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Coordination and reactivity study of titanium phenoxo complexes containing a bulky bidentate imino-*N*-heterocyclic carbene ligand

Timothy G. Larocque, Gino G. Lavoie*

Department of Chemistry, York University, 4700 Keele Street, Toronto, Canada M3J 1P3

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ABSTRACT

The synthesis and structural characterisation of early transition metal complexes containing the aryl-substituted acyclic imino-*N*-heterocyclic carbene ligand are reported. X-ray crystallographic studies of titanium phenoxo complexes confirmed that the NHC ligand coordinates through the carbenoid carbon and the imine nitrogen atoms to form an octahedral complex. NMR spectroscopic analyses revealed restricted rotation about the aryl bonds. Attempts to prepare the corresponding titanium imido complex repeatedly led to decomposition products, presumably due to the enhanced reactivity of the imine group resulting in its cleavage from the C^Imine ligand scaffold. The catalytic activities of the phenoxo complexes towards ethylene polymerisation were assessed.

1. Introduction

N-Heterocyclic carbene (NHC) ligands have played a dominant role in transition metal chemistry since the first isolation by Arduengo in 1991 [1]. The strong σ-donating and weak π-accepting capabilities of NHCs have contributed to the widespread application of NHCs as ancillary ligands [2–5]. Despite the overwhelming interest of NHC coordination and their use as ancillary ligands for catalysis, little has been done in developing NHC-based catalysts for the polymerisation of ethylene and α-olefins [6–8].

Recently, we have reported NHC analogues of bulky α-diimines (**A**) and 2,6-diiminopyridines (**B**) in an attempt to generate thermally stable catalytic systems (Fig. 1) [9–11]. Our initial work with early transition metals focussed on the synthesis of group 4 and 6 metal halide complexes coordinated by C^Imine, the first free carbene of this class ever reported (Scheme 1) [12]. The catalytic activities of these new complexes towards ethylene polymerisation were assessed. $TiCl_4$(C^Imine) showed promising activities and thereby warranted further tailoring of the steric and electronic parameters of the complex through ligand variations [12]. We herein report the synthesis and isolation of the corresponding titanium aryloxo complexes and the attempted synthesis of titanium imido complexes.

2. Results and discussion

2.1. Synthesis of $TiCl_2(2,6\text{-}OC_6H_3{-}Me_2)_2$(C^Imine) (**1**)

In an attempt to improve the catalytic activity of Ti(C^Imine)-type complexes towards olefin polymerisation and oligomerisation, we decided to replace two chloride atoms with other ancillary ligands. In view of the success of catalysts bearing aryloxo and imido ancillary ligands for α-olefin polymerisation [13–23], we chose to prepare titanium complexes of 1-(1-(2,6-dimethylphenylimino)-2,2-dimethylpropyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene carbene (C^Imine) containing aryloxo or imido groups as ancillary ligands in an attempt to develop structure–property relationships for ethylene polymerisation.

Attempts to treat $TiCl_4$(C^Imine) with 2 equiv of $Na(2,6\text{-}OC_6H_3{-}Me_2)$ under a variety of reaction conditions led to a mixture of reaction products. As a result, the $TiCl_2(2,6\text{-}OC_6H_3{-}Me_2)_2(THF)_2$ metal precursor [24] was prepared and treated with 1 equiv of C^Imine in toluene to give compound **1** as an orange powder in good yield (82%). The solution ^1H NMR spectrum is consistent with the desired product. The presence of two ortho methyl resonances for the 2,6-dimethylphenoxide ligands at δ 2.58 and 2.41 is a strong indication of the cis arrangement of these ligands. A decrease in the C=N stretching frequency from 1662 cm^{-1} for the free ligand to 1609 cm^{-1} for **1** suggests coordination of the ligand to the metal centre in a bidentate mode through both the carbenoid carbon and the imine nitrogen atoms. A comparable decrease in stretching frequency was also observed in

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* Corresponding author. Tel.: +1 417 736 2100x77728; fax: +1 416 736 5936.
E-mail address: glavoie@yorku.ca (G.G. Lavoie).

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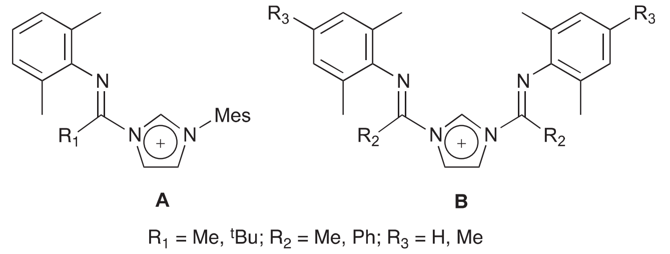


Fig. 1. Precursors to bulky (arylimino)alkylimidazol-2-ylidene carbenes.

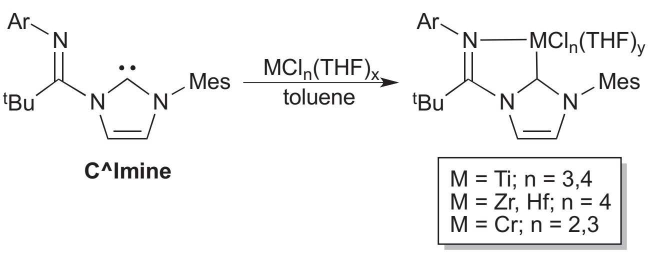
$TiCl_4$(C^Imine) and other related early transition metal complexes [12].

In order to confirm the proposed structure of **1**, we attempted to isolate single crystals suitable for X-ray crystallographic studies. Crystals of the desired product were successfully grown at −35 °C under nitrogen by slow liquid diffusion of pentane into a saturated CH_2Cl_2 solution. Analysis of the X-ray diffraction data confirmed the coordination of the ligand through the carbenoid carbon of the carbene and the imine nitrogen, with a C1–Ti1–N3 bite angle of 68.77(10)°, slightly smaller than that observed in $TiCl_4$(C^Imine) [12] (Fig. 2). The structure shows both chloride atoms trans to each other. As expected, the titanium centre of **1** exhibits a pseudo-octahedral coordination geometry, commonly observed in $TiCl_2(OAr)_2L_2$ complexes [25,26]. Angles about the metal centre range from 76.25(8)° to 100.80(10)° (Table 1).

Upon coordination of C^Imine to titanium in **1**, the C=N bond length increases slightly from 1.266(3) to 1.270(4) Å, consistent with the observed decrease in the corresponding IR stretching frequency. The strong σ-donating ability of the carbene gives rise to the trans influence and is illustrated by the longer Ti–O2 bond trans to the carbene (1.821(2) Å), compared to that for Ti–O1 cis to the carbene (1.795(2) Å). The Ti1–C1 and Ti1–N3 bond distances were determined to be 2.226(3) and 2.379(2) Å, respectively. Both values are slightly greater than those observed in the tetrachloride complex $TiCl_4$(C^Imine) [12], possibly due to the larger sterics of the phenoxide ligands or to its stronger trans influence compared to that of chlorides [27]. Interestingly, both the Ti1–O1–C26 and the Ti1–O2–C34 bond angles are equivalent at 179.1(2)°.

As expected, we see significant multiple bond character between the metal and the oxygen with the Ti1–O1 (1.795(2) Å) and Ti1–O2 (1.821(2) Å) lengths closer to the expected bond distance of a Ti=O double bond (1.74 Å) than of a Ti–O single bond (1.99 Å) [28,29]. The steric constraint imposed by the formation for the metallacycle leads to a yaw distortion of 10.0°, slightly higher than that observed in $TiCl_4$(C^Imine) (9.1°) [12] but considerably smaller than in square planar nickel complexes of C^Imine (14.5–15.7°) [9], further illustrating the effect of having a six-coordinate metal centre and sterically-demanding phenoxide ligands.

The xylyl and mesityl rings of C^Imine are almost orthogonal to the best plane formed by the imidazol-2-ylidene ring, at 82.40° and 89.26°, respectively. The phenoxide ring cis to the carbene is almost perfectly aligned with the mesityl ring, with an N2–C1–Ti1–O1 torsion angle of 0.7(3)°. These two rings are also approximately coplanar, as evidenced by the small angle (3.4°) between the mean planes formed by each ring. In contrast, the phenoxide ring trans to the carbene is neither well aligned nor coplanar with the xylyl ring of C^Imine, with a C6–N3–Ti1–O2 torsion angle of 25.1(2)° and an angle between the planes formed by each ring of 15.9°.



Scheme 1. Synthesis of group 4 and 6 metal halide complexes of C^Imine.

Interestingly, previous attempts to grow crystals of **1** from slow liquid diffusion of pentane into a saturated THF solution at −35 °C resulted in the decomposition product **2**, with two coordinated mesitylimidazole fragments bound to titanium cis to each other (Fig. 3). Nucleophilic attack of adventitious water on the iminic carbon of the bidentate ligand, which has become a better electrophile through replacement of two chlorides in $TiCl_4$(C^Imine) with the more electronegative phenoxide ligands, likely accounts for its decomposition to mesitylimidazole and *N*-(2,6-dimethylphenyl)pivaloylamide. Interestingly, such cleavage of the N1–C4 bond has not been reported for more electron-rich late transition metal analogues [9]. Compound **2** was independently synthesized by reacting 2 equiv of 1-(2,4,6-trimethylphenyl)imidazole with $TiCl_2(2,6\text{-}OC_6H_3\text{-}Me_2)_2(THF)_2$.

*2.2. Synthesis of $TiCl_2(2,6\text{-}OC_6H_4O)$(C^Imine) (**3**)*

Considering that the cis arrangement of chloride ligands is critical in the formation of active olefin polymerisation catalysts, we decided to prepare the catecholate titanium complex, with the expectation that the desired cis-chloride isomer would be produced. Similar to our observations with compound **1**, attempts to treat $TiCl_4$(C^Imine) with 1 equiv of $Li_2(2,6\text{-}OC_6H_4O)$ under a variety of reaction conditions led to a mixture of reaction products. The $TiCl_2(2,6\text{-}OC_6H_4O)(THF)_2$ metal precursor was thus prepared [30] and treated with 1 equiv of C^Imine in toluene to give compound **3** in good yield (84%) as a dark red powder (Scheme 2). Compound **3**, like compound **1**, has a lower C=N stretching frequency ($\nu_{C=N}$ 1610 cm^{-1}) than that of the free carbene, suggesting that the ligand is also coordinating through the imine nitrogen.

Crystals of **3** suitable for single crystal X-ray diffraction were successfully grown at −35 °C under nitrogen by slow liquid diffusion of pentane into a saturated CH_2Cl_2 solution. X-ray crystallographic analysis confirmed the coordination of the ligand through both the central imidazol-2-ylidene carbon and the imine nitrogen, with a slightly larger C1–Ti1–N3 bite angle (70.20(10)°) than that observed in **1**, a result of replacing two 2,6-dimethylphenoxide ligands with the smaller bidentate 2,6-catecholate (Fig. 4). This allows for the C^Imine ligand to be closer to the metal centre, resulting in shorter Ti1–C1 and Ti1–N3 bonds compared to those observed in **1**. As expected, the titanium centre adopts a pseudo-octahedral coordination geometry with bond angles about the metal centre ranging from 70.20(10) to 99.83(10)° (Table 1).

As observed for compound **1**, coordination of C^Imine results in an increase in the C=N bond length from 1.266(3) to 1.288(4) Å, which is in agreement with the related decrease in the C=N bond IR stretching frequency. The formation of the metallacycle leads to a yaw distortion of 9.0°. To our surprise, we do not see elongation of the Ti1–Cl2 bond from the trans influence of the strong σ-donating carbene. The Ti1–Cl1 and the Ti1–Cl2 bond lengths were determined to be 2.3427(9) and 2.3064(10) Å, respectively and the longer Ti1–Cl1 bond length could be a result of steric crowding of the catecholate ligand. The 2,6-dimethylphenyl and 2,4,6-trimethylphenyl rings are twisted 88.87° and 80.97° off the imidazol-2-ylidene ring, respectively. The catecholate and mesityl rings are approximately coplanar with C14 lying over O2, with an

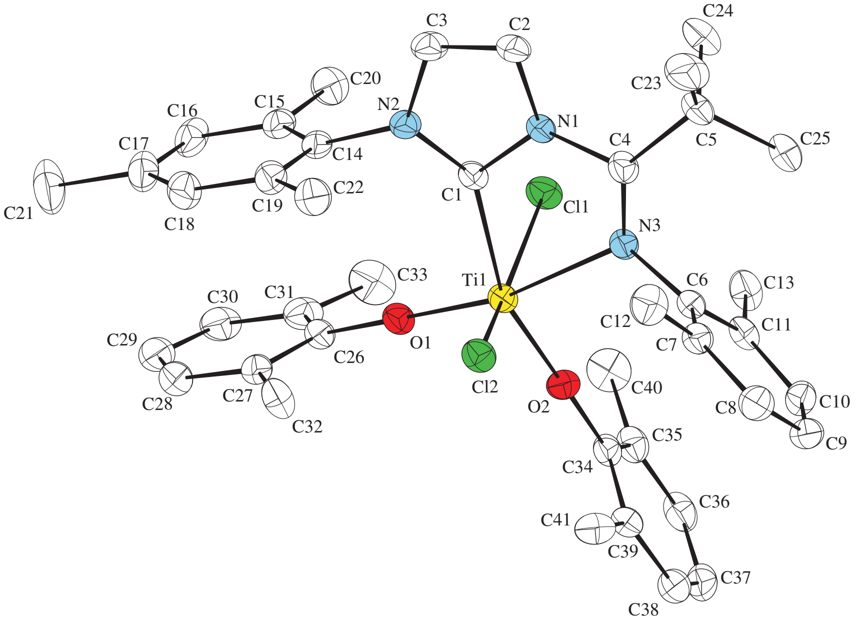


Fig. 2. ORTEP drawing (50% probability) of **1**. H atoms and a CH_2Cl_2 solvent molecule are omitted for clarity.

angle between the best planes formed by each ring of 7.94° and a C14–O2 distance of 3.388 Å. Lastly, the *ipso* carbon (C6) of the xylyl ring is in closer proximity to both Cl2 and C25, at 3.169 and 2.840 Å, respectively.

The solution ^{1}H NMR spectrum for compound **3** at room temperature was surprisingly more complicated than that of compound **1**. Broad resonances in the aromatic region at δ 6.41, 5.88 and 5.40 and in the benzylic region at δ 2.47 and 1.58, each respectively integrating to 3, 1, 1, 9 and 3 protons were observed. The broad resonance at δ 6.41 corresponds to the overlapping *para* and *meta* protons of the xylyl ring, while those at δ 5.88 and 5.40 are the inequivalent *meta* protons of the mesityl ring. The resonance at δ 2.47 corresponds to the broad ortho methyl protons of the xylyl ring and to one of the two ortho methyl groups of the mesityl ring, with the second set of inequivalent ortho methyl protons resonating at δ 1.58. The magnetic inequivalence of the protons for both the mesityl and xylyl rings, and the presence of broad resonances suggest restricted rotation for both aryl rings.

Table 1

Selected bond lengths and angles for compounds $TiCl_4$(C^Imine), **1** and **3**.

	$TiCl_4$(C^Imine) [12]	**1**	**3**
Bond lengths (Å)			
Ti–C1	2.167(5)	2.226(3)	2.186(3)
Ti–N3	2.358(4)	2.379(2)	2.336(3)
Ti–Cl1	2.2370(16)	2.3844(9)	2.3427(9)
Ti–Cl2	2.2930(18)	2.3245(9)	2.3064(10)
Ti–Cl3	2.2775(18)	–	–
Ti–Cl4	2.2808(16)	–	–
Ti–O1	–	1.795(2)	1.892(2)
Ti–O2	–	1.821(2)	1.854(2)
N1–C1	1.373(6)	1.375(4)	1.376(4)
N2–C1	1.344(6)	1.344(4)	1.338(4)
N1–C4	1.448(6)	1.431(4)	1.441(4)
N3–C4	1.288(6)	1.270(4)	1.288(4)
C2–C3	1.329(8)	1.329(4)	1.326(5)
Bond angles (°)			
C1–Ti–N3	70.42(16)	68.77(10)	70.20(10)
N1–C4–N3	112.3(4)	113.3(3)	112.9(3)
N1–C1–N2	104.7(4)	104.8(2)	105.0(3)
C1–Ti–Cl1	97.18(14)	76.25(8)	82.07(8)
Cl–Ti–Cl2	83.34(15)	83.47(8)	157.71(8)
C1–Ti–Cl3	82.16(15)	–	–
Cl1–Ti–Cl3	83.32(15)	–	–
C1–Ti–Cl4	158.65(15)	–	–
Cl2–Ti–Cl3	165.21(7)	–	–
C1–Ti–O1	–	97.73(10)	88.97(10)
C1–Ti–O2	–	160.54(10)	99.83(10)
O1–Ti–O2	–	100.80(10)	81.26(9)
Cl1–Ti–O1	–	97.17(7)	169.24(8)
Cl1–Ti–O2	–	95.49(7)	94.34(7)

This was further supported by variable-temperature NMR experiments (Fig. 5). A ^{1}H NMR spectrum of **3** in $CDCl_3$ was acquired

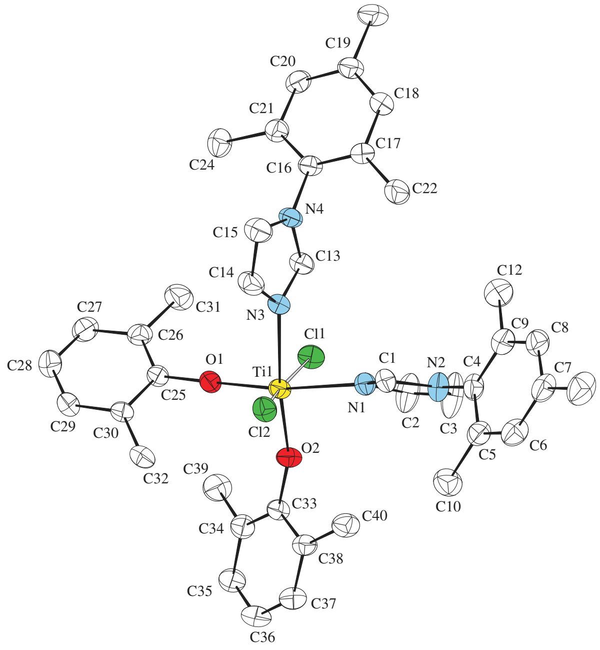
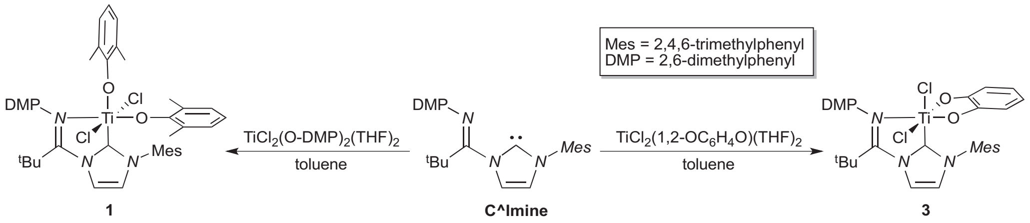


Fig. 3. ORTEP drawing (50% probability) of **2**. H atoms are omitted for clarity.



Scheme 2. Synthesis of titanium complexes **1** and **3** from free carbene, C^Imine.

at 21 °C. The temperature was gradually increased and spectra were recorded at 5 °C intervals up to a final temperature of 50 °C. Both *meta* proton resonances of the mesityl ring at δ 5.88 and 5.40 coalesced at δ 5.63 at approximately 40 °C, with estimated values for the rate constant and the free energy of activation ($\Delta G^{\ddagger}$) of 320 s^{-1} and 59 kJ mol^{-1}, respectively. The NMR spectrum recorded at 50 °C showed further line sharpening of this resonance and of that assigned to the *meta* aromatic protons of the xylyl (δ 6.41). Interestingly, in addition to becoming sharper, the relative integration of the resonance at δ 2.47 decreased from the original 9 protons at room temperature to 6 protons at 50 °C, which were assigned to the methyl protons of the xylyl ring. The elevated temperature also resulted in broadening of the ortho methyl resonance from the mesityl ring at δ 1.58, indicating the beginning of coalescence with the other resonance for the magnetically-inequivalent methyl protons at δ 2.47 (Fig. 5).

The restricted rotation likely results from the sterics about the hexacoordinate metal centre introduced by both the ortho-substituted aryl rings, the large *tert*-butyl group and by the rigid bidentate catecholate ligand. While distances of the *ipso* carbon (C6 and C14) of both aryl rings to nearby atoms (*vide supra*) may suggest a greater energy barrier for rotation of the xylyl ring compared to that of the mesityl ring, our variable-temperature experiments clearly indicate otherwise. This is reasonable considering that the dianionic catecholate ligand produces a stiff chelate with the metal centre and that the neutral iminic nitrogen atom (N3) forms a weaker and more labile dative bond with the metal centre. Upon restoring the temperature of the solution back to 25 °C, the original spectrum was restored, further supporting restricted rotation of both the xylyl and mesityl rings, and indicating no thermal decomposition.

2.3. Attempted synthesis of $TiCl_2(=N-R)$(C^Imine)

In an attempt to further expand the library of potential catalysts, we decided to prepare the titanium imido dichloride complex. Reaction of 2 equiv of *tert*-butylamine with $TiCl_4$(C^Imine) under a variety of reaction conditions led to a mixture of reaction products despite the various reaction conditions and solvents (THF, dichloromethane, chloroform) investigated. Attempts to separate the components of the reaction mixture were unsuccessful. In all cases, the resulting spectra contained a number of unidentified species. All spectra interestingly showed the same two characteristic resonances of equal intensity at δ 8.6 and 8.3 also observed for the decomposition product **2**.

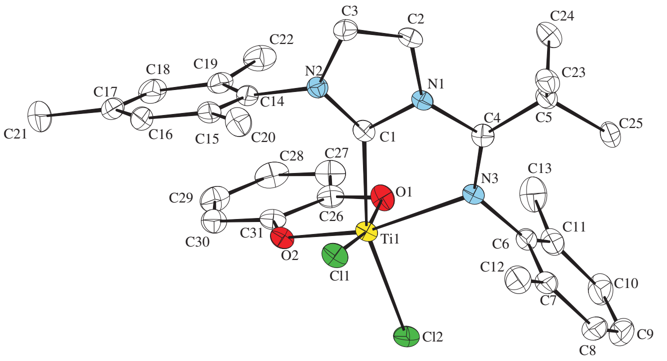


Fig. 4. ORTEP drawing (50% probability) of **3**. H atoms and a pentane solvent molecule were omitted for clarity.

As a result, we decided to adopt the same strategy used in the preparation of **1** and **3** and to attempt simple ligand displacement reactions with titanium imido precursors containing a labile ligand. Thus, $TiCl_2$(*tert*-butylimido)$(NHMe_2)_2$, $TiCl_2$(*tert*-butylimido)$(py)_3$, $TiCl_2$(*tert*-butylimido)(TMEDA) and $TiCl_2$(*tert*-butylphenylimido)(TMEDA) were prepared [31,32] and each one was treated with 1 equiv of C^Imine in several solvents (THF, toluene, diethyl ether and chloroform) and at various reaction conditions. In all cases, a complex mixture of unidentified compounds was generated and attempts to isolate the components were unsuccessful. The ^1H NMR spectra displayed the same distinctive downfield resonances reported above. We believe that upon coordination to the electropositive titanium centre, the C=N bond becomes more electrophilic and more susceptible to nucleophilic attack, thus resulting in decomposition. This decomposition pathway might be mitigated in compounds **1** and **3** thanks to the bulkier hexacoordinate metal centres and to the greater electron-donating capabilities of two phenoxide ligands, compared to one single imido ligand.

2.4. Ethylene polymerisation catalysis

The catalytic activities of compounds **1** and **3** towards ethylene polymerisation in toluene were studied at atmospheric pressure and room temperature in the presence of 1000 equiv methylaluminoxane (MAO) as cocatalyst. In both cases, only trace amounts of polyethylene (PE) were recovered and no soluble waxes or low molecular weight oligomers were generated. In contrast, the parent $TiCl_4$(C^Imine) complex showed productivities of 40 kg PE mol M^{-1} h^{-1} [12]. Coordination of the iminic nitrogen (N3) to the more Lewis acidic metal centre enhances the electrophilicity of the iminic carbon (C4) in compounds **1** and **3**, making it more susceptible to nucleophilic attack and to decomposition into complexes such as compound **2**, which was itself also found to be inactive in ethylene polymerisation under comparable conditions.

3. Conclusions

New titanium complexes containing a bidentate imino-*N*-heterocyclic carbene were prepared as potential catalysts for olefin polymerisation. The metal electronics and sterics about the metal centre were tuned through coordination of either two phenoxide ligands (**1**) or one catecholate ligand (**3**). NMR experiments

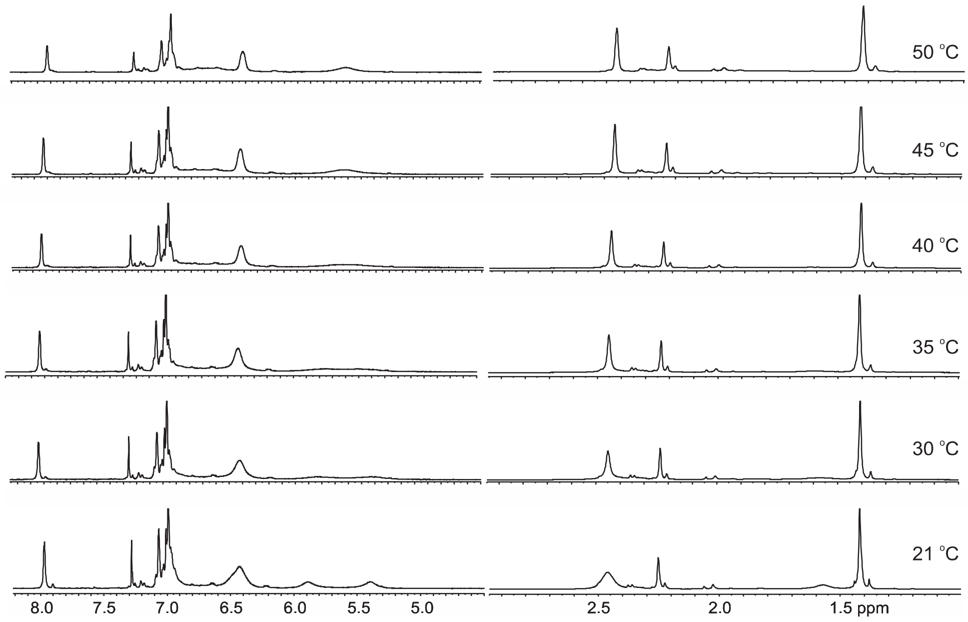


Fig. 5. Selected regions of the ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **3** at temperatures ranging from 21 to 50 °C.

revealed restricted rotation of both aryl rings that are part of the imino-carbene ligand scaffold. The solid-state structure of both complexes was confirmed by X-ray diffraction studies. Attempts to make a related titanium imido complex failed, presumably due to the sensitivity of the imine group towards nucleophilic attack, as evidenced by the formation of the bis(imidazole) decomposition product **2**. The catalytic activities of the phenoxide complexes towards ethylene polymerisation were assessed and found to be significantly lower than that previously reported for the tetrachloride complex.

4. Experimental

4.1. General methods

All manipulations were performed under a dinitrogen atmosphere in a drybox or using standard Schlenk techniques. Solvents used in the preparation of air and/or moisture sensitive compounds were dried using an MBraun Solvent Purification System fitted with alumina columns and stored over molecular sieves under a positive pressure of dinitrogen. Deuterated solvents were degassed using three freeze–pump–thaw cycles. C_6D_6 and $CDCl_3$ were vacuum distilled from sodium and CaH_2, respectively, and stored under dinitrogen. NMR spectra were recorded on a Bruker DRX 600 (^{1}H at 600 MHz, ^{13}C at 150.9 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 75.5 MHz) spectrometer and are at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^{1}H) and solvent (^{13}C) resonances and chemical shifts were reported with respect to $\delta = 0$ for tetramethylsilane. Elemental compositions and exact masses were determined by either ANALEST Laboratory of the University of Toronto or by Guelph Chemical Laboratories Inc. located in Guelph, Ontario.

All metal precursors were purchased from either BDH or Sigma–Aldrich. *N*-(2,6-Dimethylphenyl)acetamide was purchased from Sigma–Aldrich or Alfa Aesar and used without further purification. 1-(1-(2,6-Dimethylphenylimino)-2,2-dimethylpropyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene (C^Imine) was prepared using the published procedure [12]. $TiCl_2(2,6\text{-}OC_6H_3\text{–}Me_2)_2(THF)_2$ and $TiCl_2(1,2\text{-}OC_6H_4O)(THF)_2$ were prepared analogous to the literature procedure. The product was further purified by dissolving it in THF with subsequent precipitation from pentane to yield the THF adduct [24,30]. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories. MAO was graciously donated by Albemarle Corp.

4.2. Synthesis of complexes 1–3

4.2.1. Synthesis of $TiCl_2(2,6\text{-}OC_6H_3\text{–}Me_2)_2$(C^Imine) (1)

A solution of C^Imine (107 mg, 0.287 mmol) dissolved in toluene (5 mL) was added to a toluene solution of $TiCl_2(2,6\text{-}OC_6H_3\text{–}Me_2)_2(THF)_2$ (145 mg, 0.287 mmol) and the dark red solution was stirred at room temperature for 4 h. Volatiles were removed under reduced pressure and the product was washed with pentane (15 mL) to yield a bright orange-red powder. A spectroscopically pure product was acquired by recrystallisation from CH_2Cl_2 and pentane (172 mg, 82%). Crystals suitable for X-ray diffraction study were grown at −35 °C under nitrogen by slow liquid diffusion of pentane into a saturated CH_2Cl_2 solution. ^{1}H NMR (400 MHz, C_6D_6): δ 6.93 (d, J = 2.0, 1H, $NCHCN_{(mesityl)}$), 6.77–6.49 (m, 9H, $p\text{-}CH_{(2,6\text{-}xylyl)}$ + $p\text{-}CH_{(phenoxide)}$ + $p\text{-}CH_{(phenoxide)}$ + $m\text{-}CH_{(2,6\text{-}xylyl)}$ + $m\text{-}CH_{(phenoxide)}$ + $m\text{-}CH_{(phenoxide)}$), 6.47 (s, 2H, $m\text{-}CH_{(mesityl)}$), 5.94 (d, J = 2.0, 1H, $NCCHN_{(mesityl)}$), 2.58 (s, 6H, $o\text{-}CH_{3(phenoxide)}$), 2.55 (s, 6H, $o\text{-}CH_{3(2,6\text{-}xylyl)}$), 2.43 (s, 6H, $o\text{-}CH_{3(mesityl)}$), 2.41 (s, 6H, $o\text{-}CH_{3(phenoxide)}$), 1.84 (s, 3H, $p\text{-}CH_{3(mesityl)}$), 0.88 (s, 9H, $(CH_3)_3C$); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 201.2 (NCN), 167.9 ($C_{ipso(phenoxide)}$), 165.7 ($C_{ipso(phenoxide)}$), 162.9 (C=N), 146.0 ($C_{ipso(2,6\text{-}xylyl)}$), 139.8 ($p\text{-}C_{(mesityl)}$), 135.6 ($o\text{-}C_{(mesityl)}$), 131.6 ($o\text{-}C_{(2,6\text{-}xylyl)}$), 131.2 ($o\text{-}C_{(phenoxide)}$), 130.5 ($o\text{-}C_{(phenoxide)}$), 129.7 ($m\text{-}CH_{(mesityl)}$), 129.1 ($C_{ipso(mesityl)}$), 129.0 ($m\text{-}CH_{(2,6\text{-}xylyl)}$), 128.7 ($m\text{-}CH_{(phenoxide)}$), 128.6 ($m\text{-}CH_{(phenoxide)}$), 126.0 ($p\text{-}CH_{(2,6\text{-}xylyl)}$), 122.1 ($p\text{-}CH_{(phenoxide)}$), 121.7 ($NCCN_{(mesityl)}$), 121.3 ($p\text{-}CH_{(phenoxide)}$), 119.6 ($NCCN_{(mesityl)}$), 40.7 ($(CH_3)_3C$), 30.2 ($(CH_3)_3C$), 22.0 ($o\text{-}CH_{3(2,6\text{-}xylyl)}$), 21.3 ($p\text{-}CH_{3(mesityl)}$), 20.5 ($o\text{-}CH_{3(phenoxide)}$), 19.8 ($o\text{-}CH_{3(mesityl)}$), 19.2 ($o\text{-}CH_{3(phenoxide)}$). FTIR (cast film) $\nu_{C=N}$ 1616 cm^{-1}. Anal. Calcd for $C_{41}H_{49}Cl_2N_3O_2Ti$ (%): C, 67.03; H, 6.72; N, 5.72. Found (%): C, 66.84; H, 7.01; N, 5.69.

4.2.2. *Synthesis of $TiCl_2(2,6\text{-}OC_6H_3{-}Me_2)_2(1\text{-}(2,4,6\text{-}trimethylphenyl)imidazole)_2$ (**2**)*

A solution of 1-(2,4,6-trimethylphenyl)imidazole (144 mg, 0.776 mmol) dissolved in toluene (5 mL) was added to a toluene solution of $TiCl_2(2,6\text{-}OC_6H_3{-}Me_2)_2(THF)_2$ (196 mg, 0.388 mmol) and the dark red solution was stirred at room temperature for 3 h. Volatiles were removed under reduced pressure and the product was purified by multiple recrystallisations from CH_2Cl_2 and pentane (201 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 2H, NC*H*N$_{\text{(mesityl)}}$), 7.74 (s, 2H, NCC*H*N$_{\text{(mesityl)}}$), 6.94 (s, 4H, m-C*H*$_{\text{(mesityl)}}$), 6.87 (d, *J* = 7.4, 4H, *m*-C*H*$_{\text{(phenoxide)}}$), 6.77 (s, 2H, NC*H*CN$_{\text{(mesityl)}}$), 6.70 (t, *J* = 7.4, 2H, *p*-C*H*$_{\text{(phenoxide)}}$), 2.33 (s, 18H, *o*-C*H*$_{3\text{(phenoxide)}}$, *p*-C*H*$_{3\text{(mesityl)}}$), 1.95 (s, 12H, *o*-C*H*$_{3\text{(mesityl)}}$); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.4 (*C*$_{ipso\text{(phenoxide)}}$), 141.2 (NCHN), 139.6 (*p*-*C*$_{\text{(mesityl)}}$), 134.8 (*o*-*C*$_{\text{(mesityl)}}$), 132.4 (*C*$_{ipso\text{(mesityl)}}$), 130.8 (NC*C*N), 129.4 (o-*C*$_{\text{(phenoxide)}}$), 129.2 (*m*-CH$_{\text{(mesityl)}}$), 127.9 (*m*-CH$_{\text{(phenoxide)}}$), 121.7 (*p*-CH$_{\text{(phenoxide)}}$), 118.8 (NCCN), 21.0 (*p*-CH$_{3\text{(mesityl)}}$), 17.5 (*o*-CH$_{3\text{(phenoxide)}}$), 17.3 (*o*-CH$_{3\text{(mesityl)}}$). Anal. Calcd for $C_{40}H_{46}Cl_2N_2O_2Ti$ (%): C, 65.49; H, 6.32; N, 7.64. Found (%): C, 65.72; H, 6.13; N, 7.77.

4.2.3. *Synthesis of $TiCl_2(1,2\text{-}OC_6H_4O)$(C^Imine) (**3**)*

A solution of C^Imine (150 mg, 0.401 mmol) dissolved in toluene (2 mL) was added to a toluene solution (5 mL) of $TiCl_2(1,2\text{-}OC_6H_4O)(THF)_2$ (149 mg, 0.401 mmol). The dark red solution was allowed to stir for 4 h. The volume was reduced under reduced pressure and the product was precipitated with pentane. The supernatant was removed and the product was dried *in vacuo* to yield a dark red powder. An analytically pure product was isolated by recrystallisation from CH_2Cl_2 and pentane (202 mg, 84%). Crystals suitable for X-ray diffraction study were grown at −35 °C under nitrogen by slow liquid diffusion of pentane into a saturated CH_2Cl_2 solution. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 2.0, 1H, NC*H*CN$_{\text{(mesityl)}}$), 7.07 (d, *J* = 2.0, 1H, NCC*H*N$_{\text{(mesityl)}}$), 7.03–6.99 (m, 4H, C*H*$_{\text{(aryl)}}$), 6.41 (br s, 3H, *m*-C*H*$_{\text{(2,6-xylyl)}}$, *p*-C*H*$_{\text{(2,6-xylyl)}}$), 5.88 (br s, 1H, *m*-C*H*$_{\text{(mesityl)}}$), 5.40 (br s, 1H, *m*-C*H*$_{\text{(mesityl)}}$), 2.47 (br s, 9H, *o*-C*H*$_{3\text{(aryl)}}$), 2.24 (s, 3H, *p*-C*H*$_{3\text{(mesityl)}}$), 1.58 (br s, 3H, *o*-C*H*$_{3\text{(aryl)}}$), 1.43 (s, 9H, (C*H*$_3$)$_3$C); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 197.2 (NCN), 166.9 (*C*=N), 158.7 (*C*$_{\text{(aryl)}}$), 145.2 (*C*$_{\text{(aryl)}}$), 139.4 (*p*-*C*$_{\text{(mesityl)}}$), 134.8 (*C*$_{\text{(aryl)}}$), 133.9 (*C*$_{\text{(aryl)}}$), 129.3 (*m*-CH$_{\text{(mesityl)}}$), 129.0 (*C*$_{\text{(aryl)}}$), 128.3 (*m*-CH$_{\text{(2,6-xylyl)}}$), 126.7 (*p*-CH$_{\text{(2,6-xylyl)}}$), 123.8 (NCCN$_{\text{(mesityl)}}$), 119.9 (NCCN$_{\text{(mesityl)}}$), 111.2 (*o*-C$_{\text{(mesityl)}}$), 40.7 ((CH$_3$)$_3$*C*), 30.4 ((*C*H$_3$)$_3$C), 21.0 (*p*-CH$_{3\text{(mesityl)}}$), 20.0 (*o*-CH$_{3\text{(mesityl)}}$), 19.0 (*o*-CH$_{3\text{(2,6-xylyl)}}$), 16.6 (*o*-CH$_{3\text{(mesityl)}}$). Not all ^{13}C assignments could be made due to poorly defined correlations from the broad resonances. FTIR (cast film) $\nu_{\mathrm{C}} =_{\mathrm{N}}$ 1610 cm^{-1}. Anal. Calcd for $C_{31}H_{35}Cl_2N_3O_2Ti$ (%): C, 62.01; H, 5.88; N, 7.00. Found (%): C, 61.78; H, 6.12; N, 6.47.

4.3. *General procedure for ethylene polymerisation*

Ethylene polymerisation was performed at atmospheric pressure and room temperature in a 200-mL Schlenk flask containing a magnetic stir bar. The flask was conditioned in an oven at 160 °C for at least 12 h prior to use. The hot flask was brought to room temperature under dynamic vacuum, and back-filled with ethylene. This cycle was repeated a total of three times. Under an atmosphere of ethylene, the flask was charged with 20 mL of dry toluene and 1000 equiv of methylaluminoxane (MAO). The solution was stirred for 15 min before a solution of the catalyst in toluene was introduced into the flask via a syringe. The reaction mixture was vigorously stirred for 10 min after the addition of the catalyst, and subsequently quenched with a 50:50 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 60 °C for several hours.

4.4. *X-ray crystallographic studies*

X-ray crystallographic data for compounds **1** and **2** were collected at the University of Toronto on a Bruker-Nonius Kappa-CCD diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K and were measured using a combination of φ scans and ω scans with κ offsets, to fill the Ewald sphere. Intensity data were processed using the Denzo-SMN package [33]. Absorption corrections were carried out using SORTAV [34]. X-ray crystallographic data for compound **3** was collected at McMaster University on a Bruker APEX2 diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K and were measured using φ and ω scans. Unit cell parameters were determined using at least 50 frames from three different orientations. Data were processed using SAINT, and corrected for absorption with accurate face-indexing as well as redundant data (SADABS), and solved using direct methods and the SHELX program suite. The structures were solved and refined using SHELXTL V6.1 [35] for full-

Table 2
Crystal data and structure refinement details for compounds **1**, **2** and **3**.

	1	**2**	**3**
Empirical formula	$C_{41.5}H_{50}Cl_3N_3O_2Ti$	$C_{40}H_{46}Cl_2N_4O_2Ti$	$C_{38.5}H_{52.5}Cl_2N_3O_2Ti$
Formula weight/g mol^{-1}	777.10	733.61	708.14
Crystal size/mm	0.25 × 0.22 × 0.20	0.26 × 0.20 × 0.14	0.31 × 0.27 × 0.23
θ Range/deg	2.64–27.50	2.55–27.50	1.73–26.36
h; *k*; *l* Range	−23,22; −12,13; −26,27	±11; ±17; −20,21	−17,16; −20,19; −22,16
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	*P*-1	$P2_1/c$
a/Å	18.2261(5)	8.8050(2)	13.7876(18)
b/Å	10.6412(3)	13.5093(4)	16.111(2)
c/Å	21.3160(6)	16.7090(4)	18.264(2)
α/°	90	98.6120(12)	90
β/°	110.3690(10)	104.3730(16)	109.588(2)
γ/°	90	91.6390(16)	90
Z	4	2	4
D_{calcd}/Mg m^{-3}	1.332	1.283	1.231
F(000)	1636	772	1506
No. of reflns collected/unique	21,314/8744	22,446/8648	42,162/7768
No. data/restrnts/params	8744/0/482	8648/0/452	7768/7/421
Final *R* indices [$F^2 < 2\sigma(F^2)$]: R_1, wR_2	0.0612, 0.1498	0.0589, 0.1453	0.0561, 0.1464
R indices (all data): R^1, wR^2	0.1234, 0.1850	0.1199, 0.1811	0.0882, 0.1711
Goodness-of-fit on F^2	1.040	1.035	1.045

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 Uiso-tied to the carrier atom. Details of the X-ray crystal data and structure refinement details are listed in Table 2. Other crystallographic data (tables of atomic coordinates with isotropic and anisotropic displacement parameters, bond lengths and angles) are provided as Supplementary material.

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Appendix A. Supplementary material

CCDC 856682 (for **1**), CCDC 856683 (for **2**), and CCDC 856684 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.cccdc.cam.ac.uk/data-request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2012.05.018.

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