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PAPER

# Titanium(IV) imido complexes of imine imidazol-2-imine ligands†

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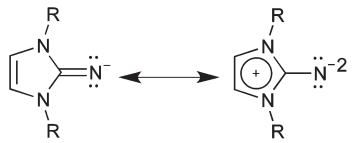
Free imine imidazol-2-imine ligands with two different substitution patterns have been isolated for the first time and they were found to exist as an equilibrium mixture of geometric and mesomeric isomers. The relative ratios of these isomers are dependent on both the nature of the substituents and of the solvent. The synthesis of the titanium(IV) alkyl and arylimido complexes of these ligands was unexpectedly found to be very selective and was successfully achieved only with the lesser sterically-demanding 2,4,6-trimethylphenyl derivative IMesN^Imine **2a**. The solid-state structure of the alkylimido complex further confirms the zwitterionic character of the ligand. The isolated titanium imido complexes were found to be active catalysts for the polymerisation of ethylene.



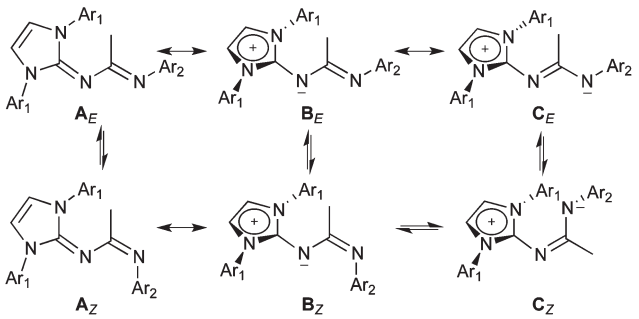
## Introduction

Transition metal complexes containing metal nitrogen multiple bonds play critical roles in a number of biological, industrial and catalytic processes.[1–8] For example, metal imido (M═NR) complexes based on group 4 transition metals undergo a wide variety of organic transformations such as [2 + 2] cycloaddition,[3,9] metathesis,[9–11] insertion,[3,12,13] C–H bond activation[3,14] and 1,2-addition reactions such as hydroamination.[9,14–18] In all these cases, the polarisable metal(IV)–imido bond is responsible for enhanced reactivity that can be controlled through the coordination geometry and electronics of the metal centre. In addition, imido groups have been also used as robust ancillary ligands in ring-opening metathesis polymerisation[11] and Ziegler–Natta olefin polymerisation.[3,19]

Since the discovery of a stable *N*-heterocyclic carbene (NHC) by Arduengo *et al.*,[20] the chemistry of these potent ligands has witnessed an extensive growth due to their similarities to tertiary phosphines in terms of thermodynamics and coordination chemistry.[21–24] More recently, these carbenes have been used in reactions with organic azides to produce imidazol-2-imines.[25,26] Deprotonation of these cyclic guanidine analogues yields a new class of highly basic monoanionic ligands that arises from the ability of the 5-membered imidazole ring to stabilise the resulting positive charge (Scheme 1).[27,28] The ligand can thus be considered isoelectronic with phosphinimides ($R_3PN^-$), cyclopentadienyls ($C_5R_5^-$), bulky alkoxides ($R_3CO^-$), siloxides ($R_3SiO^-$), and even with imido ligands ($RN^{-2}$) thanks to its amphielectronic nature, formally donating as many as six (2σ and 4π) electrons to the metal centre (Scheme 1).[29,30]



**Scheme 1** Mesomeric structures for imidazol-2-imine.



**Scheme 2** Isomeric structures for imine imidazol-2-imine ligands.

We have recently exploited the concept and developed a new family of ligands based on the imine imidazol-2-imine scaffold **A** (Scheme 2). Although the ligand is overall neutral, both exocyclic nitrogen atoms are electron-rich, as illustrated by the mesomeric structures **B** and **C**. The ligand scaffold is analogous to amidines, where one of the nitrogen atoms has been substituted with an imidazol-2-ylidene fragment allowing for further tailoring of the ligand electronics. Moreover, this fragment effectively shifts the steric bulk from the first to the second coordination sphere, leading to a more open metal centre that is still protected from bimolecular decompositions. This shift emulates the steric feature typically offered by cyclopentadienyl, bulky

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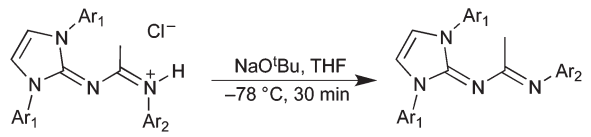
†Electronic supplementary information (ESI) available: NMR spectra for **2a** and **2b**. Crystallographic data for **4a**, CCDC reference number 842511. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31004j




**1a,b** **2a,b**

$Ar_1$ = 2,4,6-trimethylphenyl (**a**); 2,6-diisopropylphenyl (**b**)
$Ar_2$ = 2,6-dimethylphenyl

**Scheme 3** Synthesis of imine imidazol-2-imine ligand precursors.

alkoxide, siloxide, amide and phosphinimide ligand systems and has led to enhanced catalytic activities in reactions such as olefin polymerisation mediated by early transition metals.[30,31]

Considering the importance of metal imido (M═NR) complexes and the critical role of ancillary ligands in controlling their reactivity, we decided to use our recently reported *N*-(1-(2,6-dimethylphenylimino)ethyl)-1,3-bis(aryl)imidazol-2-imine hydrochloride salts, wherein aryl = 2,4,6-trimethylphenyl and 2,6-diisopropylphenyl, abbreviated as IMesN^Imine·HCl (**1a**) and IPrN^Imine·HCl (**1b**), respectively, as ligand precursors to prepare titanium(IV) imido complexes. We herein describe the synthesis and characterisation of the ligand itself and the effect of the substitution pattern on the coordination to titanium.

## Results and discussion

### Synthesis and characterisation of IMesN^Imine (2a) and IPrN^Imine (2b)

The protonated ligands IMesN^Imine·HCl (**1a**) and IPrN^Imine·HCl (**1b**) were obtained as air-stable white solids by reaction of the corresponding imidazol-2-imine and imidoyl chloride in toluene (125 °C) for 12 h.[32] Deprotonation of the amidinium salts **1a** and **1b** with NaO$^t$Bu in THF cleanly produces the imine imidazol-2-imine products as moisture-sensitive white solids in 74% (**2a**) and 90% (**2b**) yields, respectively (Scheme 3). While **1a** exists as one single species in solution,[32] the $^1$H NMR spectrum of IMesN^Imine (**2a**) shows evidence of three isomers in relative ratios that are highly solvent-dependent. As such, the three isomers are present in 12 : 4 : 1 and 4 : 3 : 1 ratios in benzene-$d_6$ and in dichloromethane-$d_2$, respectively. Considering that the X-ray structures of **1a** and **1b**, and of the corresponding titanium and palladium complexes show little double bond character between the azole ring central carbon atom and the exocyclic nitrogen,[32] the three isomers are believed to be *E*- and *Z*-conformers of the zwitterionic structures **B** and **C**, as defined in Scheme 2. A series of NMR correlation experiments using the well-resolved and unambiguously assigned $^{13}$C NMR resonances for **2a** (benzene-$d_6$ and dichloromethane-$d_2$) and **2b** (toluene-$d_8$) allowed us to identify $\mathbf{B}_Z$ as the major component of the equilibrium mixture. The exact nature of the minor component could not however be unequivocally assigned to any of the three remaining zwitterionic structures ($\mathbf{B}_E$, $\mathbf{C}_E$ and $\mathbf{C}_Z$) due to limitations of NMR spectroscopy experiments. Exchange peaks in the NOESY spectrum suggest that all species are in equilibrium with each other, albeit slow on the NMR timescale as evidenced by the absence of line broadening. The dynamic equilibrium is further supported by variations in relative ratios of isomers observed during variable-temperature NMR experiments.

The major isomer of **2a** shows characteristic resonances in benzene-$d_6$ for the mesityl *para*- and *ortho*-$CH_3$ protons in a 1 : 2 ratio at $\delta$ 2.08 and 2.25, whereas the other two minor isomers show two sets of resonances at $\delta$ 2.12 and 1.91, and at $\delta$ 2.25 and 2.11. The resonances arising from the iminic methyl protons for the major isomer were observed at $\delta$ 1.54, while the corresponding resonances for the two minor isomers were observed at $\delta$ 1.80 and 1.91, as unresolved resonances. The benzylic protons of the 2,6-dimethylphenyl ring appeared as a singlet at $\delta$ 1.77 for the major isomer and as broad unresolved singlets with the expected integration at $\delta$ 2.03 and 1.77 for the minor ones. The characteristic higher frequency resonances for the imidazole backbone (–NC*H*C*H*N–) protons were observed at $\delta$ 5.81 and at $\delta$ 5.70 and 5.64 for the major and minor isomers, respectively.

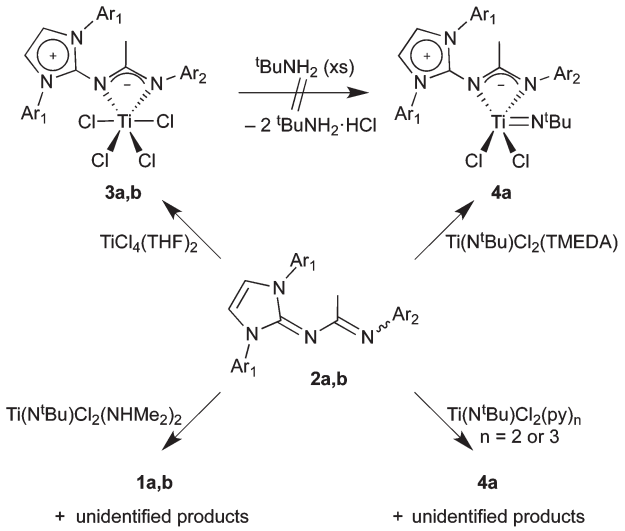
Unlike the $^1$H NMR spectrum in dichloromethane-$d_2$ for **2a**, that for the bulkier **2b** shows the presence of only two isomers in a 12 : 1 ratio. Interestingly, the $^1$H NMR spectrum in toluene-$d_8$ for **2b** is further simplified and shows the presence of only one isomer ($\mathbf{B}_Z$). A typical $AX_2$ spectrum for the methyl protons of the isopropyl groups was observed as a set of two doublets at $\delta$ 1.29 and 1.16 each integrating to 12H, whereas the corresponding septet for the methine protons was observed at $\delta$ 3.19 with vicinal coupling of 6.9 Hz. The resonance for the iminic methyl protons was observed at $\delta$ 1.40, while those for the benzylic protons of the 2,6-dimethylphenyl ring appeared as a singlet at $\delta$ 1.62. The characteristic downfield resonance for the imidazolium backbone (–NC*H*C*H*N–) was observed at $\delta$ 6.01.

In the $^{13}$C{$^1$H} NMR spectrum for **2a** (benzene-$d_6$), the exocyclic iminic carbon resonate at the characteristic high frequency shifts at $\delta$ 158.9 (major isomer) and 152.9 (minor isomer) respectively, whereas the corresponding resonance for the single isomer of **2b** (toluene-$d_8$) was observed at $\delta$ 157.5. The $^{13}$C{$^1$H} NMR resonance for the exocyclic iminic carbon for the third isomer of **2a** was not observed presumably due to the combination of its long relaxation time, quaternary nature and low relative contribution (6%) in the equilibrium mixture. The central imidazol-2-imine carbon for **2a** (major isomer) and **2b** was observed at $\delta$ 148.7 and 148.6, respectively. The corresponding resonances for the minor isomer of **2a** appeared at $\delta$ 143.1 and 151.9. Full $^1$H and $^{13}$C{$^1$H} assignments for **2a** and **2b** are detailed in the Experimental section.

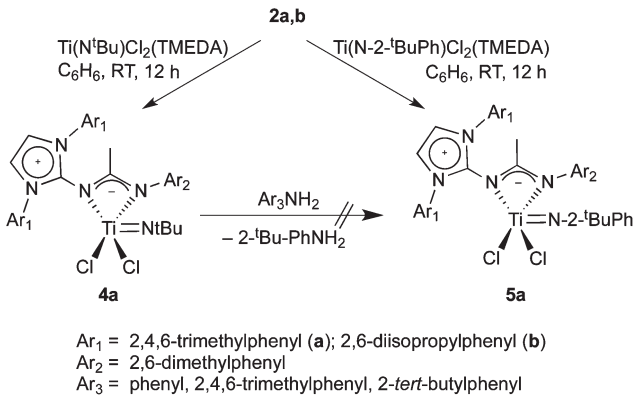
### Synthesis, characterisation and catalytic activity of Ti(IV) imido complexes

The preparation of the five coordinated titanium(IV) imido complexes of ligand **2a** and **2b** was first attempted by reaction of Ti(IMesN^Imine)$Cl_4$ (**3a**)[32] and Ti(IPrN^Imine)$Cl_4$ (**3b**)[32] with an excess of $^t$BuN$H_2$ (Scheme 4). In a typical experiment, a cold ($CH_2Cl_2$ or toluene) solution of **3a** or **3b** was treated with 3, 4 or 6 equivalents of $^t$BuN$H_2$ under conditions similar to those used for the synthesis of analogous complexes.[33–35] Upon workup, the sample showed complete decomposition of the starting complexes **3a** or **3b** with the formation of the protonated ligand (**1a** or **1b**) and other unidentified species. After the initial




**Scheme 4** Synthesis of titanium(IV) *tert*-butylimido complexes.




**Scheme 5** Synthesis of titanium(IV) arylimido complexes.

disappointing results, simple ligand displacement on the readily prepared [Ti(N$^t$Bu)Cl$_2$(NHMe$_2$)$_2$] and [Ti(N$^t$Bu)Cl$_2$(py)$_n$] ($n$ = 2 or 3) complexes was investigated. To our surprise, under varying conditions, the reaction of either **2a** or **2b** with [Ti(N$^t$Bu)Cl$_2$(NHMe$_2$)$_2$] only resulted in the protonation and decomposition of the ligand with the formation of unidentified species. The reaction of ligand **2a** with [Ti(N$^t$Bu)Cl$_2$(py)$_n$] ($n$ = 2 or 3) results in the formation of the desired product **4a** in 30% yield by NMR with some other unidentified products. All our attempts to increase the yield or to isolate the required product from the reaction mixture failed. Substitution of pyridine for TMEDA in the imido metal precursor allowed for the isolation of **4a** in spectroscopically-pure form after solvent evaporation and recrystallisation from dichloromethane/pentane (Scheme 5). Unfortunately, all our attempts to react ligand **2b** in similar ways to form the corresponding titanium imido complex failed to show any ligand displacement reaction with either [Ti(N$^t$Bu)Cl$_2$(py)$_n$] or [Ti(N$^t$Bu)Cl$_2$(TMEDA)] and only led to slight decomposition of the ligand and of the imido precursors. This selectivity in the ligand coordination is presumably due to the interaction of the steric bulk of the ligand in the second coordination sphere with the sterically demanding *tert*-butylimido group.

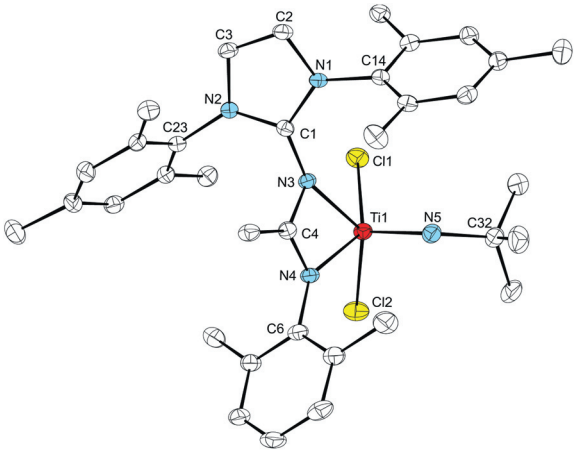



**Fig. 1** ORTEP drawing (30% probability level) of the molecular structure of **4a**. Hydrogen atoms and dichloromethane molecule omitted for clarity.

The $^1$H NMR spectrum (chloroform-d) of **4a** shows singlet resonances at $\delta$ 0.63 and 1.26 for the *tert*-butyl and for the iminic methyl protons, respectively. A prominent high-frequency chemical shift for the imidazole backbone (–NC*H*C*H*N–) protons was observed at the $\delta$ 6.88 and found to be consistent with the coordination of the ligand, when compared with the corresponding resonances observed for **2a**. The *ortho*-C*H*$_3$ and the *meta*-C*H* protons of the mesityl ring appeared as broad resonances at $\delta$ 2.26 and 6.94, respectively, indicating a restricted rotation around N–C$_{ipso}$ bond. This further translated in broad resonances in the $^{13}$C{$^1$H} spectrum for the *ortho*-C*H*$_3$ and the *meta*-C*H* of the mesityl ring at $\delta$ 19.3 and 130.4, respectively. As expected, a high-frequency chemical shift at $\delta$ 168.3 was observed for the endocyclic iminic carbon atom, in agreement with coordination of the ligand in a bidentate fashion. Full $^1$H and $^{13}$C{$^1$H} NMR assignments are detailed in the Experimental section.

The coordination environment around the titanium(IV) centre for **4a** was elucidated by X-ray diffraction studies on single crystals grown at room temperature by layering a saturated dichloromethane solution with pentane. The solid-state structure (Fig. 1) confirms the bidentate coordination mode of the ligand to form a distorted square-pyramidal geometry metal complex, with the imido group formally occupying the apical position and the chloride ligands *cis* with respect to each other. The metal centre is displaced from the basal plane formed by Cl1, Cl2, N3 and N4 by 0.666 Å. Selected bond lengths and angles for **4a** are summarised in Table 1, along with the corresponding values for **1a** and **3a**.[18] The bond angles around the titanium atom are in the range of 50.35 to 99.05°, with the smallest angle attributed to the amidinate N3–Ti–N4 bite angle and the largest one to the Cl1–Ti–Cl2 angle. The lengthening of the C4–N3 (1.363(4) Å) and the shortening of C4–N4 (1.299(5) Å), along with the reduction of the N1–C1–N2 bond angle to 106.4° compared to that observed for **2a**, are due to the delocalisation of the electron density over the C1–N3–C4–N4 π-system. Similar trends were observed in the solid-state structure of **3a**, which also shows bidentate coordination of the ligand.[32] These changes in bond

**Table 1** Comparison of selected bond lengths (Å) and bond angles (deg) for **4a** with those reported for **1a** and **3a**

| | IMesN^Imine·HCl (**1a**)[a] | Ti(IMesN^Imine)$Cl_4$ (**3a**)[a] | Ti(IMesN^Imine)$_2$($N^tBu$)$Cl_2$ (**4a**) |
|---|---|---|---|
| *Bond lengths (Å)* | | | |
| C1–N1, C1–N2 | 1.354(4), 1.356(4) | 1.365(5), 1.349(5) | 1.359(4), 1.361(4) |
| N1–C2, N2–C3 | 1.396(4), 1.397(4) | 1.386(5), 1.400(5) | 1.391(5), 1.393(5) |
| C2–C3 | 1.336(5) | 1.341(6) | 1.339(5) |
| N1–$C_{ipso}$, N2–$C_{ipso}$ | 1.448(4), 1.450(3) | 1.455(5), 1.449(5) | 1.447(5), 1.448(4) |
| C1–N3 | 1.338(4) | 1.354(5) | 1.340(4) |
| C4–N3, C4–N4 | 1.311(4), 1.330(4) | 1.361(5), 1.312(5) | 1.363(4), 1.299(5) |
| Ti–N5 | — | — | 1.678(3) |
| Ti–N3, Ti–N4 | — | 2.253(3), 2.106(3) | 2.267(3), 2.172(3) |
| Ti–$Cl_{(trans\ to\ N3)}$ | — | 2.2480(13) | 2.3375(12) |
| Ti–$Cl_{(trans\ to\ N4)}$ | — | 2.2913(13) | 2.3371(12) |
| *Bond angles (deg)* | | | |
| N1–C1–N2 | 109.0(3) | 106.5(3) | 106.4(3) |
| N1,2–C1–N3 | 123.3(3), 129.6(3) | 127.2(4), 126.2(4) | 123.5(3), 130.0(3) |
| C1–N3–C4 | 122.7(3) | 122.3(4) | 125.5(3) |
| N3–C4–N4 | 118.8(3) | 110.7(4) | 111.3(3) |
| C4–N4–C6 | 125.3(3) | 122.3(3) | 121.3(3) |
| C32–N5–Ti | — | — | 160.6(3) |

[a] Ref. 32.

lengths and the 52.02° angle formed between the imidazole ring and the diazametallacyclobutene further support zwitterionic character of the ligand through enhanced delocalisation of the π-electrons over the entire imine imidazol-2-imine framework.

In contrast to compound **3a**, the ability of the apical imido ligand to act as a 2σ,4π-donor ligand to the highly electrophilic $d^0$ titanium(IV) centre in **4a** likely leads to a decrease in π-donation from the basal chlorine and nitrogen donors. This results into a marked elongation of the corresponding Ti–Cl and Ti–N bonds (Table 1). Such electronic effects are further supported by the short Ti–N5 bond length (1.678(3) Å) for **4a**, which is indicative of significant Ti≡N triple bond character, and are in agreement with theoretical models and symmetry arguments presented in previous studies.[1,36,37] The Ti–N5 bond is shorter than the corresponding bond in either Heyduk's (tmp-BIAN)Ti(=N$^t$Bu)$Cl_2$ (1.690(4) Å)[35] or Mountford's (py)$_3$Ti(=N$^t$Bu)$Cl_2$ (1.705(3) Å)[34] complexes but is comparable to that observed in Winter's (TMEDA)Ti(=N$^t$Bu)$Cl_2$ (1.662(4) Å)[38] complex. The slightly non-linear Ti–N5–C32 bond angle of 160.6(3)°, in comparison to the corresponding bond angle of 164.1(4)° observed in both [(tmp-BIAN)Ti(=N$^t$Bu)$Cl_2$][20] and [(TMEDA)Ti(=N$^t$Bu)$Cl_2$],[23] is probably due to the large repulsion between the *tert*-butyl imido group and the steric bulk in the second coordination sphere from the mesityl and xylyl substituents on the bidentate ligand.[39,40] This repulsion results in the *tert*-butyl group tilting towards the chloride ligands, with C34 and C35 approximately eclipsing Cl1 and Cl2, respectively, when the molecule is viewed along the Ti1–N5 bond. The angles between the basal plane and the best plane formed by either the imidazole ring or the 2,6-dimethylphenyl group are comparable at 71.8° and 73.2°, respectively. The average angle between all four apical planes containing the titanium imido (Ti=N3) bond and the basal plane is 87.9°. All the remaining bond lengths and angles are unexceptional and lie within the expected range.

Previous studies using early and late transition metals have shown that *tert*-butylimido/arylamine exchange is thermodynamically favourable due to a greater reactivity of the *tert*-butylimido group compared to that of the resulting arylimido complexes.[34,35,41–45] To synthesise the corresponding aryl imido complex **5a**, we therefore attempted the reactions of **4a** with aniline, 2,4,6-trimethylaniline and 2-*tert*-butylaniline under various conditions (Scheme 5). To our surprise, the *tert*-butylimido/arylamine exchange did not readily proceed under reported conditions[34,35] and further attempts to promote the exchange by prolonged heating in different solvent systems only resulted in the formation of the protonated imidazol-2-imine with some unidentified species. Similar to our approach to prepare **4a**, reaction of **2a** with the TMEDA adduct of Ti(=N-2-$^t$BuPh)$Cl_2$[46] in benzene at room temperature produced the targeted titanium complex Ti(IMesN^Imine)Ti(=N-2-$^t$BuPh)$Cl_2$ (**5a**) as a faint orange solid in 78% yield. Our attempts to synthesise the analogous Ti(IPrN^Imine)Ti(=N-2-$^t$BuPh)$Cl_2$ (**5b**) in a similar way were not successful, again suggesting a greater repulsion between the imido substituents and the more sterically demanding bis-1,3-(2,6-diisopropylphenyl)imizol-2-imine moiety.

The substituents on imido ligands have been shown to have a significant impact on the polymerisation activities of related titanium dichloride complexes of neutral four- and six-electron donor ligands, with some complexes being completely inactive and others producing polyethylene at a rate of 10 000 kg mol$^{-1}$ h$^{-1}$ bar$^{-1}$.[46,47] The catalytic activities for compounds **4a** and **5a** towards ethylene polymerisation in toluene were thus evaluated at atmospheric pressure and room temperature, with 1000 equivalents of methylaluminoxane. While complexes **4a** and **5a** showed relatively low activities for ethylene polymerisation, with respective rates of 6.5 and 7.8 kg PE mol$^{-1}$ h$^{-1}$ bar$^{-1}$, our initial results demonstrate the impact of the imido substituents on the performance of the catalysts, with an increase in catalyst activities observed upon replacing the electron-rich *tert*-butyl group with the electron-poor and sterically-demanding 2-*tert*-butylphenyl group. In both cases, the formation of soluble waxes or low molecular weight oligomers was not observed.

## Summary

We have isolated and characterised a family of free imine imidazol-2-imine ligands. An interesting solvent dependent equilibrium between the different geometric and mesomeric structures for the ligands was observed by NMR spectrometry. The synthesis of titanium(IV) imido complexes was unexpectedly found to be very selective and was successfully achieved only with the lesser sterically-demanding 2,4,6-trimethylphenyl derivative IMesN^Imine **2a**.


## Experimental

### General comments

All manipulations of air and/or moisture sensitive materials were carried out under an inert atmosphere of dinitrogen using standard Schlenk vessel techniques, or in an inert-atmosphere glovebox containing dinitrogen. Dinitrogen used for the Schlenk manifolds was further purified by passage through columns filled with molecular sieves (4 Å) and manganese(II) oxide suspended on vermiculite. Solvents used in the preparation of air and/or moisture sensitive compounds were dried using an MBraun Solvent Purification System fitted with alumina columns. Solvents were deoxygenated by bubbling dry dinitrogen through the dried solvents for twenty minutes before use. Solvents and solutions were transferred through stainless steel cannulae using a positive pressure of dinitrogen. Deuterated solvents were degassed using three freeze–pump–thaw cycles and were vacuum distilled from sodium ($C_6D_6$ and toluene-$d_8$) or $CaH_2$ ($CDCl_3$, $CD_2Cl_2$ and $CD_3CN$) and stored in an inert-atmosphere glovebox. Filtrations of air and/or moisture-sensitive compounds were achieved by using modified stainless steel cannulae fitted with glass fibre filter discs at one end. All glassware and cannulae were dried at 120 °C for 24 h before use. NMR spectra were recorded on a Bruker DRX 600 ($^1$H at 600 MHz, $^{13}$C at 150 MHz), Bruker AV 400 ($^1$H at 400 MHz, $^{13}$C at 100 MHz) or Bruker AV 300 ($^1$H at 300 MHz, $^{13}$C at 75 MHz) spectrometer at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protiosolvent ($^1$H) and solvent ($^{13}$C) resonances and chemical shifts were reported with respect to $\delta = 0$ for tetramethylsilane. Microanalyses were performed either by ANALEST of the Department of Chemistry, University of Toronto or by Guelph Chemical Laboratories, Guelph, Ontario, Canada, N1G 5G5. Exact masses were determined by the AIMS Laboratory of the Department of Chemistry, University of Toronto or by the microanalytical laboratory of the Department of Chemistry, McMaster University.

All reagents were purchased from Aldrich or Alfa Aesar with the exception of $TiCl_4$, which was purchased from BDH. They were used as received with the exception of NaO$^t$Bu, which was sublimed and kept in an inert-atmosphere glovebox. Methylaluminoxane (MAO) was graciously donated by Albemarle Corp. IMes·HCl,[48] IPr·HCl,[48] IMes,[49] IPr,[49] imidazol-2-imines,[28] IMesN^Imine·HCl (**1a**),[32] IPrN^Imine·HCl (**1b**),[32] $TiCl_4(THF)_2$,[50] Ti(N$^t$Bu)$Cl_2$(TMEDA),[38] Ti(N-2-$^t$BuPh)$Cl_2$(TMEDA)[46] and *N*-(2,6-Dimethylphenyl)acetimidoyl chloride[51] were prepared using published procedures.

### Synthesis of ligand precursors

***N*-(1-(2,6-Dimethylphenylimino)ethyl)-1,3-bis(2,4,6-trimethylphenyl)imidazol-2-imine; IMesN^Imine (2a).** To a suspension of IMesN^Imine·HCl (4.30 g, 8.61 mmol) in THF (40 mL) at −78 °C was added a cold THF (25 mL) solution of sodium *tert*-butoxide (868 mg, 9.03 mmol). The reaction mixture was stirred for 30 min at this temperature, and then slowly warmed to room temperature and stirred for an additional 4 h. During this time, the color of the reaction mixture changed to pale yellow. The mixture was subsequently filtered through a plug of Celite. Volatiles were removed at reduced pressure and the resulting solid was extracted with toluene (30 mL). The desired product was recovered by removing the solvent *in vacuo*. Yield: 2.94 g (74%).

$^1$H NMR (600 MHz, $C_6D_6$): *Major isomer (72%):* $\delta$ 7.03 (d, 2H, $^3J$ = 7.4 Hz, *m*-C$H_{(2,6\text{-xylyl})}$), 7.03 (t, 1H, $^3J$ = 7.4 Hz, *p*-C$H_{(2,6\text{-xylyl})}$), 6.69 (s, 4H, *m*-C$H_{(\text{mesityl})}$), 5.81 (s, 2H, –NC*H*C*H*N–), 2.25 (s, 12H, *o*-C$H_{3(\text{mesityl})}$), 2.08 (s, 6H, *p*-C$H_{3(\text{mesityl})}$), 1.77 (s, 6H, *o*-C$H_{3(2,6\text{-xylyl})}$), 1.54 (s, 3H, C$H_{3(\text{imine})}$); *Minor isomer 1 (22%):* $\delta$ 7.03 (d, 2H, $^3J$ = 7.3 Hz, *m*-C$H_{(2,6\text{-xylyl})}$), 7.03 (t, 1H, $^3J$ = 7.3 Hz, *p*-C$H_{(2,6\text{-xylyl})}$), 6.76 (s, 4H, *m*-C$H_{(\text{mesityl})}$), 5.64 (s, 2H, –NC*H*C*H*N–), 2.12 (s, 6H, *p*-C$H_{3(\text{mesityl})}$), 2.03 (s, 6H, *o*-C$H_{3(2,6\text{-xylyl})}$), 1.91 (s, 12H, *o*-C$H_{3(\text{mesityl})}$), 1.80 (s, 3H, C$H_{3(\text{imine})}$); *Minor isomer 2 (6%):* $\delta$ 7.12 (t, 2H, $^3J$ = 7.6 Hz, *m*-C$H_{(2,6\text{-xylyl})}$), 7.10 (d, 1H, $^3J$ = 7.6 Hz, *p*-C$H_{(2,6\text{-xylyl})}$), 6.76 (s, 4H, *m*-C$H_{(\text{mesityl})}$), 5.70 (s, 2H, –NC*H*C*H*N–), 2.25 (s, 6H, *p*-C$H_{3(\text{mesityl})}$), 2.11 (s, 12H, *o*-C$H_{3(\text{mesityl})}$), 1.91 (s, 3H, C$H_{3(\text{imine})}$), 1.77 (s, 6H, *o*-C$H_{3(2,6\text{-xylyl})}$).

$^1$H NMR (400 MHz, $CD_2Cl_2$): *Major isomer (49%):* $\delta$ 6.89 (s, 4H, *m*-C$H_{(\text{mesityl})}$), 6.73–6.69 (br m, 2H, *m*-C$H_{(2,6\text{-xylyl})}$), 6.54 (t, 1H, $^3J$ = 7.4 Hz, *p*-C$H_{(2,6\text{-xylyl})}$), 6.46 (s, 2H, –NC*H*C*H*N–), 2.26 (s, 6H, *p*-C$H_{3(\text{mesityl})}$), 2.17 (s, 12H, *o*-C$H_{3(\text{mesityl})}$), 1.42 (s, 6H, *o*-C$H_{3(2,6\text{-xylyl})}$), 1.22 (s, 3H, C$H_{3(\text{imine})}$); *Minor isomer 1 (38%):* $\delta$ 6.91 (s, 4H, *m*-C$H_{(\text{mesityl})}$), 6.73–6.69 (br m, 2H, *m*-C$H_{(2,6\text{-xylyl})}$), 6.60–6.57 (br m, 1H, *m*-C$H_{(2,6\text{-xylyl})}$), 6.41 (s, 2H, –NC*H*C*H*N–), 2.30 (s, 6H, *p*-C$H_{3(\text{mesityl})}$), 1.91 (s, 12H, *o*-C$H_{3(\text{mesityl})}$), 1.53 (s, 6H, *o*-C$H_{3(2,6\text{-xylyl})}$), 1.50 (s, 3H, C$H_{3(\text{imine})}$); *Minor isomer 2 (13%):* $\delta$ 6.93 (s, 4H, *m*-C$H_{(\text{mesityl})}$), 6.73–6.69 (br m, 2H, *m*-C$H_{(2,6\text{-xylyl})}$), 6.60–6.57 (br m, 1H, *m*-C$H_{(2,6\text{-xylyl})}$), 6.17 (s, 2H, –NC*H*C*H*N–), 2.26 (s, 6H, *p*-C$H_{3(\text{mesityl})}$), 2.13 (s, 12H, *o*-C$H_{3(\text{mesityl})}$), 1.91 (s, 6H, *o*-C$H_{3(2,6\text{-xylyl})}$), 1.53 (s, 3H, C$H_{3(\text{imine})}$).

$^{13}$C{$^1$H} NMR (160 MHz, $C_6D_6$): *Major isomer (Z-isomer):* $\delta$ 158.9 (s, –N*C*$_{(\text{imine})}$N–), 150.6 (s, *C*$_{(2,6\text{-xylyl})}$), 148.7 (s, –N*C*$_{(\text{imidazole})}$N–), 138.1 (s, *p*-*C*H$_{(2,6\text{-xylyl})}$), 136.2 (s, *C*$_{(\text{mesityl})}$), 134.6 (s, *o*-*C*$_{(\text{mesityl})}$), 129.4 (s, *m*-*C*H$_{(\text{mesityl})}$), 128.8 (s, *o*-*C*$_{(2,6\text{-xylyl})}$), 120.6 (s, *m*-*C*$_{(\text{mesityl})}$ + *p*-*C*H$_{(2,6\text{-xylyl})}$), 115.6 (s, –N*C*H*C*HN–), 20.9 (s, *p*-*C*H$_{3(\text{mesityl})}$ + *C*H$_{3(\text{imine})}$), 18.2 (s, *o*-*C*H$_{3(\text{mesityl})}$ + *o*-*C*H$_{3(2,6\text{-xylyl})}$); *Minor isomer 1:* $\delta$ 152.9 (s, –N*C*$_{(\text{imine})}$N–), 151.6 (s, *C*$_{(2,6\text{-xylyl})}$), 143.1 (s, –N*C*$_{(\text{imidazole})}$N–), 138.6 (s, *p*-*C*H$_{(2,6\text{-xylyl})}$), 136.2 (s, *C*$_{(\text{mesityl})}$), 133.2 (s, *o*-*C*$_{(\text{mesityl})}$), 129.5 (s, *m*-*C*H$_{(\text{mesityl})}$), 127.1 (s, *o*-*C*$_{(2,6\text{-xylyl})}$), 120.8 (s, *m*-*C*H$_{(2,6\text{-xylyl})}$ + *p*-*C*H$_{(2,6\text{-xylyl})}$), 114.7 (s, –N*C*H*C*HN–), 23.9 (s, *C*H$_{3(\text{imine})}$), 21.0 (s, *p*-*C*H$_{3(\text{mesityl})}$), 18.8 (s, *o*-*C*H$_{3(2,6\text{-xylyl})}$), 18.1 (s, *o*-*C*H$_{3(\text{mesityl})}$); *Minor isomer 2:* $\delta$ 151.9 (s, –N*C*$_{(\text{imidazole})}$N–), 143.1 (s, *C*$_{(\text{mesityl})}$), 151.9 (s, *C*$_{(2,6\text{-xylyl})}$), 129.5 (s, *m*-*C*H$_{(\text{mesityl})}$), 128.3 (s, *o*-*C*$_{(\text{mesityl})}$), 127.8 (s, *p*-*C*H$_{(\text{mesityl})}$), 120.8 (s, *m*-*C*H$_{(2,6\text{-xylyl})}$ + *p*-*C*H$_{(2,6\text{-xylyl})}$), 112.5

(br s, –NCHCHN–), 18.6 (s, *p*-$CH_{3(mesityl)}$), 18.2 (s, *o*-$CH_{3(mesityl)}$ + *o*-$CH_{3(2,6\text{-}xylyl)}$), 18.1 (s, $CH_{3(imine)}$).

Anal. Calcd for $C_{31}H_{36}N_4$ (%): C, 80.13; H, 7.81; N, 12.06; Found (%): C, 79.86; H, 7.97; N, 11.88. HRMS ($ESI^+$, $CH_3CN$): Calculated for $C_{31}H_{36}N_4$, *m*/*z* = 464.2948 $[M]^+$; Found: 464.2940 $[M]^+$; FTIR (thin film): $\nu_{C=N}$ 1616 $cm^{-1}$, $\nu_{C=C}$ 1520 $cm^{-1}$.

***N*-(1-(2,6-Dimethylphenylimino)ethyl)-1,3-bis(2,6-diisopropyl phenyl)imidazol-2-imine; IPrN^Imine (2b).** To a suspension of IPrN^Imine·HCl (6.11 g, 10.5 mmol) in THF (40 mL) at −78 °C was added a cold THF (25 mL) solution of sodium *tert*-butoxide (1.06 g, 11.0 mmol). The reaction mixture was stirred for 30 min at this temperature, and then slowly warmed to room temperature and stirred for an additional 4 h. During this time, the color of the reaction mixture changed to pale yellow. The mixture was subsequently filtered through a plug of Celite. Volatiles were removed at reduced pressure and the resulting solid was extracted with a toluene–pentane (3 : 1) mixture (3 × 30 mL). The desired product was recovered by removing the solvent *in vacuo*. Yield: 5.16 g (90%).

$^1H$ NMR (400 MHz, toluene-$d_8$): $\delta$ 7.16 (t, 2H, *J* = 7.7 Hz, *p*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 7.05 (d, 4H, *J* = 7.8 Hz, *m*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 6.92 (d, 2H, *J* = 7.4 Hz, *m*-$CH_{(2,6\text{-}xylyl)}$), 6.75 (t, 1H, *J* = 7.4 Hz, *p*-$CH_{(2,6\text{-}xylyl)}$), 6.01 (s, 2H, –NC*H*C*H*N–), 3.19 (sept, 4H, *J* = 6.9 Hz, $CH_{(2,6\text{-}diisopropylphenyl)}$), 1.62 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)}$), 1.40 (s, 3H, $CH_{3(imine)}$), 1.29 (d, 12H, *J* = 6.9 Hz, $CH_{3(2,6\text{-}diisopropylphenyl)}$), 1.16 (d, 12H, *J* = 6.9 Hz, $CH_{3(2,6\text{-}diisopropylphenyl)}$).

$^1H$ NMR (400 MHz, $CD_2Cl_2$): *Major isomer (92%):* $\delta$ 7.33 (t, 2H, *J* = 7.7 Hz, *p*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 7.18 (d, 4H, *J* = 7.7 Hz, *m*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 6.69 (d, 2H, *J* = 7.4 Hz, *m*-$CH_{(2,6\text{-}xylyl)}$), 6.52 (t, 1H, *J* = 7.4 Hz, *p*-$CH_{(2,6\text{-}xylyl)}$), 6.46 (s, 2H, –NC*H*C*H*N–), 3.04 (sept, 4H, *J* = 6.9 Hz, $CH_{(2,6\text{-}diisopropylphenyl)}$), 1.32 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)}$), 1.25 (s, 3H, $CH_{3(imine)}$), 1.17 (d, 12H, *J* = 7.0 Hz, $CH_{3(2,6\text{-}diisopropylphenyl)}$), 1.14 (d, 12H, *J* = 7.0 Hz, $CH_{3(2,6\text{-}diisopropylphenyl)}$); *Minor isomer (8%):* $\delta$ 7.40 (t, 2H, *J* = 7.8 Hz, *p*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 7.22 (d, 4H, *J* = 7.8 Hz, *m*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 6.59–6.55 (d+ br, 3H, *m*-$CH_{(2,6\text{-}xylyl)}$ + *p*-$CH_{(2,6\text{-}xylyl)}$), 6.25 (s, 2H, –NC*H*C*H*N–), 2.69 (sept, 4H, *J* = 6.9 Hz, $CH_{(2,6\text{-}diisopropylphenyl)}$), 1.35 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)}$), 1.19 (s, 3H, $CH_{3(imine)}$), 1.06 (d, 12H, *J* = 6.9 Hz, $CH_{3(2,6\text{-}diisopropylphenyl)}$), 1.02 (d, 12H, *J* = 7.0 Hz, $CH_{3(2,6\text{-}diisopropylphenyl)}$).

$^{13}C\{^1H\}$ NMR (100 MHz, toluene-$d_8$): $\delta$ 157.5 (s, –$NC_{(imine)}$N–), 150.6 (s, $C_{(2,6\text{-}xylyl)}$), 148.6 (s, –$NC_{(imidazole)}$N–), 146.8 (s, *o*-$C_{(2,6\text{-}diisopropylphenyl)}$), 135.1 (s, $C_{(2,6\text{-}diisopropylphenyl)}$), 129.6 (s, *p*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 128.5 (s, *m*-$C_{(2,6\text{-}xylyl)}$), 124.2 (s, *m*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 121.0 (s, *p*-$CH_{(2,6\text{-}xylyl)}$), 116.7 (s, –NCHCHN–), 29.2 (s, $CH_{(2,6\text{-}diisopropylphenyl)}$), 24.6 (s, $CH_{3(2,6\text{-}diisopropylphenyl)}$), 23.5 (s, $CH_{3(2,6\text{-}diisopropylphenyl)}$), 21.5 (s, $CH_{3(imine)}$), 18.5 (s, *o*-$CH_{3(2,6\text{-}xylyl)}$).

$^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$): *Major isomer:* $\delta$ 157.5 (s, –$NC_{(imine)}$N–), 150.8 (s, $C_{(2,6\text{-}xylyl)}$), 148.6 (s, –$NC_{(imidazole)}$N–), 147.1 (s, *o*-$C_{(2,6\text{-}diisopropylphenyl)}$), 135.1 (s, $C_{(2,6\text{-}diisopropylphenyl)}$), 129.6 (s, *p*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 128.9 (s, *o*-$C_{(2,6\text{-}xylyl)}$), 127.1 (s, *m*-$CH_{(2,6\text{-}xylyl)}$), 124.3 (s, m-$CH_{(2,6\text{-}diisopropylphenyl)}$) 120.3 (s, *p*-$CH_{(2,6\text{-}xylyl)}$), 117.3 (s, –NCHCHN–), 28.9 (s, $CH_{(2,6\text{-}diisopropylphenyl)}$), 24.7 (s, $CH_{3(2,6\text{-}diisopropylphenyl)}$), 23.3 (s, $CH_{3(2,6\text{-}diisopropylphenyl)}$), 20.9 (s, $CH_{3(imine)}$), 18.1 (s, *o*-$CH_{3(2,6\text{-}xylyl)}$); *Minor isomer:* $\delta$ 153.9 (s, –$NC_{(imine)}$N–), 145.6 (s, –$NC_{(imidazole)}$N–), 131.1 (s, *p*-$CH_{(2,6\text{-}diisopropylphenyl)}$), 127.3 (s, *m*-$CH_{(2,6\text{-}xylyl)}$), 124.7 (s, *p*-$CH_{(2,6\text{-}diisopropylphenyl)}$) 120.6 (s, *p*-$CH_{(2,6\text{-}xylyl)}$), 113.9 (s, –NCHCHN–), 28.9 (s, $CH_{(2,6\text{-}diisopropylphenyl)}$), 25.5 (s, $CH_{3(2,6\text{-}diisopropylphenyl)}$), 23.7 (s, $CH_{3(imine)}$), 22.4 (s, $CH_{3(2,6\text{-}diisopropylphenyl)}$), 17.3 (s, *o*-$CH_{3(2,6\text{-}xylyl)}$).

Anal. Calcd for $C_{37}H_{48}N_4$ (%): C, 80.98; H, 8.82; N, 10.21; Found (%): C, 81.13; H, 8.63; N, 10.28; HRMS ($ESI^+$, $CH_3CN$): Calculated for $C_{37}H_{48}N_4$, *m*/*z* = 548.3872 $[M]^+$; Found: 548.3879 $[M]^+$; FTIR (thin film): $\nu_{C=N}$ 1610 $cm^{-1}$, $\nu_{C=C}$ 1519 $cm^{-1}$.

**(*N*-(1-(2,6-Dimethylphenylimino)ethyl)-1,3-bis(2,4,6-trimethyl phenyl)imidazol-2-imine)-*tert*-butylimidodichlorotitanium(IV); Ti-(IMesN^Imine)(N$^t$Bu)$Cl_2$ (4a).** To a solution of Ti(N$^t$Bu)-$Cl_2$(TMEDA) (61.1 mg, 0.199 mmol) in benzene (2 mL) was added dropwise a benzene (5 mL) solution of IMesN^Imine (102 mg, 0.219 mmol) at room temperature. The reaction mixture changed to a bright orange-red color from the original lemon yellow. The reaction mixture was stirred for 12 h at this temperature and was subsequently filtered through a plug of Celite. Volatiles were removed at reduced pressure and the crude was redissolved in minimum amount of methylene chloride and layered with pentane. Yellow needles formed overnight and were collected, washed with pentane and dried *in vacuo*. Yield: 107 mg (82%). Single crystals suitable for X-ray diffraction study were grown by layering a saturated methylene chloride with pentane at room temperature.

$^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.94 (br s, 4H, *m*-$CH_{(mesityl)}$), 6.94–6.91 (br m, 3H, *m*-$CH_{(2,6\text{-}xylyl)}$ + *p*-$CH_{(2,6\text{-}xylyl)}$), 6.88 (s, 2H, –NC*H*C*H*N–), 2.32 (s, 6H, *p*-$CH_{3(mesityl)}$), 2.26 (br s, 12H, *o*-$CH_{3(mesityl)}$), 2.03 (s, 6H, *o*-$CH_{3(2,6\text{-}xylyl)}$), 1.26 (s, 3H, $CH_{3(imine)}$), 0.63 (s, 9H, *tert*-butyl-$CH_3$).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 168.3 (s, –$NC_{(imine)}$N–), 146.8 (s, $C_{(2,6\text{-}xylyl)}$), 144.9 (s, –$NC_{(imidazole)}$N–), 140.2 (s, *p*-$C_{(mesityl)}$), 134.1 (br s, $C_{(mesityl)}$), 131.6 (s, *o*-$C_{(mesityl)}$), 131.1(s, *o*-$C_{(2,6\text{-}xylyl)}$), 130.4 (br s, *m*-$CH_{(mesityl)}$), 128.1 (s, *m*-$CH_{(2,6\text{-}xylyl)}$), 125.1 (s, *p*-$CH_{(2,6\text{-}xylyl)}$), 119.1 (s, –NCHCHN–), 71.5 (s, $C_{(tert\text{-}butyl)}$), 30.4 (s, $CH_{3(tert\text{-}butyl)}$), 21.1 (s, *p*-$CH_{3(mesityl)}$), 19.3 (br s, *o*-$CH_{3(mesityl)}$), 18.6 (s, *o*-$CH_{3(2,6\text{-}xylyl)}$), 18.1 (s, $CH_{3(imine)}$).

Anal. Calcd for $C_{35}H_{45}Cl_2N_5Ti$ (%): C, 64.22; H, 6.93; N, 10.70; Found (%): C, 64.39; H, 6.98; N, 10.58.

**(*N*-(1-(2,6-Dimethylphenylimino)ethyl)-1,3-bis(2,4,6-trimethyl phenyl)imidazol-2-imine)-(2-tert-butylphenylimido)dichloro titanium(IV); Ti(IMesN^Imine)(N-2-$^t$BuPh)$Cl_2$ (5a)**

To a solution of Ti(N-2-$^t$BuPh)$Cl_2$(TMEDA) (191 mg, 0.502 mmol) in benzene (10 mL) was added dropwise a benzene (10 mL) solution of IMesN^Imine (245 mg, 0.527 mmol) at room temperature. The color of the reaction mixture turned from brown to bright orange-yellow. The reaction mixture was stirred for 12 h at this temperature. The precipitated off-white was filtered and washed with benzene (5 mL), pentane (5 mL) and dried under reduced pressure. The crude was redissolved in methylene chloride (2 mL) and layered with pentane. The

resulting pale orangish off-white solid was collected, washed with pentane and dried *in vacuo*. Yield: 285 mg (78%).

$^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ 6.94 (br s, 4H, *m*-C$H_{(mesityl)}$), 6.93 (s, 2H, –NC*H*C*H*N–), 6.83 (br s, 3H, *m*-C$H_{(2,6\text{-xylyl})}$ + *p*-C$H_{(2,6\text{-xylyl})}$), 6.81 (d, 1H, $J$ = 7.8 Hz, *o*-C$H_{(2\text{-}t\text{-BuPh})}$), 6.61 (t, 1H, $J$ = 7.4 Hz, *m*-C$H_{(2\text{-}t\text{-BuPh})}$), 6.49 (t, 1H, $J$ = 7.4 Hz, *p*-C$H_{(2\text{-}t\text{-BuPh})}$), 5.93 (d, 1H, $J$ = 7.7 Hz, *m*-C$H_{(2\text{-}t\text{-BuPh})}$), 2.25 (br s, 18H, *o*-C$H_{3(mesityl)}$ + *p*-C$H_{3(mesityl)}$), 1.78 (s, 6H, *o*-C$H_{3(2,6\text{-xylyl})}$), 1.33 (s, 3H, C$H_{3(imine)}$), 1.22 (s, 9H, *t*-butyl C$H_3$).

$^{13}$C{$^1$H} NMR (100.6 MHz, $CD_2Cl_2$): $\delta$ 170.4 (s, –N*C*$_{(imine)}$N–), 161.2 (s, *C*$_{(2\text{-}t\text{-BuPh})}$), 146.9 (s, –N*C*$_{(imidazole)}$N–), 143.6 (s, *C*$_{(2,6\text{-xylyl})}$), 140.8 (s, *o*-*C*$_{(mesityl)}$), 140.5 (s, *o*-*C*$_{2(2\text{-}t\text{-BuPh})}$), 132.2 (s, *o*-*C*$_{(2,6\text{-xylyl})}$), 131.6 (s, *m*-*C*$_{3(2\text{-}t\text{-BuPh})}$), 130.8 (s, *p*-*C*$_{(mesityl)}$), 130. 8 (*m*-*C*H$_{(mesityl)}$), 130.2 (br s, *C*$_{(mesityl)}$), 128.4 (s, *m*-*C*H$_{(2,6\text{-xylyl})}$), 125.6 (s, *p*-*C*H$_{(2,6\text{-xylyl})}$), 125.2 (s, *m*-*C*$_{5(2\text{-}t\text{-BuPh})}$), 124.7 (s, *o*-*C*$_{6(2\text{-}t\text{-BuPh})}$), 124.7 (s, *p*-*C*$_{4(2\text{-}t\text{-BuPh})}$), 120.3 (s, –NC*H*C*H*N–), 35.3 (s, *C*$_{(tert\text{-}butyl)}$), 30.4 (s, *C*H$_{3(tert\text{-}butyl)}$), 21.2 (s, *p*-*C*H$_{3(mesityl)}$), 19.6 (br s, *o*-*C*H$_{3(mesityl)}$), 18.7 (s, *C*H$_{3(imine)}$), 18.6 (s, *o*-*C*H$_{3(2,6\text{-xylyl})}$).

Anal. Calcd for $C_{41}H_{49}Cl_2N_5Ti$ (%): C, 67.40; H, 6.76; N, 9.59; Found (%): C, 67.24; H, 6.82; N, 9.85.

### General procedure for ethylene polymerisation

Ethylene polymerisation was performed at atmospheric pressure and room temperature in a 500 mL Schlenk flask containing a magnetic stir bar. The flask was conditioned in an oven at 130 °C for at least 18 h prior to use. The hot flask was brought to room temperature under dynamic vacuum and backfilled with ethylene. Under an atmosphere of ethylene, the flask was charged with 30 mL of dry toluene and 1000 equivalents of MAO with respect to the catalyst (10.9 μmol). The solution was stirred for 10–15 min before a solution of the catalyst in toluene was injected into the flask. The reaction mixture was vigorously stirred for 10 min after the addition of the catalyst and subsequently quenched with a 1 : 1 mixture of concentrated hydrochloric acid and methanol. The resulting mixture was filtered, and any solid collected was washed with distilled water. Solids collected were dried under vacuum at approximately 50 °C for 24 h.

### X-Ray crystallography

X-Ray crystallographic data for **4a** was collected at the University of Toronto on a Bruker-Nonius Kappa-CCD diffractometer using monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å) at 150 K and were measured using a combination of $\phi$ scans and $\omega$ scans with $\kappa$ offsets, to fill the Ewald sphere. Intensity data were processed using the Denzo-SMN package.[52] Absorption corrections were carried out using SORTAV.[53] The structures were solved and refined using SHELXTL V6.1[54] for full-matrix least-squares refinement was based on $F^2$. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with $U_{iso}$-tied to the carrier atom. Crystallographic data (tables of atomic coordinates with isotropic and anisotropic displacement parameters, bond lengths and angles) are provided as ESI.†

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