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Synthesis, Isolation and Structural Investigation of Schiff-Base Alkoxytitanium Complexes: Steric Limitations of Ligand Coordination

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This paper reports the reaction of Ti(O*i*Pr)$_4$ with a series of Schiff-base ligands. The Schiff-base proligands **1a**–**l** are synthesised by the condensation of salicylaldehyde with a range of primary alkylamine and aniline derivatives. The treatment of **1a**–**f** with Ti(O*i*Pr)$_4$ yields the octahedral bis(aryloxy–imine)Ti(O*i*Pr)$_2$ complexes **2a**–**f**. X-ray crystal structure analysis of **2c**, **2d** and **2e** reveals complexes with a *trans*-aldiminato oxygen atom and *cis*-N,*cis*-alkoxide ligand arrangement about the central metal atom. The reactions of Ti(O*i*Pr)$_4$ with the ligands **1g** and **1h** result in a sterically induced ligand rearrangement to form the octahedral complexes **2g** and **2h**, also characterised by X-ray diffraction experiments, in which the nitrogen atoms of the O,N-chelate are now *trans*-orientated at the titanium centre. ^{1}H NMR analysis reveals significant deshielding of the isopropoxide methine proton, induced by this coordination mode. In contrast, reactions of **1i** and **1j** with Ti(O*i*Pr)$_4$ result in the formation and isolation of the complexes **2i** and **2j**. X-ray crystal structure analysis shows complex **2j** to have a previously unobserved ligand orientation, in which both ligands are *trans*-orientated, with respect to the aldiminato oxygen atoms, about the titanium centre, but steric bulk of the ligand inhibits the bidentate coordination of both O,N-ligands. Further increase in the steric bulk of the imine substituent results in a reduced reactivity for ligands **1k** and **1l**, such that Ti(O*i*Pr)$_4$ reacts with **1k** to form the dimeric mono(Schiff-base) complex **2k** (characterised by X-ray analysis). No reaction is observed for **1l**.

Introduction

In recent years the development of new and increasingly active homogeneous catalysts for polymerisations has been one of the driving forces behind the advances in organometallic chemistry, the most significant progress having been made in the area of metallocene chemistry.[1–5] Much of this chemistry has focused on the development of new non-Cp ligands for alkyl d^0 metal compounds, which enhance α-olefin polymerisation, in the presence of co-catalysts, such as methylaluminoxane (MAO). A variety of ligands have been explored in recent years, including, for example, alkoxides and chelating alkoxides such as hydroxybenzaldehydes,[6–9,10] N$_2$O$_2$ Schiff-base ligands,[11–18] and bidentate N,O ligands such as 8-quinolinolato and pyridine–alkoxides.[19–22] Much of this work has focused on the formation of complexes that incorporate bidentate ligands to afford metal complexes possessing *cis*-located “active” sites, a prerequisite for effective olefin polymerisation. Recently, a family of group 4 transition-metal complexes, possessing just such a *cisoid* arrangement of two aryloxy–imine ligands, have been shown to be highly active catalysts for olefin polymerisation.[23–30] Considerable attention has also focused on the use of group 4 metal alkoxide complexes in the ring-opening polymerisations of cyclic esters such as lactic acid and ε-caprolactone.[31–35]

As part of a more general study of the chemistry of titanium alkoxides, we and others have been interested in the use of similar complexes for a range of Lewis acid mediated reactions and polymerisations.[31,32,36,37] Herein we report the results of a synthetic and structural investigation of the stereochemical control possible by steric variation of ligands, specifically at the imine substituent.

It has been shown previously that *ortho* substitution of the aryloxy–imine ligands (R position) can have a marked effect upon the structure and fluxional properties as well as the activity of the Schiff-base metal complexes as olefin polymerisation catalysts.[38,39]

Previous X-ray crystallographic studies have established that of the five possible isomeric structures of (bidentate)$_2$-MX$_2$ complexes (bidentate = aryloxy–imine ligand, X = unidentate ligand) (Figure 1) the preferred structure is a distorted octahedron with *trans*-O,*cis*-N,*cis*-X ligand arrangement [Figure 1(i)],[14,23–30,40,41] a feature that has also

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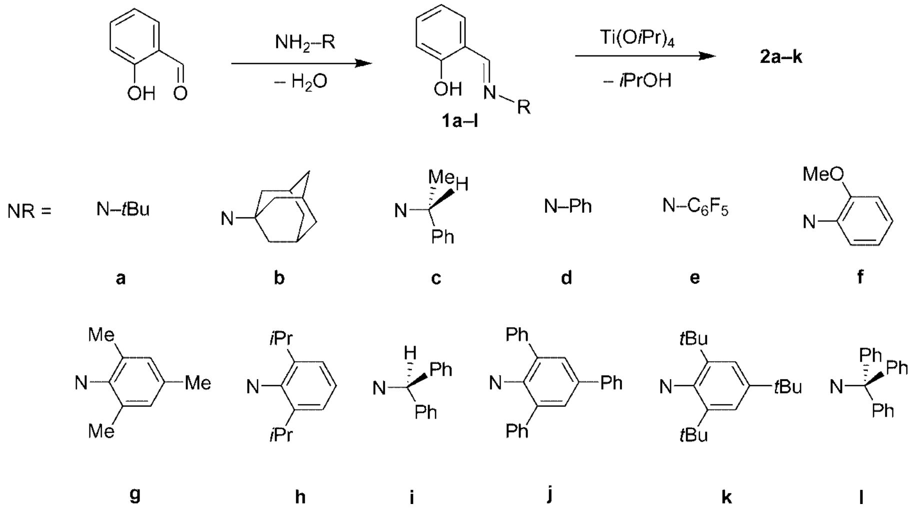

Scheme 1. Synthesis of ligands **1a**–**l** and Ti complexes **2a**–**k**.

been rationalised in terms of simple VSEPR concepts.[42] DFT calculations have also shown this conformation to be favoured in the gas phase.[23] Complexes with a *trans*-N,*cis*-O,*cis*-X ligand arrangement have also been reported.[29]

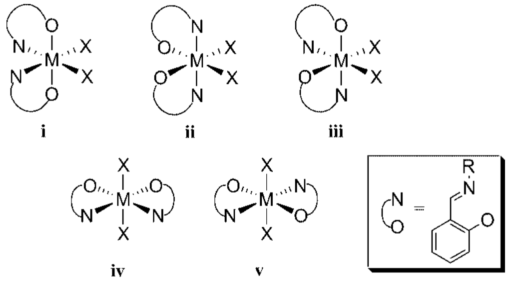

Figure 1. Depiction of the conformational isomers possible for (bidentate)$_2$MX_2 complexes.

Results and Discussion

The aryloxy–imine ligands **1a**–**l** were readily prepared by the condensation of salicylaldehyde with commercially available primary amines or aniline derivatives in methanol using standard procedures (Scheme 1)[43] and isolated as sharp-melting white to yellow crystalline solids following recrystallisation in 70–98% yields. The range of amine and aniline derivatives used in this study were chosen because of their potential to impart different steric demands at metal centres.

Synthesis and Structural Characterisation of Schiff Base Complexes

During the course of this study clear differences in the stereochemistry of metal complexes isolated, facilitate the

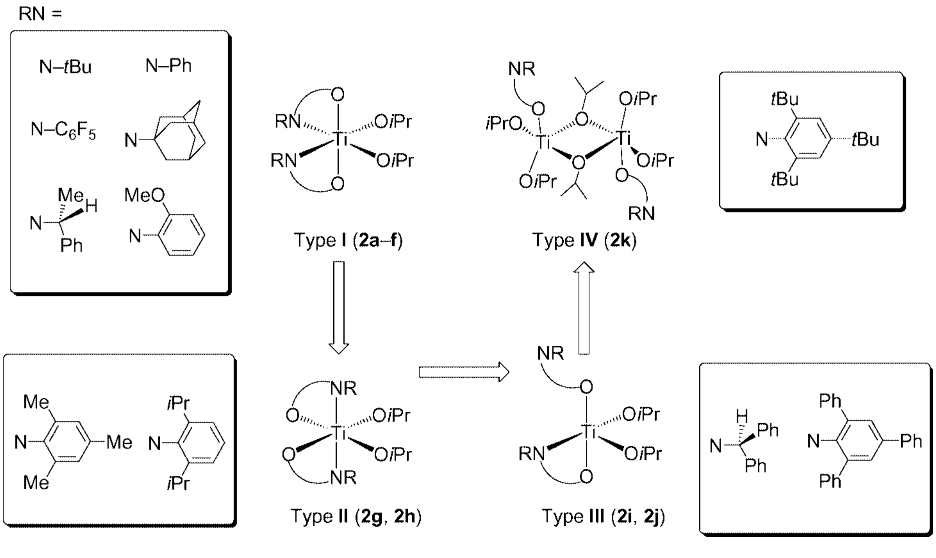

Figure 2. Structural classes of Schiff-base complexes **I**–**IV**.

division of their discussion into four distinct categories: bis(η^2-*trans*-O,O) complexes, type **I**; bis(η^2-*trans*-N,N) complexes, type **II**; bis(η^2,η^1-*trans*-O,O) complexes, type **III**; and mono(η^1) complexes, type **IV** (Figure 2). ^{1}H NMR spectroscopic data and X-ray data are discussed below. ^{13}C NMR spectroscopic data and elemental analyses are reported in the Experimental Section and are consistent with the structures proposed.

Type I Complexes, Bis(η^2-*trans*-O,O) Coordination

The reactions of Ti(O*i*Pr)$_4$ with 2 equiv. of **1a**–**f** proceed rapidly at room temperature in toluene to afford HO*i*Pr and the bis(ligand) complexes [{RN=C(C$_6$H$_4$O)}$_2$Ti(O*i*Pr)$_2$] (**2a**–**f**) in high yield (Scheme 1). The complexes **2** were isolated as analytically pure crystalline solids by recrystallisation from concentrated toluene solutions.

^{1}H NMR spectra of **2a**–**f** at room temperature contain one single set of sharp resonances, for both Schiff-base ligands and isopropoxide groups. Despite the variation in imine substituents in the complexes **2a**–**f**, signals due to the isopropoxide ligands do not vary significantly (i.e., δ = 4.6–4.9 ppm for the isopropoxide methine proton). It is well documented that six-cordinate bis(chelate) complexes of the structure types **I** and **II** (Figure 2) can undergo inversion of configuration at the metal centre, exhibiting rapid $\Delta \rightleftharpoons \Lambda$ isomerisation and isopropoxide rotation and/or exchange at ambient temperatures.[44–47] The observation of only one set of resonances for each ligand type in the ^{1}H and ^{13}C NMR spectra of **2a**–**f** is consistent with a C_2-symmetric structure. In the specific case of the complexes **2c**–**e**, single-crystal X-ray diffraction studies confirm the complexes to be type **I** (Figure 2) C_2-symmetric complexes in the solid state.

In order to probe this fluxional behaviour further, low-temperature ^{1}H NMR spectra of **2c**, which incorporates an enantiomerically pure chiral ligand, are particularly informative, because the presence of chiral ligands leads to the formation of diastereoisomers.[20] Variable-temperature ^{1}H NMR spectra for the imine CH region are shown in Figure 3. At room temperature (23 °C) the ^{1}H NMR spectrum of **2c** shows one broad resonance each for the imine CH, the methine proton of the isopropoxide ligand, and the methine proton of the chiral imine substituent. Cooling of the sample to –20 °C results in resolution of each of these resonances into two peaks of intensity ratio 1:2.1, corresponding to the two diastereoisomers possible for complexes of type **I** shown in Figure 2. {It is likely that the two major isomers observed in solution correspond to the two diastereoisomers of the (*trans,cis,cis*) isomer [Figure 1(i)] as non-bulky ligands prefer a *trans*-O,*cis*-N conformation.} Cooling of the sample to –30 °C results in further changes in the relative intensities of these signals until at –80 °C the relative intensities are found in a 1:3.6 ratio. Although the absolute stereochemistry of the major diastereoisomer observed in the solution state cannot be determined unequivocally, it may be inferred from the molecular structure determination of **2c**. Compound **2c** crystallises in a chiral space group as only one diastereoisomer (see below), It is therefore likely that this is also the thermodynamically more stable isomer observed in solution.

The fluctional behaviour observed for **2c** at low temperatures is fully reversible, and warming of the sample to 60 °C shows a slight sharpening of the signals in the ^{1}H NMR spectrum relative to the room-temperature spectrum, but no evidence for metal-based isomerisation is observed.

The molecular structures of **2c**, **2d**, and **2e** are shown in Figures 4, 5 and 6, respectively, and key parameters are summarised in Tables 1 and 5. All three complexes adopt a distorted octahedral structure of type **I**, with a *trans*-aldiminato,*cis*-alkoxide,*cis*-imine ligand arrangement.

The asymmetric unit of **2c** contains crystallographically independent molecules, both of which possess the same chirality but which differ marginally in the relative orientations of the isopropoxide groups. The coordination geometry

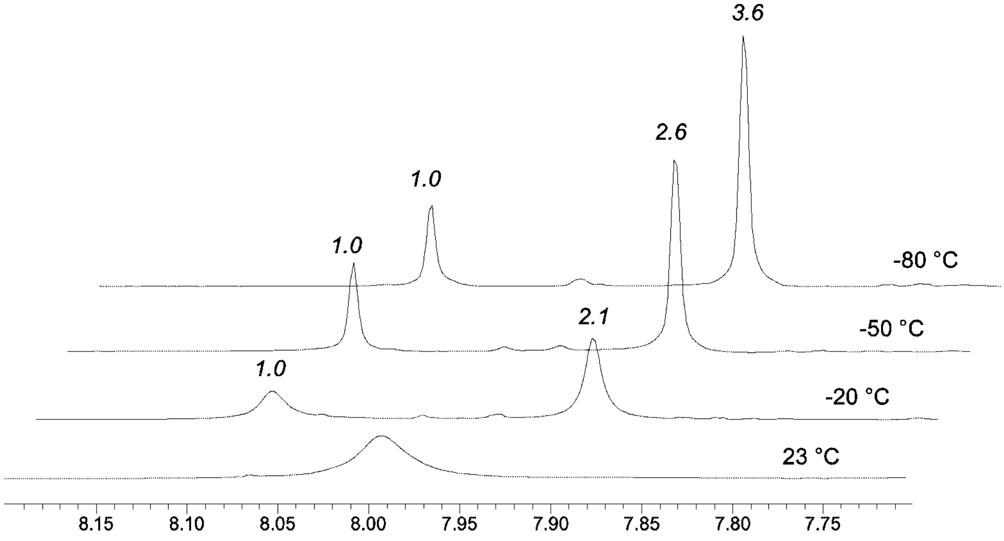

Figure 3. Variable-temperature ^{1}H NMR spectra of **2c** showing the imine CH region of the ligand (relative integrals shown in italics above peaks).

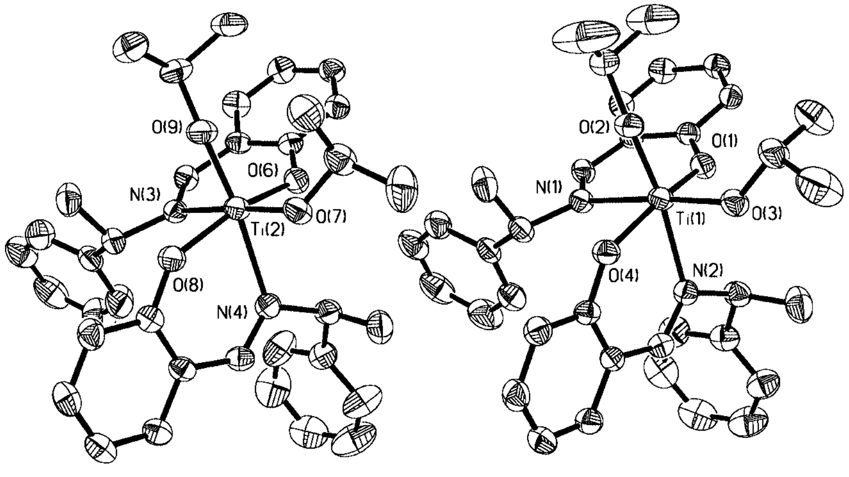

Figure 4. Molecular structures of the two independent molecules, **A** and **B**, in complex **2c**. Structures are shown with 50% displacement ellipsoids; hydrogen atoms have been omitted for clarity.

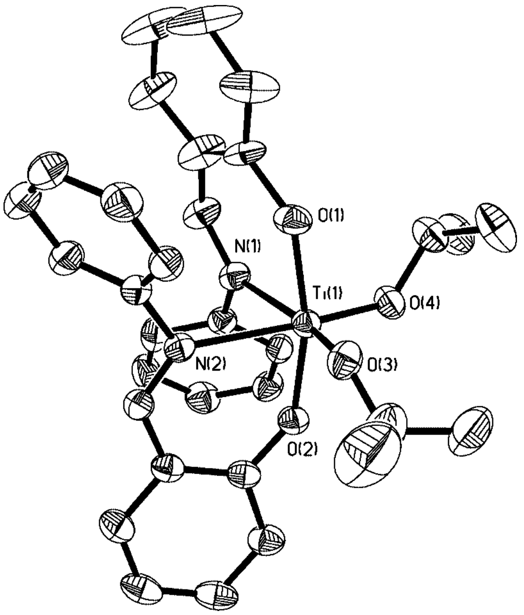

Figure 5. Molecular structure of complex **2d**. The structure is shown with 50% displacement ellipsoids. Hydrogen atoms have been omitted for clarity. Disorder in the aryloxy unit (O1–N1) is not shown.

around the central titanium atom is close to octahedral. The axial O–Ti–O bond angle is distorted away from linearity [O(1)–Ti(1)–O(4), 161.65(8)°; O(6)–Ti(2)–O(8), 161.95(8)°] such that there is a displacement of the aldiminato ring away from the isopropoxide ligands. The Ti–O*i*Pr moieties exhibit bond lengths of 1.777(2) Å [Ti(1)–O(2)], 1.817(2) Å [Ti(1)–O(3)], 1.826(2) Å [Ti(2)–O(7)], and 1.778(2) Å [Ti(2)–O(9)], with O–Ti–O angles of 99.85(9)° and 101.04(8)° about Ti(1) and Ti(2), respectively. As expected, the Ti–N(imine) bonds are considerably longer: Ti(1)–N(1) 2.347(2), Ti(1)–N(2) 2.299(2), Ti(2)–N(3) 2.321(2), Ti(2)–N(4) 2.300(2) Å. The coordination geometries in complexes **2d** and **2e** are similar to that observed in **2c**, although subtle differences between the complexes are apparent (Table 1).

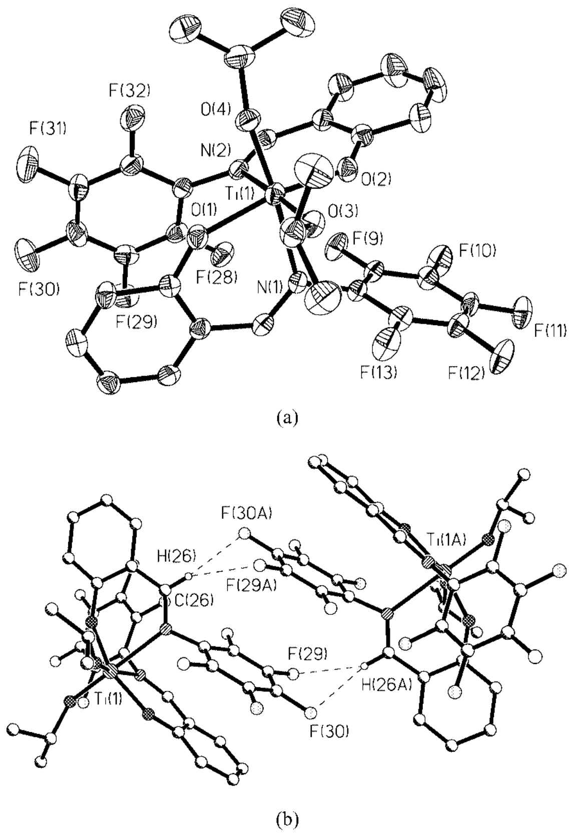

Figure 6. (a) Molecular structure of complex **2e**, shown with 50% displacement ellipsoids. Hydrogen atoms have been omitted for clarity. (b) Supramolecular structure of **2e** highlighting the intermolecular C–H···F interactions C(26)···F(29A) 3.550(4) Å, C(26)···F(30A) 3.406(4) Å, C(26)–H(26)···F(29A) 154.6°, C(26)–H(26)···F(30A) 140.1°.

Previous work has highlighted the role of the imine C–H group in promoting weak intermolecular interactions in the solid-state structures of Schiff-base complexes.[11] Of the titanium compounds described in this work, only **2e** exhibits significant intermolecular interactions involving this hydrogen-bond donor group: pairs of monomers are associ-

Table 1. Selected bond lengths [Å] and angles [°] for complexes **2c** (molecules A and B), **2d** and **2e**.

	2c		**2d**	**2e**
	A	B		
Ti–OAr	1.9262(18)	1.9417(18)	1.8945(14)	1.9190(16)
	1.9312(18)	1.9181(18)	1.9042(13)	1.9327(18)
Ti–N	2.299(2)	2.300(2)	2.350(16)	2.328(2)
	2.347(2)	2.321(2)	2.3278(16)	2.340(2)
Ti–OR	1.7767(19)	1.7778(18)	1.8126(14)	1.7791(19)
	1.8170(18)	1.8257(18)	1.8186(14)	1.7979(17)
ArO–Ti–OAr	161.65(8)	161.95(8)	165.35(7)	156.71(9)
N–Ti–N	83.72(8)	84.55(8)	75.98(5)	82.81(7)
O–Ti–N	81.02(7)	81.14(7)	81.06(6)	79.95(7)
RO–Ti–OR	99.85(9)	101.04(8)	104.26(7)	101.96(9)

ated through mutual C–H···F interactions as shown in Figure 6(b). In related complexes, in which the imine group is an *ortho*-F-substituted phenyl ring, C–H···F interactions between the imine substituent and the β-H atoms of the growing polymer chain have been cited as the reason for the remarkable stability and catalytic behaviour of such complexes.[48,49]

Type II Complexes, Bis(η^2-*trans*-N,N) Coordination

Upon increasing the steric bulk of the imine substituent, beyond that of *o*-methoxyaniline, significant changes in the ^{1}H NMR spectra are observed, such that the isopropoxide methine resonances shift from δ = 4.6–4.9 ppm in **2a**–**f** to δ = 3.4 and 3.7 ppm in **2g** and **2h**, respectively. We believe this change is indicative of a transformation from a type **I** to a type **II** structure. As with complexes **2a**–**f**, NMR spectra of **2g** and **2h** are consistent with C_2-symmetric complexes. A single-crystal X-ray structure of **2h** confirms the type **II** structure, in which the bidentate ligands adopt a mutually *trans*-N,*cis*-O(Ar),*cis*-O(R) arrangement, as shown in Figure 7; although there are no significant differences in Ti–N and Ti–O(Ar) bond lengths in **2h** relative to type **I** complexes **2c**–**e** (Tables 1 and 2), there is movement of the axial nitrogen atoms away from the isopropoxide ligands such that the N–Ti–N angle in **2h** is 164.61(8)°. As in the case of **2c**–**e**, the geometry of the aryloxy–imine ligands forces the chelate angles around the Ti atom to deviate from the ideal octahedral geometry, with a "bite" angle [N(1)–Ti(1)–O(1)] of 82.33(10)°, which is comparable to the average "bite" angles found in **2c**–**e** [81.02(7)° (**2cA**), 81.14(7)° (**2cB**), 81.06(6)° (**2d**) and 79.95(7)° (**2e**)]. Erker et al. have previously observed this unusual configuration in Schiff-base Ti and Zr chloride complexes of the ligand **1h**.[29]

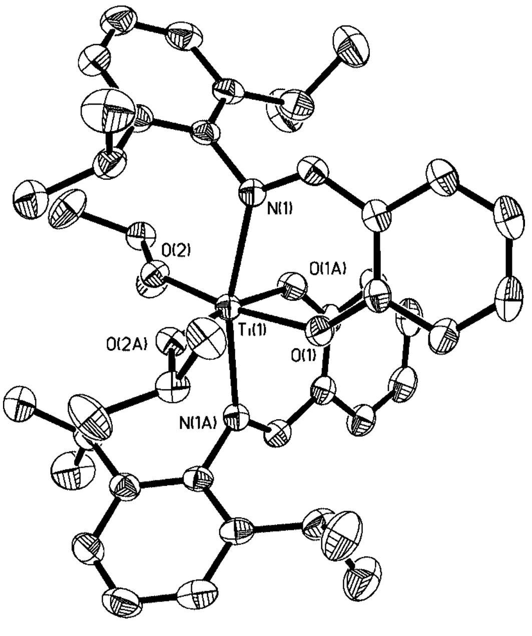

Figure 7. Molecular structure of **2h**. Ellipsoids are shown with 50% displacement probability. Hydrogen atoms have been omitted for clarity. Equivalent atoms (*A) are generated by the symmetry transformations $-x+1$, y, $-z+1/2$, and $-x+1/2$, $-y+1/2$, $-z+1$.

Table 2. Selected bond lengths [Å] and angles [°] for complex **2h**.

Ti(1)–O(1)	1.975(1)	O(1)–Ti(1)–O(1*)	85.30(8)
Ti(1)–O(2)	1.805(1)	O(1)–Ti(1)–O(2)	171.27(6)
Ti(1)–N(1)	2.228(1)	O(2)–Ti(1)–O(2*)	95.87(8)
N(1)–Ti(1)–N(1*)	164.61(8)	O(1)–Ti(1)–N(1)	82.33(6)

The significant shift observed in the ^{1}H NMR spectra of the isopropoxide ligands on changing from type **I** to type **II** complexes is not reflected in the Ti–O(isopropoxide) bond lengths, which remain similar in both type **I** and **II** complexes (see Tables 1 and 2). This suggests that the deshielding observed for type **II** complexes (**2g** and **2h**) is due to the proximity of the methine proton to an *N*-aryl group of the Schiff-base ligand rather than due to a differing *trans* effect caused by reorientation of the ligands. This inference is supported by the solid-state structures of type **I** and type **II** complexes, in which the isopropoxide methine proton is directed towards an aryl ring in type **II** complexes but not in type **I**. These orientations are apparent from Figures 5 and 7, type **I** and **II** complexes, respectively. Overall, the steric environment surrounding the metal centre is altered significantly because of the reorientation of the Schiff-base ligands as highlighted by the space-filling diagrams shown in Figure 8. It would be surprising if these changes did not influence the reactivity of the metal complexes, and it is interesting to note that a recent report by Matsui et al. suggests that very bulky imine substituents inhibit the activity of Schiff-base Zr complexes as polyolefin precatalysts.[23]

Type III Complexes, Bis($\eta^2\eta^1$-*trans*-O,O) Coordination

An additional increase in the steric bulk of the imine substituents (ligands **1i** and **1j**) leads to the formation of complexes **2i** and **2j** (Scheme 1). Characterisation of **2i** and **2j** by ^{1}H NMR spectroscopy indicates the presence of the same ligand set as for **2a**–**h**. However, for both complexes, the isopropoxide methine proton is only slightly deshielded in comparison to the type **I** complexes **2a**–**f** implying that the isopropoxide group no longer experiences the deshield-

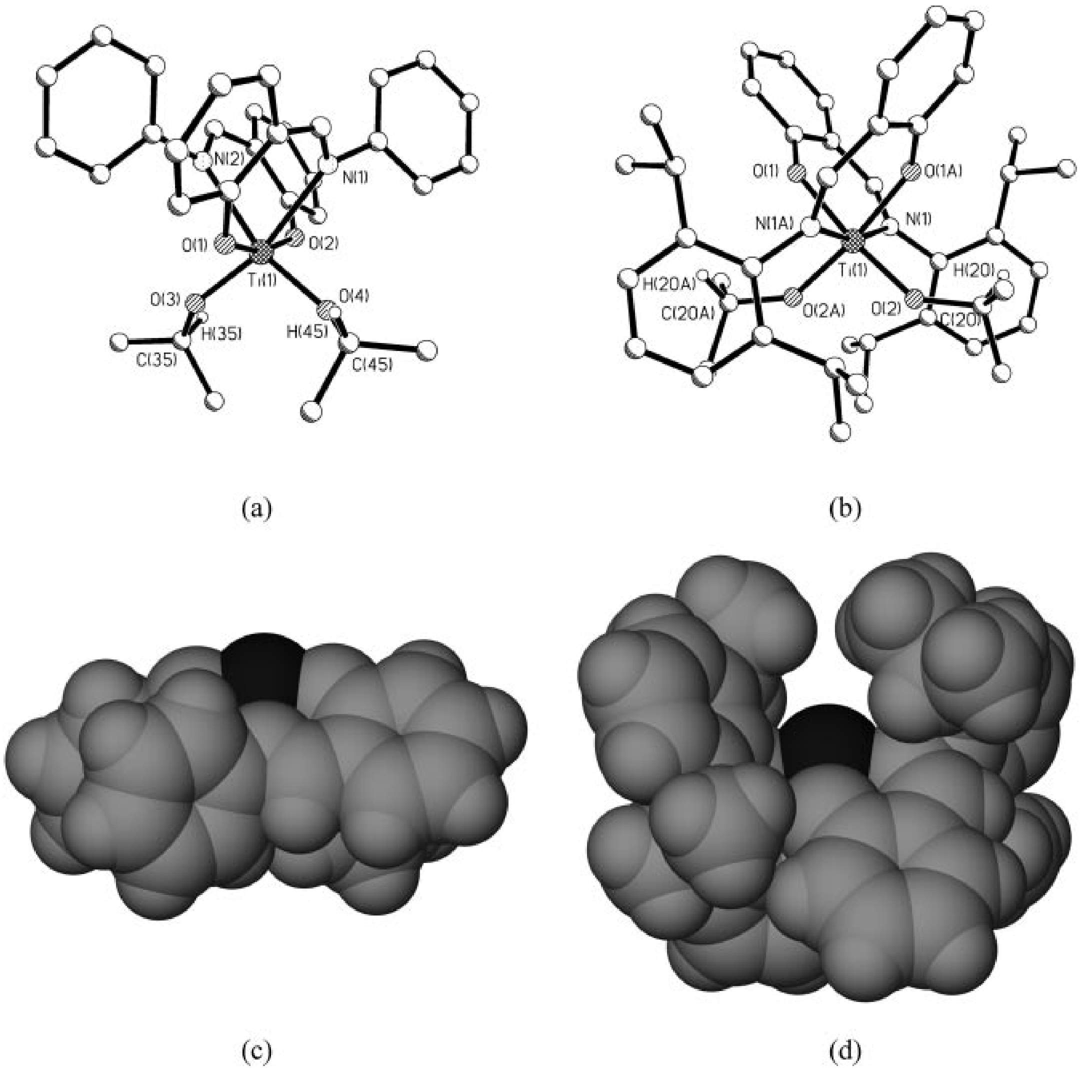

Figure 8. Complexes **2d** [(a) and (c)] and **2h** [(b) and (d)] highlighting orientation of the chelating ligands relative to the isopropoxide methine protons [(a) and (b)] and the difference in the steric environment of the active site in type **I** and type **II** complexes [isopropoxide groups have been omitted in (c) and (d) for clarity].

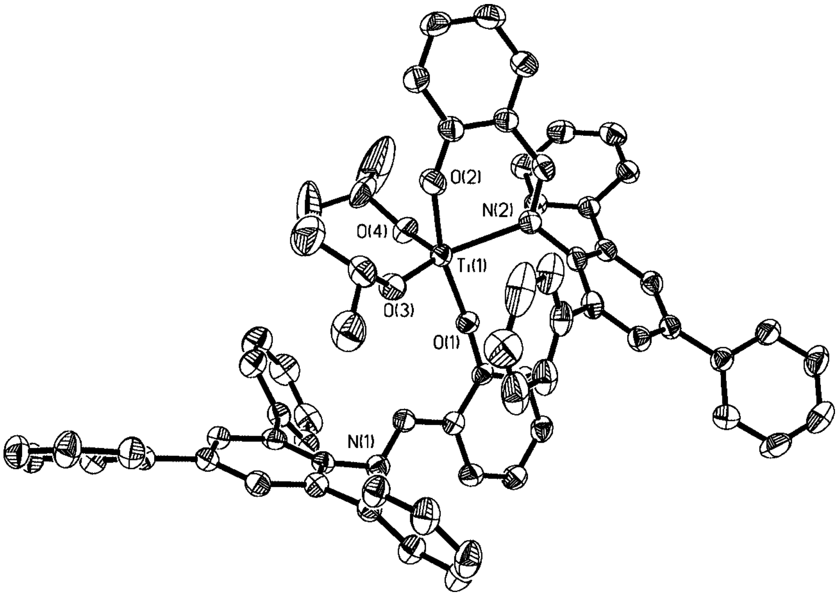

Figure 9. Molecular structure of complex **2j**, shown with 50% displacement ellipsoids; hydrogen atoms have been omitted for clarity.

ing effects observed in **2g** and **2h**, and that a further structural change has taken place.

X-ray structural analysis of complex **2j** (Figure 9) reveals the nature of this change and represents a previously uncharacterised structure for disubstituted Schiff-base titanium or zirconium complexes. Complex **2j** exhibits a five-coordinate titanium centre, with a distorted square-pyramidal geometry, supporting two alkoxide ligands and two aryloxide ligands, each exhibiting different bonding modes. One ligand forms a chelate to the metal centre in the expected η^2 fashion, while the second binds in η^1 mode solely through the aryloxide group. The 2,4,6-triphenylphenyl group of this monodentate ligand is orientated such that it is remote from the metal centre, thus relieving steric congestion. Selected bond lengths and angles for **2j** are given in Table 3. Complex **2j** may be viewed as a structural model for the proposed intermediate in the $\Delta \rightleftharpoons \Lambda$ enantiomerisation process of octahedral $(AB)_2MX_2$ complexes. The enantiomerisation process is reasoned to proceed via a five-coordinate intermediate formed by the rupture of a metal–ligand bond as shown in Figure 10.[19–21,44–47]

Table 3. Selected bond lengths [Å] and angles [°] for complex **2j**.

Ti–O(1)	1.862(2)	O(2)–Ti–O(1)	164.72(8)
Ti–O(2)	1.942(2)	O(3)–Ti–O(4)	112.11(9)
Ti–O(3)	1.791(2)	O(3)–Ti–N(2)	140.21(8)
Ti–O(4)	1.774(2)	O(4)–Ti–N(2)	106.25(8)
Ti–N(2)	2.215(2)	O(2)–Ti–N(2)	80.27(7)
C(7)–N(1)	1.276(3)		
C(46)–N(2)	1.441(3)		

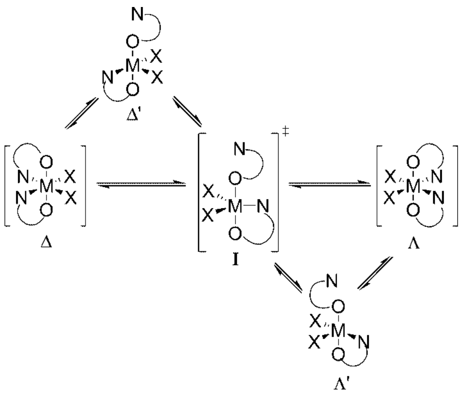

Figure 10. Proposed mechanism of racemisation for interchange of Δ and Λ forms of the bis(aryloxy–imine)titanium complexes. Complexes Δ′ and Λ′ represent the stable five-coordinate species, such as **2j**.[44–47]

Type IV Complexes, Mono(η^1) Coordination

Further increases in the steric bulk of the imine substituent (ligand **1k**, Scheme 1) inhibits formation of disubstituted complexes analogous to **2a**–**j**, and results in only monosubstitution of $Ti(OiPr)_4$ to yield **2k**, even in the presence of excess **1k** and in refluxing toluene. Under similar reaction conditions, **1l** is recovered intact and no evidence for even monosubstitution is observed.

In the solid state, **2k** has a dimeric structure (Figure 11, Table 4) consisting of two terminal alkoxide and two bridging μ-O*i*Pr groups, as well as one monodentate aryloxide ligand coordinated to each Ti atom. This is structurally similar to the previously reported (alkoxide)(phenoxide)-titanium complex $[Ti_2(O\text{-}2,4,6\text{-}Me_3C_6H_2)_2(OiPr)_4(\mu\text{-}OiPr)_2]$.[18,50] Each titanium centre in **2k** possesses a trigonal-bipyramidal geometry, with one μ^2-O*i*Pr group in an axial and one in an equatorial site (Figure 12). The terminal alkoxy–imine ligand occupies an equatorial site, and within

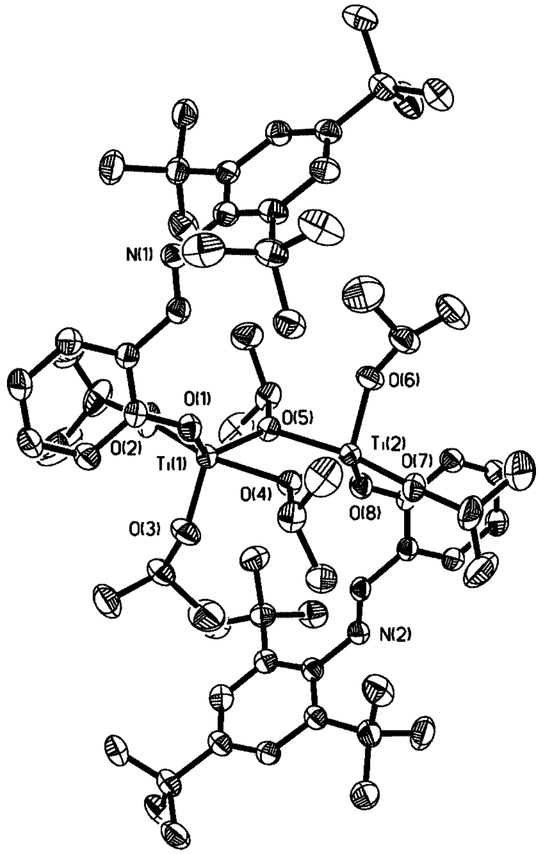

Figure 11. Molecular structure of complex **2k**, shown with 50% displacement ellipsoids; hydrogen atoms have been omitted for clarity.

Table 4. Selected bond lengths [Å] and angles [°] for complex **2k**.

Ti(1)–Ti(2)	3.263(2)	Ti(1)–O(4)–Ti(2)	107.05(9)
		Ti(1)–O(5)–Ti(2)	107.63(9)
Ti(1)–O(1)	1.882(2)	O(4)–Ti(1)–O(5)	72.30(8)
Ti(1)–O(2)	1.762(2)	O(4)–Ti(2)–O(5)	72.56(8)
Ti(1)–O(3)	1.778(2)		
Ti(1)–O(4)	2.120(2)	O(2)–Ti(1)–O(4)	167.09(10)
Ti(1)–O(5)	1.929(2)	O(1)–Ti(1)–O(5)	125.83(9)
C(7)–N(1)	1.270(4)	O(1)–Ti(1)–O(3)	111.71(10)
		O(1)–Ti(1)–O(5)	125.83(9)
Ti(2)–O(8)	1.883(2)		
Ti(2)–O(6)	1.788(2)	O(5)–Ti(2)–O(7)	170.29(9)
Ti(2)–O(7)	1.766(2)	O(4)–Ti(2)–O(6)	115.90(10)
Ti(2)–O(4)	1.924(2)	O(4)–Ti(2)–O(8)	122.29(9)
Ti(2)–O(5)	2.112(2)	O(6)–Ti(2)–O(8)	174.69(10)
C(87)–N(2)	1.272(4)		

the dimer both ligands are arranged *trans* to each other such that the molecule has crystallographic C_i symmetry. The bridging alkoxide ligands do so unsymmetrically, with the equatorial Ti–O bonds [Ti(1)–O(5) 1.929(2) Å, Ti(2)–O(4) 1.924(2) Å] being shorter than the axial [Ti(1)–O(4) 2.120(2) Å, Ti(2)–O(5) 2.112(2) Å] ones. Other bond lengths and angles found in the structure of **2k** are as expected.

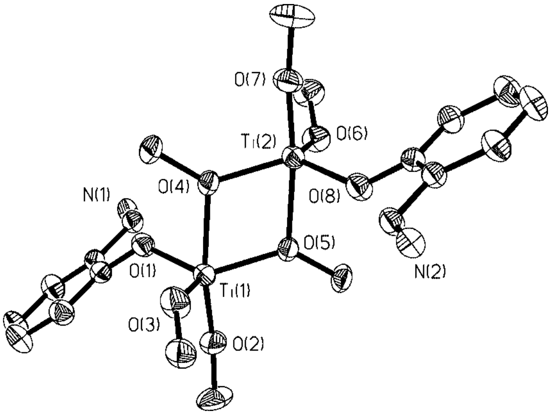

Figure 12. Structure of **2k**, showing the distorted trigonal-bipyramidal geometry about the two titanium centres, with 50% displacement ellipsoids; hydrogen atoms, methyl groups and the imine substituents have been omitted for clarity.

Conclusions

We have synthesised, isolated and structurally characterised Schiff-base complexes of titanium with the previously observed C_2-symmetric type **I** (**2a**–**f**) and type **II** (**2g** and **2h**) structures. Type **II** complexes are characterised in their ^{1}H NMR spectra by deshielding of the isopropoxide methine protons which highlights a significant change in the steric characteristics of the metal centre. A further increase in the steric demands of the imine substituent results in the isolation of complexes with the hitherto unknown five-coordinate type **III** structure (**2i** and **2j**), which can be viewed as a structural model for the proposed intermediate in $\Delta \rightleftharpoons \Lambda$ racemisation of C_2-symmetric complexes of this type. Increasing the steric bulk of the ligand still further induces a decrease in reactivity of the ligands towards Ti(O*i*Pr)$_4$. Thus, ligand **1k** substitutes only one alkoxide to form the bridged alkoxide complex **2k**, and **1l** is unreactive towards Ti(O*i*Pr)$_4$.

The ability to control molecular structure and particularly the environment about Lewis acidic metal centres, by steric variation at a ligands periphery, described here, clearly shows that, although somewhat distant from the metal centre, the choice of imine substituent is critical to the ligand coordination geometry about the central metal, and points to possible the rational design of metallo-organic complexes for use in catalysis.

Experimental Section

General Remarks: All manipulations were carried out under dry argon using standard Schlenk and glove-box techniques. Solvents were purified by conventional procedures and distilled prior to use. Ti(O*i*Pr)$_4$ was purchased from Aldrich and used as received, without further purification. The ligands **1a**–**m** were prepared using the appropriate amine and salicylaldehyde, all purchased from Aldrich, using standard literature techniques.[51] Solution ^{1}H, and ^{13}C NMR experiments were performed at ambient temperature with a Bruker Avance-300. ^{1}H NMR spectroscopic data are referenced to residual non-deuterated solvent.

Syntheses of Complexes

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)N*t*Bu}$_2$] (2a): To a stirred solution of **1a** (0.36 g, 2 mmol) in 20 mL of toluene was added Ti(O*i*Pr)$_4$ (0.3 mL, 1 mmol) dropwise by syringe, at 0 °C. The mixture was heated at reflux for 2 h. The solution was cooled to room temperature before removal of solvent under reduced pressure. The yellow residue was dissolved in a minimum of fresh toluene (6 mL), warmed to ca. 40 °C, and filtered through a Celite pad into a Schlenk flask. The filtrate was layered with 5 mL of dry pentane and allowed to stand at 4 °C for 2 days after which the solid microcrystalline product was collected by filtration, washed with 5 mL of cold hexane and dried in vacuo. Yield: 0.36 g (70%). $C_{28}H_{42}N_2O_4Ti$ (518.3): calcd. C 64.86, H 8.10, N 5.40; found C 65.1, H 8.17, N 5.41. ^{1}H NMR (300 MHz, 23 °C, CDCl$_3$): δ = 1.17 [br. s, 12 H, OCH(C*H*$_3$)$_2$], 1.36 [s, 18 H, NC(C*H*$_3$)$_3$], 4.62 [sept, $^3J_{HH}$ = 6 Hz, OC*H*(CH$_3$)$_2$, 2 H], 6.6–6.85 (br. m, 4 H, CH$_{arom}$), 7.18–7.26 (br. m, 2 H, CH$_{arom}$), 7.27–7.45 (br. m, 2 H, CH$_{arom}$), 8.34 [s, 2 H, C(*H*)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 25.8, 30.9, 61.4, 77.6, 118.5, 119.3, 123.8, 132.5, 133.2, 160.1, 166.5 ppm.

Complexes **2b**–**2k** were prepared in a manner analogous to that of **2a**.

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)N(C$_{10}$H$_{15}$)}$_2$] (2b): Yield: 0.38 g (57%). $C_{40}H_{54}N_2O_4Ti$ (674.4): calcd. C 71.20, H 8.07, N 4.15; found C 71.60, H 8.01, N 4.09. ^{1}H NMR (300 MHz, 23 °C, CDCl$_3$): δ = 1.22 [br . s, 12 H, OCH(C*H*$_3$)$_2$], 1.53–2.09 (br. m, 30 H, NC$_{10}$*H*$_{15}$), 4.69 [br. m, 2 H, OC*H*(CH$_3$)$_2$], 6.67–6.82 (br. m, 4 H, CH$_{arom}$), 7.14–7.28 (br. m, 2 H, CH$_{arom}$), 7.32–7.47 (br. m, 2 H, CH$_{arom}$), 8.32 [s, 2 H, C(*H*)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 25.9, 30.2, 36.7, 43.3, 78.4, 117.8, 118.7, 119.4, 131.7, 132.5, 160.4, 164.9 ppm.

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)N[(*R*)-CHMePh]}$_2$] (2c): Yield: 0.44 g (72%). $C_{36}H_{42}N_2O_4Ti$ (614.3): calcd. C 70.36, H 6.84, N 4.56; found C 69.60, H 6.84, N 4.42. ^{1}H NMR (300 MHz, 23 °C, CDCl$_3$): δ = 1.02 [br. s, 12 H, OCH(C*H*$_3$)$_2$], 1.45 [br. s, 6 H, CH(C*H*$_3$)Ph], 4.67 [sept, OC*H*(CH$_3$)$_2$, $^3J_{HH}$ = 6 Hz, 2 H], 5.29 (br. m, 2 H, C*H*MePh) 6.58–6.66 (br. m, 2 H, CH$_{arom}$), 6.76–6.82 (br. m, 2 H, CH$_{arom}$), 6.97 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2 H, CH$_{arom}$), 7.06–7.15 (br. m, 10 H, CH$_{arom}$), 7.23 (ddd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, CH$_{arom}$), 7.88 [s, 2 H, C(*H*)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 21.6, 25.7, 62.5, 78.6, 117.5, 119.4, 123.0, 126.9, 127.6, 128.8, 128.9, 134.18, 134.52, 163.7, 164.7 ppm.

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)NC$_6$H$_5$}$_2$] (2d): Yield: 0.38 g (68%). $C_{32}H_{34}N_2O_4Ti$ (558.2): calcd. C 68.80, H 6.09, N 5.01; found C 68.50, H 6.13, N 4.98. ^{1}H NMR (300 MHz, 23 °C, CDCl$_3$): δ = 1.23 [br. s, 12 H, OCH(C*H*$_3$)$_2$], 4.9 [sept, $^3J_{HH}$ = 6 Hz, 2 H, OC*H*(CH$_3$)$_2$], 6.11–6.17 (m, 2 H, CH$_{arom}$), 6.49 (ddd, $^3J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.2 Hz, 2 H, CH$_{arom}$), 6.78–7.04 (m, 14 H, CH$_{arom}$), 7.87 [s, 2 H, C(*H*)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 25.9, 79.0, 117.8, 119.8, 123.1, 126.2, 128.4, 134.3, 135.2, 154.3, 163.7, 166.3 ppm.

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)NC$_6$F$_5$}$_2$] (2e): Yield: 0.6 g (81%). $C_{32}H_{24}F_{10}N_2O_4Ti$ (738.1): calcd. C 52.03, H 3.25, N 3.79; found C

51.8, H 3.28, N 3.78. ^{1}H NMR (400 MHz, 23 °C, CDCl$_3$): δ = 1.11 [br. s, 12 H, OCH(CH_3)$_2$], 4.77 [sept, $^3J_{HH}$ = 5.8 Hz, 2 H, OCH(CH$_3$)$_2$], 6.45–6.47 (m, 2 H, CH$_{arom}$), 6.74–6.78 (m, 2 H, CH$_{arom}$), 7.20 (dd, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1.6 Hz, 2 H, CH$_{arom}$), 7.34 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 2 Hz, 2 H, CH$_{arom}$), 8.07 [s, 2 H, C(H)=N] ppm. ^{13}C NMR (100 MHz, 23 °C, CDCl$_3$): δ = 25.5, 80.7, 118.0, 118.9, 121.2, 135.0, 136.5, 156.5, 164.9, 171.8 ppm. ^{19}F NMR (376 MHz, 23 °C, CDCl$_3$): δ = –148.3 (m), –160.1 (t, J = 21 Hz), –164.0 (m) ppm.

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)NC$_6$H$_4$-*o*-OCH$_3$}$_2$] (2f): Yield: 0.46 g (74%). $C_{34}H_{38}N_2O_6Ti$ (618.2): calcd. C 66.02, H 6.15, N 4.53; found C 66.50, H 6.09, N 4.45. ^{1}H NMR (300 MHz, 23 °C, CDCl$_3$): δ = 1.19 [br. s, 12 H, OCH(CH_3)$_2$], 3.38 (s, 6 H, OCH_3), 4.88 [sept, $^3J_{HH}$ = 6 Hz, 2 H, OCH(CH$_3$)$_2$], 5.99–6.08 (m, 2 H, CH$_{arom}$), 6.20–6.28 (m, 2 H, CH$_{arom}$), 6.36–6.47 (m, 2 H, CH$_{arom}$), 6.62–6.97 (m, 8 H, CH$_{arom}$), 7.43–7.56 (m, 2 H, CH$_{arom}$), 7.89 [s, 2 H, C(H)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 26.8, 56.0, 79.5, 111.7, 117.7, 119.8, 120.6, 123.8, 126.9, 127.8, 134.5, 135.2, 143.6, 151.6, 136.9, 169.7 ppm.

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)NC$_6$(CH$_3$)$_3$H$_2$}$_2$] (2g): Yield: 0.37 g (58%). $C_{38}H_{46}N_2O_4Ti$ (642.3): calcd. C 71.03, H 7.17, N 4.36; found C 71.30, H 7.15, N 4.32. ^{1}H NMR (300 MHz, 23 °C,

Table 5. Crystal data and structure refinement for compounds **2c**, **2d**, **2e**, **2h**, **2j** and **2k**.

Compound	**2c**	**2d**	**2e**
Empirical formula	$C_{36}H_{42}N_2O_4Ti$	$C_{32}H_{34}N_2O_4Ti$	$C_{32}H_{24}F_{10}N_2O_4Ti$
Formula mass	614.62	558.51	738.43
T [K]	150(2)	150(2)	396(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/a$	$P2_1/c$
a [Å]	18.1430(3)	16.7770(1)	14.3970(2)
b [Å]	10.1730(2)	9.9880(2)	20.1450(4)
c [Å]	18.3320(4)	17.2620(3)	21.5010(4)
β [°]	106.635(1)	90.143(1)	149.477(1)
V [Å^3]	3241.91(11)	2892.56(8)	3167.10(10)
Z	4	4	4
D_c [g cm^{-3}]	1.259	1.283	1.549
μ [mm^{-1}]	0.305	0.334	0.370
F(000)	1304	1176	1496
Crystal size [mm]	0.28 × 0.08 × 0.08	0.22 × 0.15 × 0.10	0.25 × 0.17 × 0.15
θ range [°]	3.52–26.38	3.54–27.48	3.60–27.49
Reflections collected	57745	41742	10943
Independent reflections [R(int)]	13136 [0.0516]	6582 [0.0380]	6613 [0.0326]
Reflections [$I > 2\sigma(I)$]	10091	5305	4509
Data/restraints/parameters	13136/1/788	6582/24/411	6613/0/446
Goodness-of-fit on F^2	0.994	1.030	1.011
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0423, 0.1024	0.0470, 0.1218	0.0466, 0.1121
Final R_1, wR_2 (all data)	0.0670, 0.1161	0.0615, 0.1304	0.0814, 0.1304
Max/min difference [e·Å^{-3}]	0.523/–0.308	1.236/–0.756	0.602/–0.525
Absolute structure parameter	–0.017(16)	–	–

Compound	**2h**	**2j**	**2k**
Empirical formula	$C_{51}H_{65}N_2O_4Ti$	$C_{75}H_{66}N_2O_4Ti$	$C_{75}H_{118}N_2O_8Ti_2$
Formula mass	817.95	1107.20	1271.51
T [K]	150(2)	150(2)	150(2) K
Crystal system	monoclinic	orthorhombic	triclinic
Space group	C_2/c	$Pbca$	$P\bar{1}$
a [Å]	23.1450(4)	18.2330(2)	15.3200(3)
b [Å]	17.0660(4)	24.8400(2)	15.6480(3)
c [Å]	14.5820(4)	26.3420(3)	18.1500(4)
α [°]			75.569(1)
β [°]	126.617(1)		65.055(1)
γ [°]			85.119(1)
V [Å^3]	4623.03(18)	11930.5(2)	3819.69(13)
Z	4	8	2
D_c [g cm^{-3}]	1.175	1.233	1.106
μ [mm^{-1}]	0.230	0.197	0.259
F(000)	1756	4672	1380
Crystal size [mm]	0.25 × 0.17 × 0.15	0.25 × 0.15 × 0.08	0.175 × 0.175 × 0.075
θ range [°]	3.63–27.46	3.54–27.49.	3.91–24.98
Reflections collected	39356	26279	37007
Independent reflections [R(int)]	5270 [0.1181]	13649 [0.0620]	13339 [0.0752]
Reflections [$I > 2\sigma(I)$]	3287	7735	8557
Data/restraints/parameters	5270/0/275	13649/0/768	13339/24/868
Goodness-of-fit on F^2	1.027	0.969	0.996
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0511, 0.1131	0.0552, 0.1351	0.0556, 0.1355
Final R_1, wR_2 (all data)	0.1035, 0.1332	0.1209, 0.1651	0.1004, 0.1637
Max/min difference [e·Å^{-3}]	0.346/–0.356	0.648/–0.482	0.746/–0.373

CDCl$_3$): δ = 0.38 [d, $^3J_{HH}$ = 12 Hz, 12 H, OCH(CH_3)$_2$], 2.21 (s, 3 H, *p*-CH$_3$) 2.38 (s, 6 H, *o*-CH_3), 3.45 [sept, $^3J_{HH}$ = 9 Hz, 2 H, OCH(CH$_3$)$_2$], 6.52 (ddd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 0.9 Hz, 2 H, CH$_{arom}$) 6.59–6.62 (m, 2 H, CH$_{arom}$), 6.83 (s, 4 H, CH$_{arom}$), 7.08 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.8 Hz, 2 H, CH$_{arom}$) 7.22 (ddd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.8 Hz, 2 H, CH$_{arom}$), 7.88 [s, 2 H, C(H)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 19.8, 21.1, 24.9, 77.7, 115.7, 119.9, 121.7, 129.0, 131.5, 134.6, 135.4, 135.7, 151.7, 167.8, 169.2 ppm.

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)NC$_6$[CH(CH$_3$)$_2$]$_2$H$_3$}$_2$] (2h): Yield: 0.6 g (83%). C$_{44}$H$_{58}$N$_2$O$_4$Ti (726.4): calcd. C 72.73, H 7.99, N 3.86; found C 72.30, H 8.01, N 3.76. ^{1}H NMR (300 MHz, 23 °C, CDCl$_3$): δ = 0.51 [br. s, 12 H, OCH(CH_3)$_2$], 1.25 [br. s, 24 H, CCCH(CH_3)$_2$], 3.77 [sept, $^3J_{HH}$ = 7 Hz, 2 H, OCH(CH$_3$)$_2$], 3.87 [sept, $^3J_{HH}$ = 9.2 Hz, 2 H, CCH(CH$_3$)$_2$], 6.62–6.65 (m, 4 H, CH$_{arom}$), 7.19–7.27 (m, 8 H, CH$_{arom}$), 7.35–7.39 (m, 2 H, CH$_{arom}$), 8.05 [s, 2 H, C(H)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 25.29, 27.46, 27.48, 77.8, 115.61, 120.0, 124.17, 124.17, 126.92, 134.9, 136.1, 142.2, 152.2, 167.5, 169 ppm.

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)NCH(Ph)$_2$}$_2$] (2i): Yield: 0.49 g (66%). C$_{46}$H$_{46}$N$_2$O$_4$Ti (738.3): calcd. C 74.79, H 6.23, N 3.79; found C 74.70, H 6.20, N 3.78. ^{1}H NMR (300 MHz, 23 °C, CDCl$_3$): δ = 0.92 [d, $^3J_{HH}$ = 6.4 Hz, 12 H, OCH(CH_3)$_2$], 4.5 [sept, $^3J_{HH}$ = 8.9 Hz, 2 H, OCH(CH$_3$)$_2$], 6.57–6.60 (m, 2 H, CH$_{arom}$), 6.72–6.73 (m, 2 H, CH$_{arom}$), 6.82–6.84 (m, 4 H, CH$_{arom}$), 7.02–7.27 (m, 20 H, CH$_{arom}$), 7.79 [s, 2 H, C(H)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 24.3, 70.2, 77.8, 115.9, 118.2, 121.3, 125.8, 126.9, 127.7, 128.1, 133.1, 139.9, 162.6, 166.3 ppm.

[Ti(O*i*Pr)$_2${η^2-OC$_6$H$_4$C(H)N[C$_6$H$_2$(Ph)$_3$]}{η^1-OC$_6$H$_4$C(H)NC$_6$H$_2$-(Ph)$_3$}] (2j): Yield: 0.59 g (58%). C$_{68}$H$_{58}$N$_2$O$_4$Ti (1014.4): calcd. C 80.47, H 5.71, N 2.76; found C 80.40, H 5.73, N 2.73. ^{1}H NMR (300 MHz, 23 °C, CDCl$_3$): δ = 0.69 [d, $^3J_{HH}$ = 6.4 Hz, 12 H, OCH(CH_3)$_2$], 4.14 [sept, $^3J_{HH}$ = 9 Hz, 2 H, OCH(CH$_3$)$_2$], 6.37–7.50 (m, 42 H, CH$_{arom}$), 8.29 [s, 2 H, C(H)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 25.6 80.6, 119.1, 120.2, 125.7, 127.2, 127.4, 127.5, 127.7, 128.3, 128.5, 129.3, 130.3, 130.5, 135.3, 138.3, 140.1, 141.1, 150.2, 164.3, 165.9 ppm.

[Ti(O*i*Pr)$_3$η^1-OC$_6$H$_4$C(H)N{C$_6$H$_2$(*t*Bu)$_3$}]$_2$ (2k): Yield: 0.48 g (82%, based on Ti). C$_{68}$H$_{110}$N$_2$O$_8$Ti$_2$ (1178.7): calcd. C 69.27, H 9.34, N 2.38; found C 69.02, H 9.18, N 2.39. ^{1}H NMR (300 MHz, 23 °C, CDCl$_3$): δ = 0.99 [d, $^3J_{HH}$ = 9 Hz, 36 H, OCH(CH_3)$_2$], 1.24 [s, 18 H, C(CH_3)$_3$], 1.27 [s, 36 H, C(CH_3)$_3$], 4.43 [sept, $^3J_{HH}$ = 6.3 Hz, 6 H, OCH(CH$_3$)$_2$], 6.8–6.94 (m, 4 H, CH$_{arom}$), 7.11–7.38 (m, 4 H, CH$_{arom}$), 7.96–8.14 (m, 4 H, CH$_{arom}$), 8.56 [s, 2 H, C(H)=N] ppm. ^{13}C NMR (75.5 MHz, 23 °C, CDCl$_3$): δ = 26.6, 31.9, 32.5, 35.0, 36.4, 77.6, 120.9, 121.9, 122.5, 127.8, 132.6, 138.9, 141.2, 151.9, 158.4, 165.1, 168.2 ppm.

X-ray Crystallographic Study: Crystallographic data for compounds **2c**, **2d**, **2e**, **2h**, **2j** and **2k** are summarised in Table 5. All data collections were carried out with a Nonius KappaCCD diffractometer. Structure solution and refinement were performed using SHELX86[52] and SHELX97[53] software, respectively. Experimental data relating to all structure determinations are summarised in Table 5. Full-matrix anisotropic refinement was implemented in the final least-squares cycles throughout. All data were corrected for Lorentz and polarisation and, with the exceptions of **2d**, **2e** and **2j**, for extinction effects. Hydrogen atoms were included at calculated positions throughout. In **2d**, one of the phenyl groups was seen to exhibit positional disorder. In particular, C(1)–C(6) were found to be disordered in a 1:1 ratio with C(1A)–C(6A). All carbon–carbon distances therein were refined subject to rigid-bond restraints. In complex **2h**, the asymmetric unit consisted of one half of a molecule with the central titanium atom residing on a twofold rotation axis, in addition to half of a toluene molecule proximate to a crystallographic inversion centre. The methyl group in the solvent was disordered in a 1:1 ratio by virtue of straddling this inversion centre. One full toluene molecule was also seen to be present in the structure of **2j**. In addition, one of the isopropyl groups exhibited disorder whereby C(90)–(92) were disordered in a 1:1 ratio with C(90′)–(92′). Similarly, the asymmetric unit in **2k** was also observed to contain a solvent molecule (toluene) evenly disordered over two sites. In particular, C(101)–(106) exhibited 1:1 disorder with C(201)–C(206). Both partial rings were refined as rigid hexagons. Disordered toluene methyl groups were not included in the model. Moreover, one *tert*-butyl substituent was also found to be disordered in a 70:30 ratio, whereby C(95A)–(96C) were refined at 70% occupancy and C(95D)–(95F) were refined at 30% occupancy. CCDC-239547 to -239552 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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