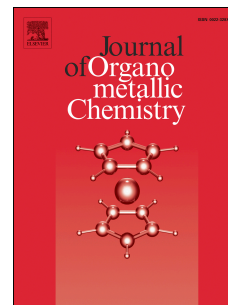


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Steric Factors on Unsymmetrical *O*-hydroxyaryl *N*-Heterocyclic Carbene Ligands Prevailing the Stabilization of Single Stereoisomer of Bis-Ligated Titanium Complexes

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Abstract

Bis-ligated titanium(IV) metal complexes supported by bidentate unsymmetrical *o*-hydroxyaryl-substituted *N*-heterocyclic carbene ligands were synthesized and structurally identified. While the direct addition of the doubly deprotonated bulky imidazolidinium chloride salts [Dipp,⁴-R^{NHC}-H]Cl (with Dipp = 2,6-diisopropylphenyl, R = H (2-hydroxyphenyl), and R = Me (2-hydroxy-4-methyl-phenyl)) with chloro-titanium precursor favors the formation of single stereoisomer corresponding to the bis-ligated titanium complexes *trans*-([κ²-C,O]-Dipp,⁴-R^{NHC})₂TiCl₂ (R = H (2-hydroxyphenyl) for **4a^H**, and R = Me (2-hydroxy-4-methyl-phenyl) for **4a^{Me}**), the reactivity with sterically less hindered imidazolidinium chloride salts [Mes,^HNHC-H]Cl and [Dep,^HNHC-H]Cl as protio-ligands (with Mes = 2,4,6-trimethylphenyl and Dep = 2,6-diethylphenyl) did not lead to single stereoisomer, but rearranged into a tetradentate salophen-like complexes *cis*-([κ⁴-O,N,N,O]-bis(imidazolidinylidene)TiCl₂) as major isomer via presumably the NHCs dimerization from bis-ligated intermediates. These results combined with topographic steric maps as well as the buried volume descriptor (%*V_{bur}*) indicate that bidentate bulky *N*-Dipp-substituted NHC ligands offer some level of steric protection preventing the formation of other possible bis-ligated (C,O)-NHC-titanium stereoisomers and constitutional isomers.

Keywords

Titanium; Bidentate ligand; Unsymmetrical *N*-heterocyclic carbene; Bis-ligated titanium complex; Ethylene polymerization.

1. Introduction

Since the first isolation and characterization of the *N*-heterocyclic carbene (NHC) by Bertrand [1] and Arduengo [2], NHCs have gained outstanding importance as ancillary ligands throughout most of the late transition metals and provided an useful hand of robust and versatile organometallic compounds for homogeneous catalysis [3]. Although late transition metal complexes show strong metal carbene bonds and slow dissociation with most of the NHC ligands, many of the early transition and *f*-block metals show the opposite trend [4]. Thus, to reduce the tendency of the NHC to dissociate from transition metal, considerable research efforts have been devoted toward the studies of multidentate anionic carbon, nitrogen, oxygen and sulfur functionalized-NHC ligands [3h, 5]. A series of anionic carbon (i.e. phenyl, cyclopentadienyl, indenyl, fluorenyl), nitrogen (i.e. amido), oxygen (i.e. alkoxide, aryloxy, enolate) and sulfur (thiolate) groups have been developed to act as tethers for holding the NHC moiety in a close proximity to oxophilic metal centers [3f, h, 4b, d, 4f-h]. For example, the use of multidentate oxygen-functionalized NHC ligands of group 4 has proven to be an effective synthetic method for developing robust catalysts for the oligomerization and (co-)polymerization of olefins [6], hydroamination/cyclization of primary aminoalkenes [7], ring-opening polymerization (ROP) of *rac*-lactide [8], and selective coupling of epoxides and CO₂ to either polycarbonates [9] or cyclic carbonates [9b]. Of particular interest, the bidentate *o*-hydroxyaryl substituted NHCs are structurally analogous to bidentate salicylaldimine ligands [10], and are amongst the most commonly studied ligand classes in coordination chemistry due to their ease of preparation, ability to stabilize various metals in different oxidation states, and particularly valuable for the fine-tuning of electronic and steric parameters in a large variety of catalytic organic and polymerization reactions [11]. Recent investigations on bis-ligated bidentate alkoxy/aryloxy-functionalized NHCs of group 4, when activated by MAO (methylaluminoxane), showed to be active in ethylene [6d, f, g, l], ethylene/1-octene and ethylene/norbornene [6d] (co-)polymerization, and stereoselective in propylene [6f, g] and styrene polymerization [6l] similarly to the class of salicylaldimine group 4 catalysts (aka phenoxy-imine, FI, Chart 1) [11e]. Following these leads, we sought to use bidentate *o*-hydroxyaryl substituted NHC-based ligands framework that are analogous to FI ligands in efforts to conceive a new class of catalysts not only for olefins polymerization, but also for the copolymerization of CO₂ and cyclohexene oxide (CHO) in order to extend our studies on active and highly selective catalysts based on tridentate bis(aryloxy) NHC ligand sets of group 4 [9]. In addition to complex developed by Grubbs, i.e. *cis*-([κ²-C,O]-Dipp,(3-Ad,5-Me)NHC)₂TiCl₂ (with 3-Ad, 5-Me = (2-hydroxy-3-(adamant-1-yl)-5-methylphenyl), and a Dipp moiety as *N*-aryl substituent, Chart 1) [6d][6l], a similar set of unsymmetrical *o*-hydroxyaryl NHC ligands was synthesized bearing sterically less-hindered substituents on the *N*-aryloxy moieties and with various *N*-aryl substituents such as Dipp, Mes and Dep groups, as well as their coordination behavior to titanium. Preliminary data concerning the ability of these titanium complexes to initiate the ethylene polymerization are also presented.

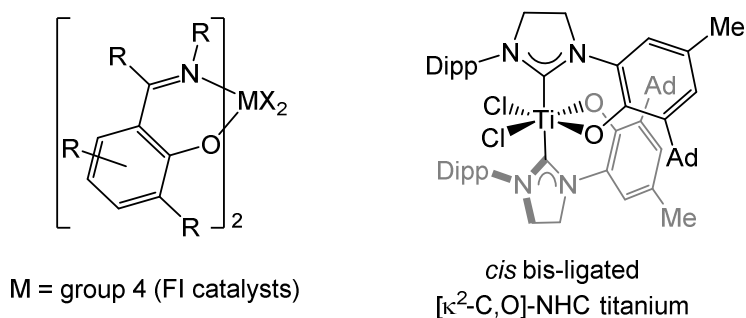
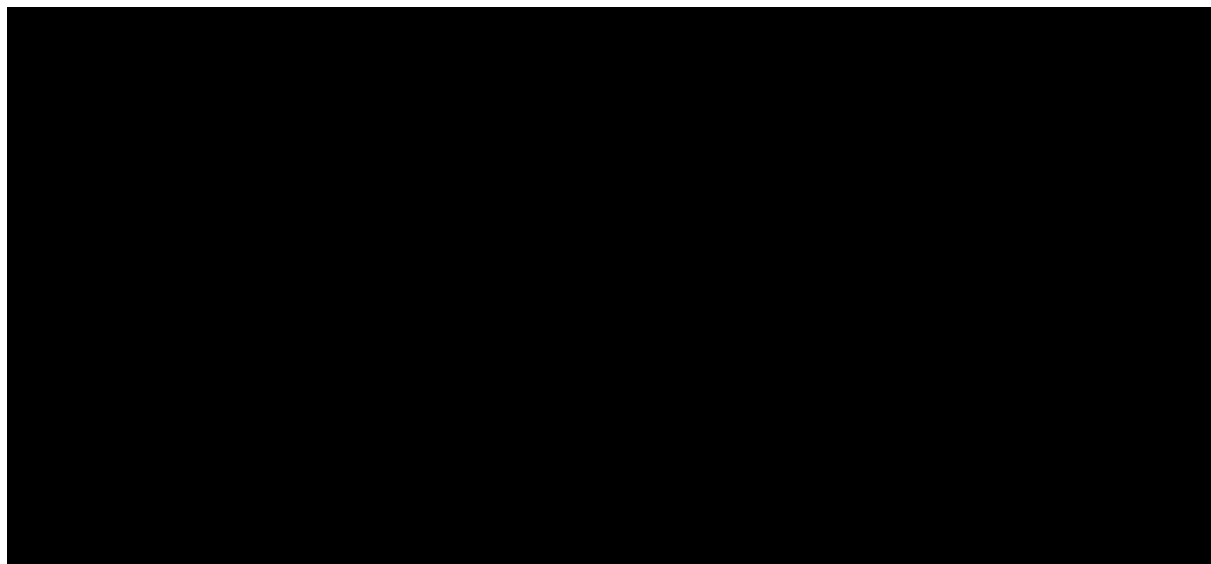


Chart 1

2. Results and Discussion

2.1. Synthesis of *o*-hydroxyaryl substituted imidazolidinium protio-ligands **3a-c**

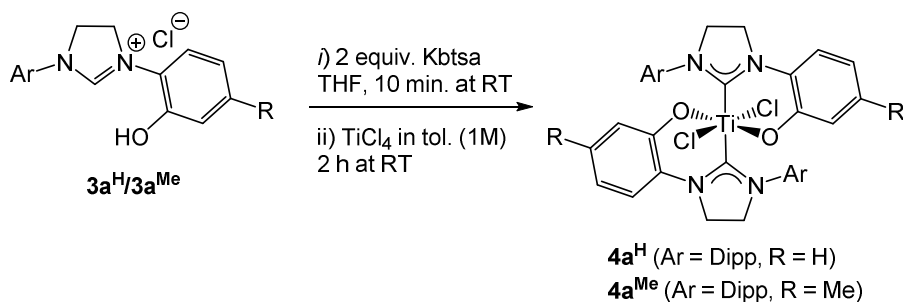
The *o*-hydroxyaryl substituted imidazolidinium chloride salts [Ar,4-H]NHC-H]Cl **3a^H** (with Ar = Dipp) and **3c** (with Ar = Mes) were prepared according to the established procedure [12], and [Dipp,4-Me]NHC-H]Cl **3a^{Me}** and [Dep,4-H]NHC-H]Cl **3b** by adapting this literature procedure: ethyl chlorooxoacetate was reacted in THF with the appropriate arylamine **a-c** in presence of triethylamine at 0 °C to give the corresponding oxanilic acid esters **1a-c**, which were treated with the suitable aminoalcohols to lead quantitatively to oxalamides **2a-c** (Scheme 1). Subsequent reduction of **2a-c** with borane THF-adduct and acidification of ethylenediamine moieties followed by their cyclization with an excess of triethyl orthoformate affords imidazolidinium protio-ligands **3a-c** in high overall yields (Scheme 1). Protio-ligand **3c** was further characterized by X-ray crystallography and crystallizes as a well-separated ion pair as found in other analogous imidazolidinium salt (Fig. S1, Table S1-3) [13]. The ¹H NMR spectra of imidazolidinium salt [Dipp,4-Me]NHC-H]Cl **3a^{Me}** and [Dep,4-H]NHC-H]Cl **3b** display the characteristic chemical resonances of the CH_{imidazolidinium} proton (singlet at δ 9.05 and 8.96 ppm, respectively) and two broad triplets for the two geminal pairs of NCH₂ protons (apparent A₂B₂ spin system, but better described as AA'XX') of the *o*-hydroxyaryl unsymmetrically substituted imidazolidinium ring (centered at δ 4.59 ppm with *v*_{AB} = 192 Hz and 4.64 ppm with *v*_{AB} = 216 Hz, respectively), which are well-in-line with the reported data for **3a^H** and **3c** (Fig. S2-3) [12]. The ¹³C NMR spectra of **3a^{Me}** and **3b** show typical chemical resonances at δ 156.6 and 157.2 ppm in chloroform-*d*, respectively, corresponding to the CH_{imidazolidinium} carbons (Fig. S4-5). The IR spectra of both protio-ligands also exhibit stretches at 1624 (ν_{C=N}) cm⁻¹ characteristic of the imidazolidinium ring.



Scheme 1. Synthetic route for unsymmetrical *o*-hydroxyaryl substituted imidazolidinium salts **3a-c** [12].

2.2. Synthesis of bis-ligated *o*-hydroxyaryl substituted NHC titanium complexes **4a^H** and **4a^{Me}**

Following the synthetic route reported previously by Grubbs [6d], the *o*-hydroxyaryl substituted imidazolidinium salts **3a^H** and **3a^{Me}** were doubly deprotonated by two equivalent of potassium bis(trimethylsilyl)amide (KbtSa) for 10 min before to be treated with a 1M solution of TiCl₄ in toluene for 1 h leading to complexes **4a^H** and **4a^{Me}** as dark-red solids (Scheme 2). Attempts using other synthetic methods for the syntheses of NHC-group 4 complexes [8b, 9a-c], such as the direct addition of imidazolidinium salts to Ti(OiPr)₄ (alcohol elimination route) under different temperature conditions (room temperature to reflux) and solvents (toluene, THF), which should give in principle similar compounds, did not lead to the bis-ligated titanium complexes. It is interesting to note that the addition of one equivalent of deprotonated imidazolidinium salts **3a^H** or **3a^{Me}** to TiCl₄ mainly leads to the formation of bis-ligated NHC complexes of titanium as major products. The ¹H NMR spectra of **4a^H** and **4a^{Me}** show similar patterns, *i.e.* the disappearance of the CH_{imidazolidinium} proton and the appearance of a centrosymmetric multiplet assigned to the two pairs of NCH₂ protons on the NHC ring (Fig. S6-7). The symmetry of the multiplet and the small chemical shift range covered by the resonances suggest a strongly coupled AA'BB' spin system where each geminal pair of spins are magnetically non-equivalent. This pattern is consistent with a higher symmetry of compounds **4a^H**/**4a^{Me}**, either C_{2h} or C_{2v}-symmetry molecule in solution (Fig. S6-7). The ¹³C NMR spectra of both complexes **4a^H** or **4a^{Me}** confirm the NHC_{carbene} ligation to the titanium central atom with typical chemical resonances of the carbene at δ 206.7 and 206.8 ppm in benzene-*d*₆, respectively, (Fig. S8-9) [4g].



Scheme 2. Syntheses of bis-ligated *o*-hydroxyaryl NHC titanium complexes.

Single crystals of **4a^H** were obtained after few days from a saturated solution of the complex in dichloromethane at -30 °C. The molecular structure of **4a^H** was determined by single-crystal X-ray diffraction that confirms the chelation of two aryloxy-NHC ligands to titanium (Fig. 1). Compound **4a^H** crystallizes in the space group $P2_1/n$, corresponding to a C_{2h} -symmetry molecule which is consistent with the observed ^1H NMR spectrum in solution. As depicted in figure 1, the structure determined for **4a^H** shows that the titanium center adopts a nearly perfect octahedral geometry (Table 1). As previously reported for similar bis-ligated NHC titanium complex, *i.e.* cis - $([\kappa^2\text{-C,O}]\text{-Dipp,(3-Ad,5-Me)NHC})_2\text{TiCl}_2$ [6d], the two neutral NHC moieties are in *trans* position to each other ($\angle\text{C}_{\text{carbene}}\text{-Ti-C}_{\text{carbene}} = 180.00(8)^\circ$) for complex **4a^H** and for the complex cis - $([\kappa^2\text{-C,O}]\text{-Dipp,(3-Ad,5-Me)NHC})_2\text{TiCl}_2$ at $178.0(9)^\circ$ occupying the axial positions (Table 1 and Table S4-5). However unlike complex cis - $([\kappa^2\text{-C,O}]\text{-Dipp,(3-Ad,5-Me)NHC})_2\text{TiCl}_2$ having both two oxygen and two chloride atoms located in *cis* position ($\angle\text{O}_{\text{Ar}}\text{-Ti-O}_{\text{Ar}} = 88.35(7)^\circ$ and $\angle\text{Cl-Ti-Cl} = 96.04(3)^\circ$, respectively), complex **4a^H** has the two oxygen and two chloride atoms in *trans* to each other ($\angle\text{O}_{\text{Ar}}\text{-Ti-O}_{\text{Ar}} = 180.0^\circ$ and $\angle\text{Cl-Ti-Cl} = 180.0^\circ$). Contrary to complex cis - $([\kappa^2\text{-C,O}]\text{-Dipp,(3-Ad,5-Me)NHC})_2\text{TiCl}_2$ (which crystallizes as a C_2 -symmetry molecule, enantiomer Λ), where the *cis*-configuration is favored to avoid the steric repulsion between Dipp and bulky Ad substituents [6d], complex **4a^H** is lacking of such bulky substituents, and thus leading to the most thermodynamically stable *trans* configuration as recently demonstrated by density functional theory calculation on bis-ligated alkoxy-functionalized NHC-Zr systems [6f, g]. Due to the more effective way that both NHC ligands wrap around titanium in **4a^H** in this *trans*-configuration, the overall bond lengths (*i.e.* Ti-C_{carbene}, and at least one of -Cl and -O bonds) are shorter, and one of the bite angles ($\angle\text{O}_{\text{Ar}}\text{-Ti-C}_{\text{carbene}}$) is larger with a less pronounced deviation from planarity ($\angle\text{O}_{\text{Ar}}\text{-C}_{\text{Ar}}\text{-N-C}_{\text{carbene}}$) for one of the NHC ligands compared to the complex cis - $([\kappa^2\text{-C,O}]\text{-Dipp,(3-Ad,5-Me)NHC})_2\text{TiCl}_2$ (Table 1).

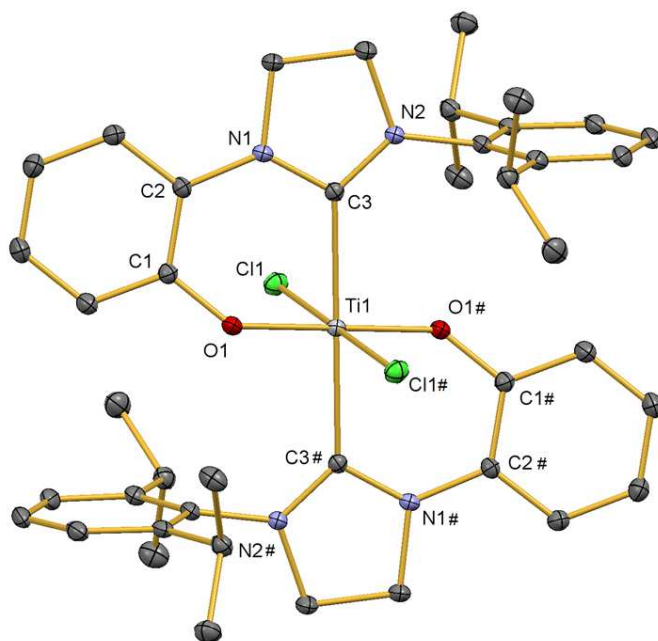


Fig. 1 Crystal structure of compound **4a^H** with anisotropic displacement parameters set at the 50% probability level. Hydrogen atoms and a co-crystallized solvent dichloromethane molecule are omitted for clarity. Selected bond distances, bond angles and torsions angles are listed in table 1. Symmetry code #: 1-x+1, -y+1, -z+1.

Table 1

Selected Bond Distances, Bond Angles and Torsion Angles for Bis-Ligated $([\kappa^2\text{-C,O}]\text{-Dipp,RNHC})_2\text{TiCl}_2$ complexes.

	<i>trans</i> - ($[\kappa^2\text{-C,O}]\text{-Dipp,4-HNHC})_2\text{TiCl}_2$ (4a^H)	<i>cis</i> - ($[\kappa^2\text{-C,O}]\text{-Dipp,(3-Ad,5-Me)NHC})_2\text{TiCl}_2$ ^a
Bond lengths (Å)		
Ti-C _{carbene}	2.2597(18)/2.2597(18)	2.264(3)/2.275(3)
Ti-O _{Ar}	1.8578(12)/1.8579(12)	1.870(1)/1.842(1)
Ti-Cl	2.3269(5)/2.3269(5)	2.337(8)/2.297(6)
Bond Angles (deg)		
C _{carbene} -Ti-C _{carbene}	180.00(8)	178.0(9)
O _{Ar} -Ti-O _{Ar}	180.0	88.35(7)
O _{Ar} -Ti-C _{carbene}	82.40(6)/82.40(6)	82.45(8)/80.43(8)
Cl-Ti-Cl	180.0	96.04(3)
O _{Ar} -Ti-Cl	90.71(4)/89.29(4)	169.14(5)/88.32(5)
C _{carbene} -Ti-Cl	84.73(4)/95.27(4)	88.15(6)/83.54(6)
Torsion Angles (deg)		
O _{Ar} -C _{Ar} -N-C _{carbene} ^b	10.65/-10.65	1.95/-19.21

^a Ref. [6d].

^b O_{Ar}-C_{Ar}-N-C_{carbene}: O1-C1-N1-C3/O1#-C1#-N1#-C3# for **4a^H** and O1-C21-N2-C1/O2-C53-N4-C33.

Although the steric hindrance could be conceptualized for both *trans* and *cis* bis-ligated complexes, the availability of solid-state molecular structures allows to calculate

the percent buried volume ($\%V_{bur}$, via SambVca 2.0 calculations) and visualize the steric maps for further comparisons of each substituents on NHC ligands [14]. To make a best comparison of both complexes, the analyses were made only by considering (κ^2 -C,O)-NHC)-Ti moiety and assuming a 3.5 Å radius of the sphere around the titanium for a Ti-C_{carbene} length of 2.26 Å. Figure 2 shows minor differences between the two unsymmetrical NHC moieties with nearly identical steric map and $\%V_{bur}$ (37.0 *vs.* 36.5); thus, making it difficult to appreciate the steric profiles of these ligands using a value of 3.5 Å, which best defines the steric hindrance in the first coordination sphere around the metal. The differences between those two ligands become more marked when increasing the spherical radius around the metal to 5.0 Å allowing taking in account the bulky groups not bound to the metal. The C_{2h} -symmetry steric map of the NHC ligand in **4a^H**, with $\%V_{bur}$ of 33.4, shows a rather flat steric map with two small bulges located in the northern and western quadrants (corresponding to the *i*Pr groups of *N*-Dipp substituent), and two large hollows which can easily accommodate two Cl atoms in *trans* to each other in the empty southern (SW, SE) and northern quadrants (NE). In contrast, the C_2 -symmetry steric map of *cis*-(κ^2 -C,O)-Dipp,(3-Ad,5-Me)NHC)₂TiCl₂ with $\%V_{bur}$ of 38.0 shows a non-flat steric map particularly in the south-eastern quadrant imposed by the upward-pointing Ad substituent and two narrow hollows (SW and NE quadrants). From these steric maps, it is clear that the *trans*-configuration observed in these bis-ligated titanium complexes (**4a^H** and **4a^{Me}**) is largely favored by the embedment of the second NHC ligand bearing a H as *ortho* substituent on the aromatic ring, and when replaced by the more hindered Ad substituent, only the *cis*-configuration with the second Ad substituent pointing downward (SW quadrant) is allowed among other configurations.

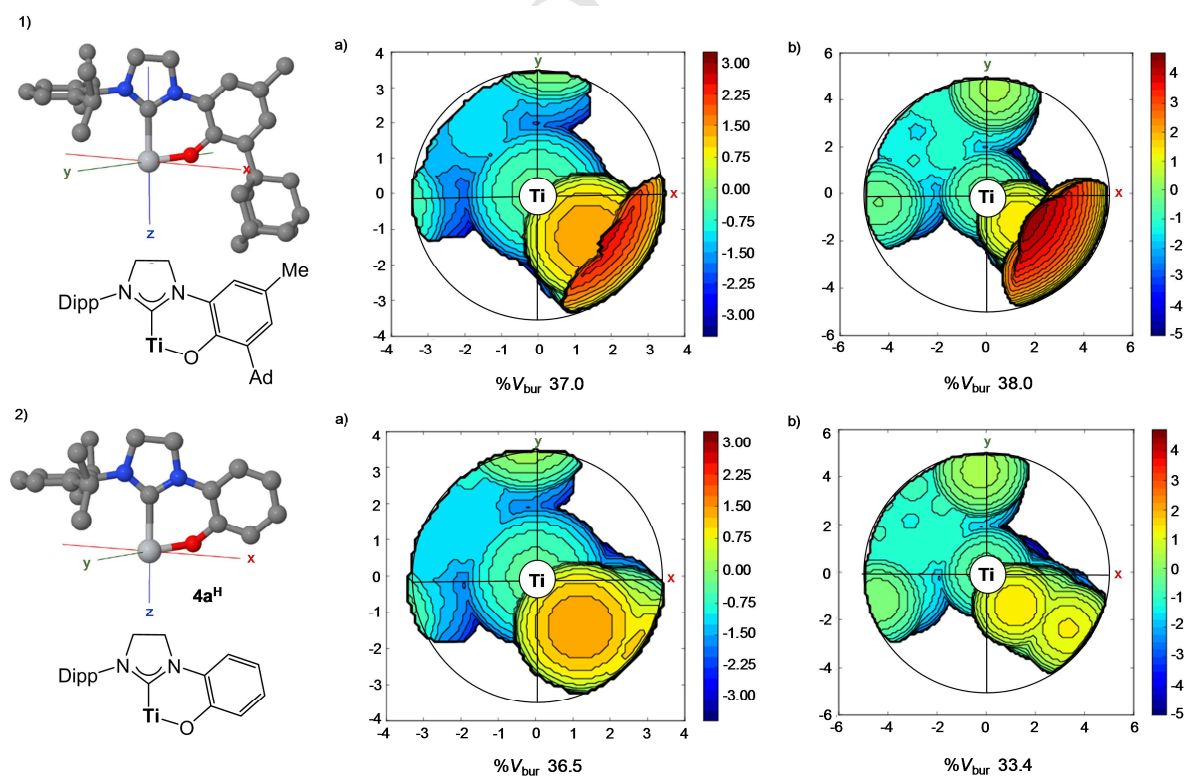
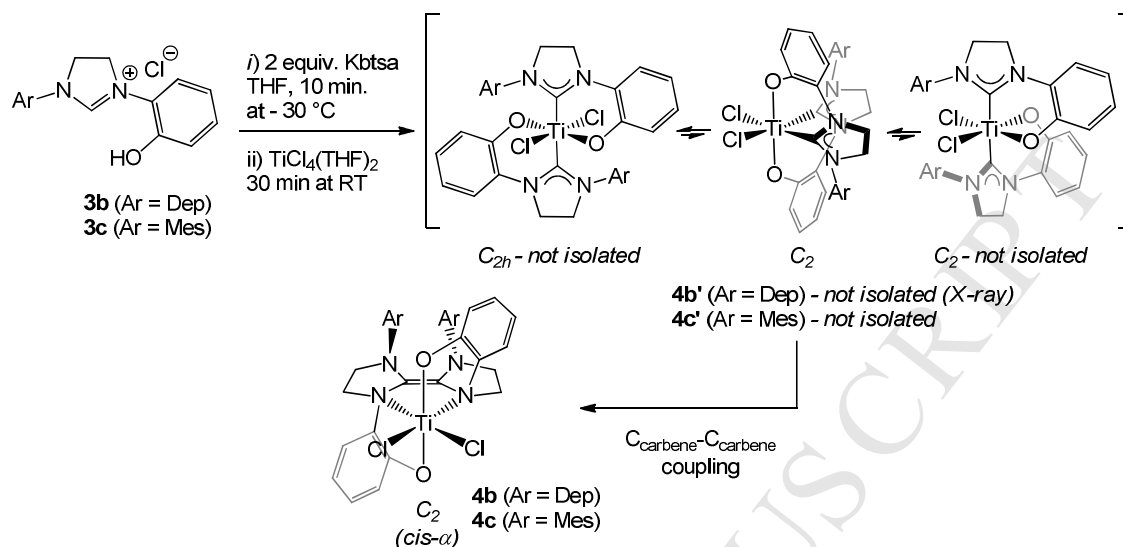


Fig. 2 Ball-and-stick representations and schemes (left) of bidentate ($[\kappa^2\text{-C,O}]\text{-NHC}$)-Ti moiety: 1) from *cis*- $[\kappa^2\text{-C,O}]\text{-Dipp,(3-Ad,5-Me)NHC}_2\text{TiCl}_2$ [6d] and 2) from complex **4a^H** with their respective steric maps (right) calculated with a sphere radius of: a) 3.5 Å and b) 5.0 Å [15]. The steric maps of these complexes are oriented in a Cartesian frame with a transverse xy-plane and a +z-axis pointing upward.

Following the synthesis route described for the aforementioned complexes **4a^H** and **4a^{Me}**, the doubly deprotonated *o*-hydroxyaryl imidazolidinium salts **3b** and **3c** bearing less sterically hindered *N*-substituents (Dep and Mes, respectively) were treated by a solution of TiCl_4 consistently giving a mixture of products. Although the disappearance of $\text{CH}_{\text{imidazolidinium}}$ and hydroxyl protons were observed for both mixtures in their respective ^1H NMR spectra, there are numerous overlapping multiple sets of signals corresponding to one or several major species in solution along with a number of other minor resonances, which are poorly resolved and nearly indiscernible from the baseline (Figure S6-7). Although the elemental analyses are reasonably consistent with the following formulation, *i.e.* bis-ligated dichlorotitanium complexes, the ^1H NMR spectra of the Dep- and Mes-substituted NHC titanium complexes show very different patterns compared to the complexes **4a^H** and **4a^{Me}** (Fig. S10-11). The notable differences are mainly observed in the splitting of resonances assigned to the two pairs of NCH_2 protons into several different proton signals with scalar couplings between all of them (for *N*-dep: three multiplets with integral ratios of 2:4:2, and for *N*-Mes: four multiplets with integral ratios of 2:2:2:2). This is in contrast to the previously observed AA'BB' spin system for **4a^H** and **4a^{Me}**. The ^{13}C NMR spectra of **4b** and **4c** (Fig. S12-13) contain no visible $\text{C}_{\text{carbene}}$ resonances in the expected range of those observed for **4a^H** and **4a^{Me}** complexes, and the combined 2D NMR analyses (^1H - ^1H COSY and ^1H - ^{13}C HSQC NMR spectra, Fig. S14-17) indicate that the major species is corresponding only to one compound in solution for both complexes. Intrigued by the observed ^1H NMR signals, further information was obtained by simulating the NMR spectra of **4b**, **4c** and **4a^H** with the Daisy module of the TopSpin program (Fig. S18-20). For **4c** the experimental data and simulations fit very well with an unambiguous, and close to first-order, AMRX spin system consisting of four chemically non-equivalent protons. The corresponding multiplets for **4b** are better denoted as an AMNX spin system as two of the multiplets almost overlap [16]. Taken together, these observations indicate that complexes **4b** and **4c** do not comprise a mirror plan anymore, contrary to *trans*-complexes **4a^H** and **4a^{Me}** with their AA'BB' spin systems (Figure S6-7). All combined results imply that complexes **4b** and **4c** have a low symmetry compared to **4a^H**/**4a^{Me}**, but still possessing two-fold symmetry, which is consistent with C_2 -symmetry molecules, meaning that four stereoisomers are structurally possible in solution (Scheme S1). Non-symmetric bis-ligated titanium complexes of C_1 -symmetry (including enantiomers Λ and Δ) were not considered here due to the unfavorable coordination mode for such bidentate aryl-substituted NHC ligands (collision between aryl-*N* substituents and the NHC ring) and the ^1H NMR pattern for the NCH_2 signals should have given rise to eight different ^1H chemical shifts for the two NCH_2 moieties. Attempts to grow crystals of suitable quality for X-ray analysis were unsuccessful, except for Dep-substituted NHC titanium complex which crystallized in a saturated solution of toluene at -30°C . The crystal structure as outlined in figure 3 reveals that out of the four expected stereoisomers for the bis-ligated titanium complexes *cis*- $[\kappa^2\text{-C,O}]\text{-dep,4-HNHC}_2\text{TiCl}_2$ none are formed, but

an unexpected complex $cis-([\kappa^4\text{-O,N,N,O}]_{\text{-dep,4-H}}\text{bis}(\text{imidazolidinylidene})\text{TiCl}_2$ (**4b**) containing a folded tetradentate salen-like ligand wraps around the titanium center in *fac-fac* binding mode with two chloride atoms in *cis* position (Scheme 3).



Scheme 3. Syntheses of **4b-c** and proposed intermediates (C_2 -enantiomer Λ of bis-ligated titanium complexes are not shown).

The X-ray structure of **4b** shows a distorted octahedral arrangement around the titanium center, with two oxygen atoms in *trans* position ($\angle \text{O}_{\text{Ar}}\text{-Ti-O}_{\text{Ar}}$ angle of $160.00(14)^\circ$) and two chloride atoms and two nitrogen atoms located in *cis* positions to each other with angles of $105.65(6)^\circ$ and $76.48(13)^\circ$, respectively. The crystal structure of **4b** shows an approximate C_2 -symmetrical isomer belonging to a rare class of *cis- α* -configuration [17] (versus the more stable *trans*- or *cis- β* -configurations [18], defined for tetradentate salen-type complexes), and reveals that the stereochemistry of the titanium center is Λ (Scheme S2). The bond lengths between Ti-O and Ti-N *ca.* 1.87 and 2.24 Å respectively, fall in the range of other known Ti-O/Ti-N bond lengths in *cis- α* -salen-like titanium complexes [17c, d, 17f-h], while the Ti-Cl bond lengths (*ca.* 2.25 Å) are shorter than those reported for the *trans*- or *cis- β* -(salen)TiCl₂ complexes (*ca.* 2.36 Å) [19]. Those observations show that the tetradentate ligand in **4b** is folded backward and is more compact around the titanium atom most likely due to the formation of five-membered rings (Ti-O-C_{Ar}-C_{Ar}-N), thus imposing such *cis- α* -configuration and short bond lengths contrary to the six-membered rings in typical salen-type complexes. The bond length of 1.345(6) Å for the dimerized $C_{\text{carbene}}\text{-}C_{\text{carbene}}$ is in the expected range for an isolated double bond and comparable to the only example reported by Lappert; *i.e.* ($[\kappa^2\text{-N,N}]$ -bis(imidazolidinylidene)-Cr(CO)₄ complex with $C_{\text{carbene}}\text{-}C_{\text{carbene}}$ bond length of 1.337(7) Å [20]. In analogy with complex **4b** featuring similar spectroscopic data (absence of NHC_{carbene} signal and same spin systems for the NCH₂ moieties) for the Mes-substituted NHC titanium complex, also probably indicate the formation of the *cis-([\kappa^4\text{-O,N,N,O}]_{\text{-Mes,4-H}}\text{bis}(\text{imidazolidinylidene})\text{TiCl}_2 (**4c**) as major isomer (Scheme 3), along with two other minor unidentified isomers (estimated by the integration of methyl groups of the *N*-mesityl substituent by ¹H NMR spectroscopy). Additional experiments in order to get more information about the other minor isomer(s) were attempted, and it was possible to cocrystallize **4b** crystals along with few other single crystals suitable for X-ray analysis.*

The crystal structure of this minor isomer reveals a bis-ligated titanium octahedral complex, *i.e.* $cis-([\kappa^2-C,O]^{-Dep,(4-H)}NHC)_2TiCl_2$ **4b'**, crystallizing as a non-crystallographic C_2 -symmetry molecule, enantiomer Λ (Scheme 3 and Scheme S1). In this case, contrary to $cis-([\kappa^2-C,O]^{-Dipp,(3-Ad,5-Me)}NHC)_2TiCl_2$, both two neutral NHC moieties and two chloride atoms are located in *cis* positions ($\angle C_{carbene}-Ti-C_{carbene} = 83.50(7)^\circ$ and $\angle Cl-Ti-Cl = 105.17(3)^\circ$, respectively), with the oxygen atoms in *trans* position ($\angle O_{Ar}-Ti-O_{Ar} = 173.25(7)^\circ$) (Figure S21 and Tables S8-10). The bond lengths Ti- $C_{carbene}$, Ti-O and Ti-Cl are in the range of those aforementioned for **4a^H** and $cis-([\kappa^2-C,O]^{-Dipp,(3-Ad,5-Me)}NHC)_2TiCl_2$. Unfortunately, due to the low amount of **4b'** further characterizations could not be achieved.

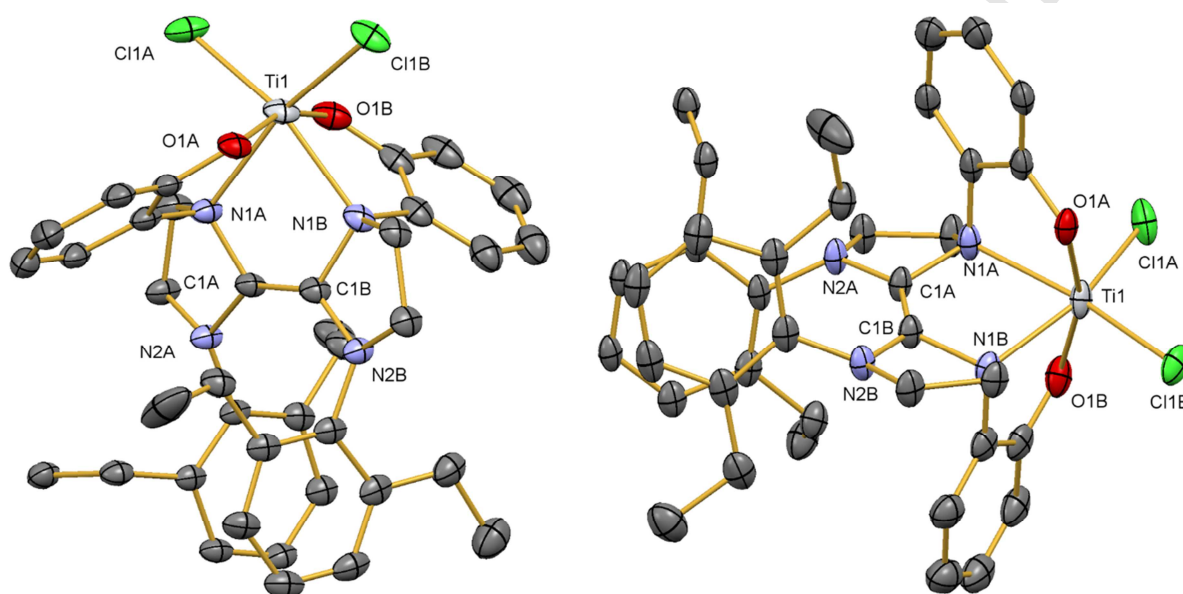


Fig. 3 Crystal structure of compound **4b** (left view along the vertical non-crystallographic C_2 -axis and right along the horizontal non-crystallographic C_2 -axis) with anisotropic displacement parameters set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances, bond angles and torsions angles are listed in tables S6-7.

In order to rationalize these results, we envisage that the steric map and the calculated $\%V_{bur}$ based on the X-ray data obtained for **4b** and **4a^H** (*i.e.* by replacing the *i*Pr groups from the *N*-Dipp substituent in **4a^H** by Me groups) could adequately mimic the *N*-dep and *N*-Mes substituents, respectively, and give an insight to the trend of reactivity (Fig. 4 and Fig. S22). Interestingly, the simulated steric maps of this bidentate NHC bearing *N*-Dep and *pseudo N*-Mes' substituent are substantially flat for both sphere radii of 3.5 and 5 Å in the NW and SE quadrants (with inferior $\%V_{bur}$), with two large hollows in the adjacent quadrants. Through these steric maps and the previous ones, it can be deduced that the *ortho* bulky *i*Pr groups on the *N*-Dipp are the steric driving force leading mostly to *trans*-configuration complexes (in absence of *ortho* bulky group on the aromatic ring). When those *N*-aryl substituents are exchanged by less bulky groups (here Et or Me), there is a lack of steric hindrance to inhibit the formation

of several species, which is leading most likely in our case to uncontrolled formation of several bis-ligated stereoisomers (Scheme S1).

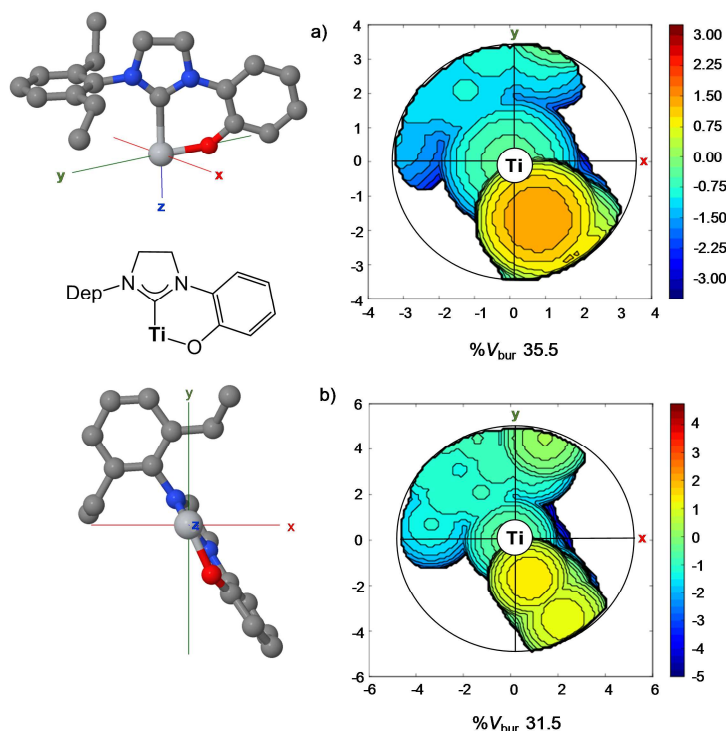


Fig. 4 Ball-and-stick representation, scheme (left) and projection (right) of the simulated steric map for a bidentate ($[\kappa^2\text{-C,O}]^{\text{-Dep,4-HNHC}}\text{-Ti}$) moiety with a sphere radius of a) 3.5 Å and b) 5.0 Å [15]. The steric maps of these complexes are oriented in a Cartesian frame with a transverse xy -plane and a $+z$ -axis pointing upward.

Although it is not clear whether the dimerization of NHCs observed for the *cis*-($[\kappa^4\text{-O,N,N,O}]\text{-bis(imidazolidinylidene)TiCl}_2$) complexes is metal-assisted or runs via a dissociated free-carbene, the ^1H NMR spectrum recorded after a couple of minutes of reaction with chloro-titanium precursor and the deprotonated **3b** protio-ligand show that several species are present in solution based on the proton signals of NCH_2 moieties. The NMR data of this mixture clearly show the formation of **4b** as the principal isomer ($\approx 48\%$) along with another major isomer ($\approx 39\%$) featuring a AMRX spin system pattern (four multiplets of 2:2:2:2 ratios) assigned to a C_2 -symmetry complex, which could correspond to one of bis-ligated titanium complexes *cis*-($[\kappa^2\text{-C,O}]^{\text{-dep,4-HNHC}}\text{)}_2\text{TiCl}_2$ (Scheme S23-24). Among the other minor isomers, only one is nearly discernible from the baseline ($\approx 13\%$) showing an AA'BB' spin system for the NCH_2 moieties (centrosymmetric multiplets) along with another doublet of doublets signal centered at 5.70 ppm (doublet of doublet assigned to Ar-H) characteristic of previous ^1H NMR pattern of **4a^H** and **4a^{Me}** suggesting the formation of a C_{2h} -symmetry bis-ligated titanium complex *trans*-($[\kappa^2\text{-C,O}]^{\text{-dep,4-HNHC}}\text{)}_2\text{TiCl}_2$. This NMR investigation confirms the conclusions obtained from the simulated steric maps with the less bulky *N*-aryl substituents (Dep and Mes), in which such substituents cannot hamper the formation of other stereoisomers of C_2 -symmetry (Scheme 3). Furthermore, the formation of several isomers suggests that the coupling of $\text{C}_{\text{carbene}}\text{-C}_{\text{carbene}}$ is most probably metal-assisted and might occur through the rearrangement of those *cis*- and *trans*-bis-ligated titanium

intermediates of C_2 - or C_{2h} -symmetry toward a C_2 -symmetric *cis*-carbene stereoisomer **4b'**, reasonably assumed to favor such coupling leading to **4b** (Scheme 3).

2.3. Polymerization Studies

Following previous studies on the copolymerization of epoxides and CO_2 catalyzed by group 4 metal complexes bearing benzotriazole alkoxide [21], bis(salphen) [22] ligands, showing structural similarities with our current 6-coordinate bis-ligated bidentate aryloxy NHC titanium complexes, and the highly selective catalysts based on the tridentate bis-aryloxy NHC complexes of group 4 [9a, c], we were interested in evaluating these complexes in the copolymerization of epoxides with CO_2 . Copolymerization experiments of CHO with CO_2 were performed by using **4a^H**, **4a^{Me}**, **4b-c** and *cis*- $([\kappa^2-C,O]-Dipp,(3-Ad,5-Me)NHC)_2TiCl_2$ compounds in the presence of most common co-catalysts such as [PPN]Cl, [PPN]N₃ and [Bu₄N]Cl to form the putative anionic catalysts [9]. The copolymerization of neat CHO with CO_2 shows no polycarbonate formation (conditions: 1 bar of CO_2 at 60 °C, ratio CHO:Ti = 2500:1) or other side-products such as cyclohexene carbonate or poly(cyclohexene oxide) ring-opening polymerization of CHO. The absence of activity is probably due to the steric congestion around the metal center and/or high stability avoiding the association of the co-catalysts nucleophile to form the “activated” species [9a, c] and/or the epoxide.

Due to the previous studies based on (non-)metallocene and phenoxy-imine catalysts development and their impact on the coordination polymerization of olefins for shaping tailored microstructure of polymers or synthesizing oligomers [11e, 23], systems based on functionalized NHC group 4 catalysts, especially the ones bearing multidentate and asymmetric auxiliary NHC ligands, have been recently explored for the α -olefins polymerization [6a-g, 6l, 24] and 1-hexene trimerization catalysis [6j]. More recently, a series of C_2 -symmetric bidentate *o*-hydroxyaryl unsymmetrically substituted NHC ligands of group 4 were found moderately active in ethylene [6d, f, g, l], ethylene/1-octene and ethylene/norbornene [6d] (co-)polymerization, and stereoselective in propylene (isotactic up to ca. 70%) [6f, g] and styrene (syndiotactic up to ca. 99% in *rrrrrr* heptads) polymerization [6l]. The preliminary reported performance on C_2 -symmetric and sterically hindered *cisoid* catalyst (*cis*- $([\kappa^2-C,O]-Dipp,(3-Ad,5-Me)NHC)_2TiCl_2$) in (co)polymerization show moderate and excellent stereoselectivity in α -olefins polymerization [6d, l], we were interested to evaluate the performance of the sterically less hindered **4a^H** and **4a^{Me}** catalysts with different spatial configuration (*transoid*). Thus, next to the *cis*- $([\kappa^2-C,O]-Dipp,(3-Ad,5-Me)NHC)_2TiCl_2$ catalyst, the newly synthesized compounds **4a^H** and **4a^{Me}** were examined for ethylene polymerization in the presence of 500 equiv. of MAO as co-catalyst. The preliminary polymerization results show that *trans*-**4a^H** and **4a^{Me}** catalysts have a moderate overall activity: 1206 and 1453 g_{PE} mmol_{Ti}⁻¹ h⁻¹ (conditions: 40 bar of ethylene at room temperature and quenched after 5 min.), respectively, which are comparable to other group 4 systems [11e, 23]. However, the activities of both catalysts remain slightly superior to the benchmark catalyst *cis*- $([\kappa^2-C,O]-Dipp,(3-Ad,5-Me)NHC)_2TiCl_2$ (1131 g_{PE} mmol_{Ti}⁻¹ h⁻¹) under similar conditions [6d, l]. The difference in activity in this case is mostly assigned to the extremely bulky bidentate aryloxy NHC ligand wrapping the titanium center, notably with its Ad substituent retarding the ethylene association to the metal rather than the *cis/transoid*

configuration itself. The reactivity in ethylene polymerization of **4b** and **4c** were also explored under the same conditions, and no significant effects were observed in term of activity for the wrapped tetradentate ligands around titanium compared to the *cis*- or *trans*-bis-ligated titanium complexes (1113 and 1047 g_{PE} mmol_{Ti}⁻¹ h⁻¹, respectively).

3. Conclusions

In summary, we have successfully synthesized a set of *o*-hydroxyaryl-substituted NHC ligands and the corresponding bis(aryloxide-NHC) titanium complexes. The bulky *N*-aryl substituent (such as Dipp *vs.* Mes and Dep) at the NHCs combined with the other *ortho*-substituent on the *N*-aryloxy moieties appear essential for leading to a single stereoisomer. Meaning that both steric factors have a significant effect on the configuration (*trans* or *cis*) of the final bis-ligated titanium complex, which can be fine-tuned by varying the size of the *N*-functional groups on the NHCs. Without such bulky *N*-aryl (*i.e.* Mes and Dep) and *ortho-N*-aryloxy (*i.e.* H) substituents, several bis-ligated stereoisomers of titanium are formed which subsequently rearrange into a tetradentate salophen-like ligand of titanium via the coupling of NHCs. The *trans*-bis(aryloxide-NHC) and *cis*-bis(imidazolidinylidene) complexes of titanium show moderate catalytic activities in ethylene polymerization, and the *N*-substituents at the NHCs and the *cis/trans*-configurations have modest effect on the activity.

4. Experimental

4.1. General procedures

All operations were performed with rigorous exclusion of air and water, using standard Schlenk, high-vacuum and glovebox techniques (MB Braun MB200B-G; <1 ppm O₂, <1 ppm H₂O). Dichloromethane, hexane, THF and toluene were purified by using Grubbs columns (MB Braun Solvent Purification System 800). Benzene-*d*₆ and chloroform-*d* (99.96%) were obtained from Aldrich, dried over sodium or CaH₂, vacuum transferred, degassed and filtered prior to use. All other chemicals were purchased from Aldrich and used as received. The oxanilic acid ethyl esters (**1a** and **1c**), oxalamides (**2a^H** and **2c**), unsymmetrical *o*-hydroxyaryl substituted imidazolidinium chloride salts (**3a^H** and **3c**) and (*cis*-[κ²-C,O]-Dipp,*3-Ad*/5-MeNHC)₂TiCl₂ were prepared according to the literature procedures [6d, 12]. The imidazolidinium chloride salt **3c** was crystallized from acetonitrile/hexane (1/5) at -30 °C. The NMR spectra of air and moisture sensitive compounds were recorded using J. Young valve NMR tubes at 298 K on Bruker BioSpin AVANCE DMX400 spectrometer (5 mm Broadband observe probehead (BBO), ¹H: 400.13 MHz; ¹³C: 100.62 MHz) and a Bruker BioSpin AVANCE AV500 (5 mm BBO, ¹H: 500.13 MHz; ¹³C: 125.77 MHz) and AV600 (5 mm triple resonance inverse CryoProbe, ¹H: 600.13 MHz; ¹³C: 150.91 MHz). ¹H and ¹³C shifts are referenced to internal solvent resonances and reported in *parts per million* (ppm) relative to TMS. Fitting of simulated spectral regions to experimental ¹H NMR data was performed with the Daisy module supplied with the TopSpin package [25]. IR spectra were recorded on a Nicolet FT-IR Protégé 460 spectrometer with a DRIFT collector. The

spectra were averaged over 64 scans; the resolution was ± 4 cm⁻¹. Elemental analyses of C, H and N were performed on an Elementar Vario EL III instrument.

4.2. Unsymmetrical *o*-hydroxyaryl-substituted imidazolidinium protio-ligand syntheses

4.2.1. 1-(2,6-diisopropylphenyl)-3-(2-hydroxy-4-methylphenyl)-4,5-dihydro-imidazolyl chloride salt (**3a^{Me}**)

Compound *N*-(2,6-diisopropylphenyl)-oxanilic acid ethyl ester **1a** (1.71 g, 6.15 mmol) and 2-amino-5-methylphenol (1 equiv., 758 mg, 6.15 mmol) were dissolved in toluene (100 mL), and 0.86 mL of NEt₃ (1 equiv., 6.15 mmol) was added under inert atmosphere. The suspension was stirred and heated to reflux overnight. After cooling down the solution, a precipitate was obtained which was dissolved in EtOAc. The solution was washed with 2 M HCl (2x100 mL). The aqueous phase was then washed with EtOAc and the combined organic phases were washed with brine, dried over MgSO₄ and dried under vacuum. The solid was crystallized from warm toluene to afford *N*-(2,6-diisopropylphenyl)-*N'*-(2-hydroxy-4-methylphenyl)-oxalamide **2a^{Me}** (1.47 g, 67% yield). ¹H NMR (400.13 MHz, chloroform-*d*): δ 9.56 (s, 1H, NH), 8.81 (s, 1H, NH), 8.25 (s, 1H, OH), 7.37 (t, *J* = 7.8 Hz, 1H, Ar_{Dipp}-H), 7.24 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.23 (d, *J* = 7.8 Hz, 1H, Ar_{Dipp}-H), 6.84 (s, 1H, Ar-H), 6.74 (d, *J* = 8.2 Hz, 1H, Ar-H), 3.02 (sept., *J* = 6.9 Hz, 2H, CH(CH₃)₂), 2.32 (s, 3H, Ar-CH₃), 1.22 (d, *J* = 6.9 Hz, 12H, CH(CH₃)₂) ppm.

Under inert atmosphere, to compound **2a^{Me}** (1.47 g, 4.15 mmol) was added 33.2 mL BH₃-THF (8 equiv., 1M in THF) and the mixture was heated to reflux overnight. After cooling down to room temperature, MeOH was added to the reaction mixture until gas evolution cease and then quenched by \approx 1.5 mL of conc. HCl. The mixture was dried, dissolved in MeOH and these steps were repeated two more times. To this pale pink solid was added 15 mL of triethyl orthoformate and the solution was stirred at room temperature overnight. The solid was filtered off, washed with Et₂O and dried under vacuum to afford **3a^{Me}** as a white solid (1.20 g, 78% yield). ¹H NMR (500.13 MHz, chloroform-*d*): δ 9.09 (s, 1H, NCHN), 7.49-7.45 (m, 2H, Ar-H), 7.24 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.85 (bs, 1H, Ar-H), 6.80 (bd, 1H, Ar-H), 4.86 (bm, 2H, NCH₂), 4.39 (bm, 2H, NCH₂), 3.00 (sept., *J* = 6.8 Hz, 2H, CH(CH₃)₂), 2.18 (s, 3H, Ar-CH₃), 1.28 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.16 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂) ppm. ¹³C NMR (125.77 MHz, chloroform-*d*): δ 156.6 (NCHN), 149.6 (*C*_{ipso}, O-Ar), 146.6 (*C*_q, Ar), 139.3 (*C*_q, Ar), 131.5 (*C*_q, Ar), 130.0 (*C*_q, Ar), 125.1 (CH, Ar), 120.5 (CH, Ar), 120.1 (CH, Ar), 119.8 (CH, Ar), 119.1 (CH, Ar), 52.5 (NCH₂), 51.0 (NCH₂), 28.9 (CH(CH₃)₂), 25.0 (CH(CH₃)₂), 24.3 (CH(CH₃)₂), 21.1 (Ar-CH₃) ppm. DRIFT (v/cm⁻¹): 2970s, 2958s, 2868s, 1624vs, 1588w, 1553w, 1526w, 1494w, 1476w, 1457m, 1420m, 1385w, 1368w, 1335w, 1311m, 1292s, 1283m, 1263s, 1185w, 1166w, 945w, 879w, 812m, 764w, 593w, 487w, 456w. Anal. Calcd for C₂₂H₂₉ClN₂O: C, 68.98; H, 7.01; N 8.47. Found: C, 69.16; H, 7.26; N, 8.40.

4.2.2. 1-(2,6-diethylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl chloride (**3b**)

2,6-diethylaniline (10 mL, 60.7 mmol) and triethylamine (1 equiv., 8.5 mL, 60.7 mmol) were dissolved in dry THF (80 mL). After cooling down the solution at 0 °C, 6.8 mL of ethyl chloroacetate (1 equiv., 60.7 mmol) was added dropwise leading to a formation of smoke and white solid. The solution was allowed to warm up at room temperature and stirred overnight. The solid was filtered off and the organic phase was washed with HCl 2M (2x100 mL). The aqueous phase was then washed with EtOAc and the combined organic phases were washed with brine, dry over MgSO₄ and dry under vacuum to afford *N*-(2,6-diethylphenyl)-oxanilic acid ethyl ester **1b** as white solid (11.23 g, 75% yield). ¹H NMR (500.13 MHz, chloroform-*d*): δ 8.40 (s, 1H, NH), 7.27 (t, *J* = 7.6 Hz, 1H, Ar_{Dep}-H), 7.15 (d, *J* = 7.6 Hz, 2H, Ar_{Dep}-H), 4.44 (q, *J* = 7.2 Hz, 2H, O-CH₂-CH₃), 2.59 (q, *J* = 7.6 Hz, 4H, CH₂-CH₃), 1.45 (t, *J* = 7.2 Hz, 3H, O-CH₂-CH₃), 1.20 (t, *J* = 7.6 Hz, 6H, CH₂-CH₃) ppm. ¹³C NMR (125.77 MHz, chloroform-*d*): δ 161.0 (CO, carbimide), 155.4 (CO, ester), 141.1 5 (C_q, Ar), 130.9 (C_q, Ar), 128.6 (CH, Ar), 126.5 (CH, Ar), 63.7 (CH₂, O-CH₂-CH₃), 24.8 (CH₂, CH₂-CH₃), 14.3 (CH₃, O-CH₂-CH₃), 14.0 (CH₃, CH₂-CH₃) ppm.

Compound **1b** (10.96 g, 43.57 mmol) and 2-aminophenol (1 equiv., 4.80 mg, 43.97 mmol) were dissolved in toluene (100 mL), and 12.3 mL of NEt₃ (1 equiv., 87.9 mmol) was added under inert atmosphere. The suspension was stirred and heated to reflux overnight. After cooling down the solution a precipitate was obtained, which was dissolved in dichloromethane. The solution was washed with 2 M HCl (2x100 mL). The aqueous phase was then washed with dichloromethane and the combined organic phases were washed with brine, dried over MgSO₄ and dried under vacuum. The solid was crystallized from warm toluene to afford *N*-(2,6-diethylphenyl)-*N'*-(2-hydroxyphenyl)-oxalamide **2b** (10.06 g, 73% yield). ¹H NMR (500.13 MHz, chloroform-*d*): δ 9.68 (s, 1H, NH), 8.88 (s, 1H, NH), 8.06 (s, 1H, OH), 7.50 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 1H, Ar_{Dep}-H), 7.30 (m, 1H, Ar-H), 7.18 (s, 1H, Ar_{Dep}-H), 7.17 (s, 1H, Ar_{Dep}-H), 7.15 (m, 1H, Ar-H), 6.97 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 1H, Ar_{Dep}-H), 6.92 (m, 1H, Ar-H), 2.61 (q, *J* = 7.6 Hz, 4H, CH₂-CH₃), 1.21 (t, *J* = 7.6 Hz, 6H, CH₂-CH₃) ppm.

Following the procedure described for **3a^{Me}**, the reaction of **2b** (1.92 g, 6 mmol) and 49.2 mL of BH₃-THF (8 equiv., 1M in THF) yielded **3b** (1.6 g, 81% yield) as a white solid. ¹H NMR (500.13 MHz, chloroform-*d*): δ 8.96 (s, 1H, NCHN), 7.57 (d, *J* = 8.2 Hz, 1H, Ar_{Dep}-H), 7.41 (t, *J* = 7.8 Hz, 1H, Ar-H), 7.20 (d, *J* = 7.8 Hz, 2H, Ar_{Dep}-H), 7.10 (d, *J* = 7.8 Hz, Ar-H), 6.96 (t, *J* = 7.7 Hz, 1H, Ar-H), 6.77 (t, *J* = 7.7 Hz, 1H, Ar-H), 4.86 (bt, *J* = 10.4 Hz, 2H, NCH₂), 4.42 (bt, *J* = 10.4 Hz, 2H, NCH₂), 2.64 (q, *J* = 7.5 Hz, 4H, CH₂-CH₃), 1.22 (t, *J* = 7.5 Hz, 6H, CH₂-CH₃) ppm. ¹³C NMR (125.77 MHz, chloroform-*d*): δ 157.2 (NCHN), 150.0 (C_{ipso}, O-Ar), 141.6 (C_q, Ar), 131.8 (C_q, Ar), 131.2 (C_q, Ar), 128.8 (CH, Ar), 127.6 (CH, Ar), 122.7 (CH, Ar), 120.3 (CH, Ar), 119.9 (CH, Ar), 118.9 (CH, Ar), 51.5 (NCH₂), 51.0 (NCH₂), 24.3 (CH₂, CH₂-CH₃), 15.2 (CH₃, CH₂-CH₃) ppm. DRIFT (v/cm⁻¹): 2971s, 2959s, 2869s, 1624vs, 1588w, 1555w, 1525w, 1494w, 1476w, 1457m, 1421m, 1385w, 1368w, 1337w, 1313m, 1292s, 1284m, 1263s, 1186w, 1166w, 945w, 880w, 812m, 763w, 593w, 487w, 455w. Anal. Calcd for C₁₉H₂₃ClN₂O: C, 68.97; H, 7.01; N 8.47. Found: C, 68.79; H, 7.26; N, 8.36.

4.3. Preparation of bis-ligated *o*-hydroxyaryl substituted NHC titanium(IV) complexes

4.3.1. *bis*(1-(2,6-diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl) titanium(IV) dichloride (**4a^H**)

In a vial 1-(2,6-diisopropylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl chloride salt **3a^H** (588.0 mg, 1.64 mmol) and potassium bis(trimethylsilyl)amide (2 equiv., 561.35 mg, 3.27 mmol) were dissolved in THF (3 mL), and the resulting yellow suspended mixture was stirred for 10 min at room temperature. To this mixture was added 0.82 mL of a solution of 1M titanium tetrachloride in toluene (0.5 equiv., 0.82 mmol) in 2 mL THF. The solution rapidly turned dark red and was allowed to stir for 2 h at room temperature. Subsequent centrifugation, filtration and evaporation to dryness afforded complex **4a^H** as a dark red solid in quantitative yield. Crystals of **4a^H** were obtained from a saturated solution of dichloromethane at -30 °C for several days. ¹H NMR (500.13 MHz, benzene-*d*₆): δ 7.42 (t, *J* = 7.7 Hz, 2H, Ar_{Dipp}-H), 7.29 (d, *J* = 7.7 Hz, 4H, Ar_{Dipp}-H), 7.01 (m, 2H, Ar-H), 6.75 (m, 2H, Ar-H), 6.37 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 2H, Ar-H), 5.26 (dd, *J* = 8.1 Hz, *J* = 1.4 Hz, 2H, Ar-H), 3.47 (sept., *J* = 6.8 Hz, 4H, CH(CH₃)₂), 3.07 (m, 4H, NCH₂), 2.95 (m, 4H, NCH₂), 1.56 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.10 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂) ppm. ¹³C NMR (125.77 MHz, benzene-*d*₆): δ 206.7 (NCN), 155.0 (*C*_{ipso}, O-Ar), 148.0 (*C*_q, Ar), 137.8 (*C*_q, Ar), 133.6 (*C*_q, Ar), 129.2 (CH, Ar), 125.3 (CH, Ar), 124.0 (CH, Ar), 119.3 (CH, Ar), 118.1 (CH, Ar), 116.7 (CH, Ar), 53.9 (NCH₂), 47.3 (NCH₂), 28.5 (CH(CH₃)₂), 26.2 (CH(CH₃)₂), 24.8 (CH(CH₃)₂) ppm. DRIFT (v/cm⁻¹): 3065w, 3031w, 2961s, 2925m, 2867m, 1610m, 1587m, 1495vs, 1474vs, 1429s, 1408s, 1385w, 1363w, 1317s, 1288vs, 1236m, 1123w, 1056w, 996w, 912m, 879m, 806w, 750m, 671m, 640w, 453w, 438w, 418m. Anal. Calcd for C₄₂H₅₀Cl₂N₄O₂Ti.2CH₂Cl₂: C, 56.73; H, 5.84; N 6.01. Found: C, 57.04; H, 6.18; N 5.94.

4.3.2. *bis*(1-(2,6-diisopropylphenyl)-3-(2-hydroxy-4-methylphenyl)-4,5-dihydro-imidazolyl) titanium(IV) dichloride (**4a^{Me}**)

Following the procedure described for **4a^H**, the reaction of 1-(2,6-diisopropylphenyl)-3-(2-hydroxy-4-methylphenyl)-4,5-dihydro-imidazolyl chloride salt **3a^{Me}** (350.8 mg, 0.94 mmol), potassium bis(trimethylsilyl)amide (2 equiv., 375.2 mg, 1.88 mmol) and titanium tetrachloride (0.5 equiv., 0.47 mL, 0.82 mmol) yielded majorly **4a^{Me}**. The residual impurities were removed by stirring compound **4a^{Me}** in toluene (5 mL) at 70 °C for two days and **4a^{Me}** was isolated after centrifugation, filtration and evaporation to dryness as a brown dark solid (241 mg, 65% yield). ¹H NMR (500.13 MHz, benzene-*d*₆): δ 7.47 (t, *J* = 7.8 Hz, 2H, Ar_{Dipp}-H), 7.32 (d, *J* = 7.8 Hz, 4H, Ar_{Dipp}-H), 6.78 (dd, *J* = 8.2 Hz, *J* = 1.5 Hz, 2H, Ar-H), 6.15 (d, *J* = 1.5 Hz, 2H, Ar-H), 5.17 (d, *J* = 8.2 Hz, 2H, Ar-H), 3.50 (sept., *J* = 6.8 Hz, 4H, CH(CH₃)₂), 3.08 (m, 4H, NCH₂), 2.87 (m, 4H, NCH₂), 2.23 (s, 3H, Ar-CH₃), 1.58 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂), 1.12 (d, *J* = 6.8 Hz, 12H, CH(CH₃)₂) ppm. ¹³C NMR (125.77 MHz, benzene-*d*₆): δ 206.8 (NCN), 153.0 (*C*_{ipso}, O-Ar), 148.1 (*C*_q, Ar), 138.0 (*C*_q, Ar), 133.2 (*C*_q, Ar), 131.3 (*C*_q, Ar), 129.1 (CH, Ar), 128.5 (CH, Ar), 125.3 (CH, Ar), 124.5 (CH, Ar), 117.7 (CH, Ar), 117.5 (CH, Ar), 54.0 (NCH₂), 47.1 (NCH₂), 28.5 (CH(CH₃)₂), 26.3 (CH(CH₃)₂), 24.9 (Ar-CH₃) ppm. DRIFT (v/cm⁻¹): 3065w, 3028w, 2965s, 2926m, 2869m, 1652w, 1615s, 1600s, 1584m, 1558w, 1539vw, 1504s, 1472 m, 1456m, 1398vw, 1386vw, 1319w, 1283vs, 1238w, 1132vw, 848w, 822w, 805w, 758w, 667w, 568w, 552m, 440w, 434vw. Anal. Calcd for

$C_{44}H_{54}Cl_2N_4O_2Ti \cdot 1/2CH_2Cl_2 \cdot 1/2C_7H_8$: C, 65.65; H, 6.77; N, 6.38. Found: C, 65.70; H, 6.49; N 6.57.

4.4. Reactivity of less-hindered unsymmetrical o-hydroxyaryl-substituted imidazolidinium salts with chloro-titanium precursor

4.4.1. Identification of the major component from the reaction of **3b** with $TiCl_4$: formation of (1,1'-(2,6-diethylphenyl)-3,3'-(2-hydroxyphenyl)bis(imidazolidin-2-ylidene) titanium(IV) dichloride (**4b**) and bis(1-(2,6-diethylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl) titanium(IV) dichloride (**4b'**) as minor isomer

In a vial 1-(2,6-diethylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl chloride salt **2b** (80.0 mg, 0.24 mmol) and potassium bis(trimethylsilyl)amide (2 equiv., 96.4 mg, 0.48 mmol) were dissolved in THF (3 mL), and the resulting yellow suspended mixture was stirred for 10 min at $-30\text{ }^{\circ}C$. After filtration, a solution of $TiCl_4(THF)_2$ (0.5 equiv., 0.12 mmol) in 2 mL THF was slowly added to this mixture. The solution rapidly turned dark red and was allowed to stir for 30 min at room temperature. Subsequent centrifugation, filtration and evaporation to dryness afforded complex **4b** along with some impurities. Most of the residual impurities were removed by stirring the mixture in hexane at room temperature overnight leading to a red dark solid. Complex **4b** was then extracted from a mixture of toluene/hexane (1:3 ratio) affording a red solid (78 mg, 90% yield). Crystals of the major isomer **4b** were obtained from a saturated solution of toluene at $-30\text{ }^{\circ}C$ for several days and crystals of the minor isomer **4b'** were co-crystallized with **4b** in a saturated solution of benzene at room temperature after three days. Major isomer **4b**: 1H NMR (500.13 MHz, benzene- d_6): δ 7.05-6.96 (m, 4H, Ar-H), 6.76-6.59 (m, 8H, Ar-H), 6.29 (bs, 1H, Ar-H), 6.27 (bs, 1H, Ar-H), 4.25-4.16 (m, 2H, NCH_2), 3.41-3.28 (m, 4H, NCH_2), 2.71-2.65 (m, 2H, NCH_2), 2.20-2.15 (m, 2H, CH_2-CH_3), 1.82-1.69 (m, 2H, CH_2-CH_3), 1.68-1.59 (m, 2H, CH_2-CH_3), 1.37-1.31 (m, 2H, CH_2-CH_3), 0.89 (t, $J = 7.6\text{ Hz}$, 6H, CH_2-CH_3), 0.77 (t, $J = 7.5\text{ Hz}$, 6H, CH_2-CH_3) ppm. ^{13}C NMR (125.77 MHz, benzene- d_6): δ 160.7 (C_{ipso} , O-Ar), 146.9 (C_q , Ar), 143.7 (C_q , Ar), 140.3 (C_q , Ar), 129.8 (CH, Ar), 128.1 (CH, Ar), 127.1 (C_q , Ar), 126.8 (CH, Ar), 126.7 (CH, Ar), 124.7 ($N_2C=CN_2$), 121.1 (CH, Ar), 120.3 (CH, Ar), 115.1 (CH, Ar), 57.0 (NCH_2), 54.8 (NCH_2), 24.5 (CH_2 , CH_2-CH_3), 22.0 (CH_2 , CH_2-CH_3), 15.4 (CH_3 , CH_2-CH_3), 14.0 (CH_3 , CH_2-CH_3) ppm. Minor isomer **4b'**: the other proton and carbon signals are nearly indiscernible from the baseline due to the low concentration of **4b'**. Anal. Calcd for $C_{38}H_{42}Cl_2N_4O_2Ti \cdot 1/3OC_4H_8 \cdot 1/2CH_3C_6H_5$: C, 66.67; H, 6.47; N, 7.10. Found: C, 66.23; H, 6.31; N 7.19.

4.4.2. Identification of the major component from the reaction of **3c** and $TiCl_4$: formation of bis(1-(2,4,6-trimethylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydroimidazolidin-2-ylidene) titanium(IV) dichloride (**4c**) and other minor isomers.

Following the procedure described for **4b**, the reaction of 1-(2,4,6-trimethylphenyl)-3-(2-hydroxyphenyl)-4,5-dihydro-imidazolyl chloride salt **3c** (70 mg, 0.22 mmol) and potassium bis(trimethylsilyl)amide (2 equiv., 88 mg, 0.44 mmol) and $TiCl_4(THF)_2$ (0.5 equiv., 0.11 mmol) affording a red solid (34 mg, 47% yield, composed of a mixture of 3 isomers **4c**:B:C = 90:8:2 based on the integration of methyl groups of the *N*-mesityl

substituent by ^1H NMR spectroscopy). For **4c**: ^1H NMR (500.13 MHz, benzene- d_6): isomer A: δ 7.06-6.98 (m, 4H, $\text{Ar}_p\text{-H}$), 6.75-6.71 (m, 2H, Ar-H), 6.68-6.32 (m, 2H, Ar-H), 6.23 (bs, 2H, Ar-H), 6.02 (bs, 2H, Ar-H), 4.25-4.16 (m, 2H, NCH_2), 3.45-3.38 (m, 2H, NCH_2), 3.26-3.18 (m, 2H, NCH_2), 2.63-2.56 (m, 2H, NCH_2), 1.91 (s, 6H, Ar-CH_3), 1.59 (s, 6H, Ar-CH_3), 1.21 (s, 6H, Ar-CH_3) ppm. For isomer B 2.17 (bd, 6H, Ar-CH_3), 1.93 (bd, 6H, Ar-CH_3), 1.67 (bd, 6H, Ar-CH_3) ppm. For isomer C: 2.49 (bs, 6H, Ar-CH_3), 2.44 (bs, 6H, Ar-CH_3), 2.00 (bs, 6H, Ar-CH_3) ppm. For **4c**: ^{13}C NMR (125.77 MHz, benzene- d_6): δ 160.8 (C_{ipso} , O-Ar), 147.3 (C_q , Ar), 137.2 (C_q , Ar), 135.7 (C_q , Ar), 134.6 (C_q , Ar), 130.2 (CH, Ar), 129.7 (CH, Ar), 129.0 (CH, Ar), 124.7 ($\text{N}_2\text{C}=\text{CN}_2$), 121.2 (CH, Ar), 120.3 (CH, Ar), 115.2 (CH, Ar), 55.0 (NCH_2), 54.9 (NCH_2), 20.7 (Ar-CH_3), 18.8 (Ar-CH_3), 16.5 (Ar-CH_3) ppm. The other proton and carbon signals are nearly indiscernible from the baseline due to the low concentration of isomers B and C. Anal. Calcd for $\text{C}_{36}\text{H}_{38}\text{Cl}_2\text{N}_4\text{O}_2\text{Ti}\cdot\text{C}_7\text{H}_8$: C, 67.11; H, 6.02; N, 7.28. Found: C, 67.45; H, 6.24; N 7.27.

4.5. General procedure for ethylene polymerization

In the glovebox, a vial was charged with a stirring bar, Ti catalyst (5 μmol) in 5 mL of toluene and 500 equiv. of MAO, and placed in an autoclave reactor. After addition of 40 bar of ethylene, the reaction was stirred 5 min and the pressure was released before to quench the reaction by 1 mL of acidified MeOH. Volatiles were removed under reduced pressure, and polymer was washed with isopropanol and dried under vacuum for 2 h at 150 $^\circ\text{C}$. The polymer yield was determined gravimetrically.

4.6. X-ray crystallography and crystal structure determination

Suitable crystals for diffraction experiments were selected in a glovebox and mounted in a minimum of Parabar 10312 oil (Hampton Research) in a nylon loop and then mounted under a nitrogen cold stream from an Oxford Cryosystems 700 series open-flow cryostat. Data collection was done on a Bruker AXS TXS rotating anode system with an APEXII Pt 135 CCD detector using graphite-monochromated Mo K_α radiation ($\lambda = 0.71073$ Å). Data collection and data processing were done using APEX2[26], SAINT[27], and SADABS[28] version 2012/1, whereas structure solution and final model refinement were done using SHELXS[29] version 2013/1 or SHELXT[30] version 2014/4 and SHELXL[31] version 2014/7. Crystal data: for **4^{aH}** obtained from a saturated solution in CH_2Cl_2 . $\text{C}_{42}\text{H}_{50}\text{Cl}_2\text{N}_4\text{O}_2\text{Ti}\cdot 2(\text{CH}_2\text{Cl}_2)$, $M = 931.51$, crystal size: $0.125 \times 0.100 \times 0.050$ mm 3 , crystal habit/color: prism/dark red, monoclinic, space group $\text{P}2_1/\text{n}$ (No.14), $a = 11.9657(7)$, $b = 12.9163(8)$, $c = 14.5572(9)$ Å, $\beta = 99.1720(10)^\circ$, $V = 2221.1(2)$ Å 3 , $Z = 2$, $\rho_{\text{calc}} = 1.393$ g.cm $^{-3}$, $F(000) = 972$, $\mu(\text{Mo-K}_\alpha) = 0.595$ mm $^{-1}$, $\lambda = 0.71073$ Å, $T = 103(2)$ K. The 28755 reflections measured on a Bruker AXS APEXII Ultra CCD area detector system yielded 4739 unique data ($2.050 < \theta < 26.776^\circ$, $R_{\text{int}} = 0.0485$) [4739 observed reflections ($I > 2\sigma(I)$)]. Goodness-of-fit on $F^2 = 1.037$, $R1 = 0.0350$, $wR2 = 0.0894$, R indices (all data) $R1 = 0.0486$, $wR2 = 0.0980$. Crystal data: for **4^b** obtained from a saturated solution in toluene at -30 $^\circ\text{C}$. $\text{C}_{38}\text{H}_{42}\text{Cl}_2\text{N}_4\text{O}_2\text{Ti}$, $M = 705.55$, crystal size: $0.247 \times 0.201 \times 0.138$ mm 3 , crystal habit/color: flat prism/Brown-black, monoclinic, space group $\text{P}2_1/\text{n}$ (No.14), $a = 9.5808(7)$, $b = 28.232(2)$, $c = 16.9105(13)$ Å, $\beta = 102.2050(10)^\circ$, $V = 4470.6(6)$ Å 3 , $Z = 4$, $\rho_{\text{calc}} = 1.048$

g.cm^{-3} , $F(000) = 1480$, $\mu(\text{Mo-K}\alpha) = 0.342 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, $T = 103(2) \text{ K}$. The 50718 reflections measured on a Bruker AXS APEXII Ultra CCD area detector system yielded 7904 unique data ($1.443 < \theta < 25.048^\circ$, $R_{\text{int}} = 0.0572$) [7904 observed reflections ($I > 2\sigma(I)$]. Goodness-of-fit on $F^2 = 1.141$, $R1 = 0.0850$, $wR2 = 0.2145$, R indices (all data) $R1 = 0.0941$, $wR2 = 0.2202$. CCDC reference codes 1579164, 1579165, 1822682 and 1822683 contain the supplementary crystallographic data for **3c**, **4^{at}**, **4b** and **4b'**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.7. $\%V_{\text{Bur}}$ and steric maps calculations

The $\%V_{\text{Bur}}$ values and steric maps were evaluated with the SambVca 2.0 package [32]. The radius of the sphere around the center atom was set to: 3.5 \AA or 5 \AA , distance from the center of the sphere: 2.26 \AA , mesh spacing: 0.1 \AA , H atoms omitted and atom radii: Bondi radii scaled by 1.17, as recommended by Cavallo [32].

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Research Highlights

- Synthesis of unsymmetrical *o*-functionalized NHC ligands
- Synthesis of single stereoisomer of bis-ligated NHC titanium complexes
- Rearrangement bis-ligated NHC titanium intermediates into tetradentate salophen-like titanium complexes via NHCs dimerization
- Calculated percentage buried volume and steric maps of half bis-ligated (C,O)-NHC titanium complexes using SambVca 2 web-tool
- MAO-activated bis-ligated NHC titanium complexes show moderate activity for ethylene polymerization