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Synthesis and characterization of titanium ketimide complexes $Ti(N{=}C^tBu_2)_nCl_{4-n}$ ($n = 1, 2$): Ethylene polymerization studies

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Abstract

Compounds $[Ti(N{=}C^tBu_2)Cl_3]_2$, **1**, $[Ti(N{=}C^tBu_2)_2Cl_2]_2$, **2**, $[Ti(N{=}C^tBu_2)(CH_2Ph)_3]$, **3**, $[Ti(N{=}C^tBu_2)_2(CH_2Ph)_2]$, **4**, $[Ti(N{=}C^tBu_2)(CH_2Ph)_2(\mu\text{-}CH_2PhB(C_6F_5)_3]$, **5** and $[Ti(N{=}C^tBu_2)_2(CH_2Ph)\ (\mu\text{-}CH_2PhB(C_6F_5)_3]$, **6**, are described. **1** was obtained from the reaction of $TiCl_4$ and $Me_3SiN{=}C^tBu_2$ and used as starting material for the preparation of **2** and **3**. Complex **4** was obtained by reaction of **2** with $PhCH_2MgCl$. Complexes **5** and **6** were prepared by addition of $B(C_6F_5)_3$ to **3** and **4**, respectively. The NMR spectra of **5** and **6** reveal that these complexes exist in solution as zwitterions with one benzyl ligand bridging the titanium and boron centres. Complexes **1** and **2** are ethylene polymerization catalysts when activated with MAO, displaying activities of 217.1 and 794.6 kg/(mol(Ti[E]) h), respectively.

Keywords: Titanium ketimide; Ethylene polymerization; MAO

1. Introduction

The diversity of Group 4 metal complexes that display extremely high activity, productivity and selectivity in α-olefin polymerization catalysis rose exponentially in recent years due to a deeper understanding of the reactions mechanisms [1–8]. It is currently recognised that the ability to modulate and control homo- and co-polymer synthesis is intrinsically associated to ligand modifications that determine stereochemical and/or electronic aspects. Subtle interactions as agostic hydrogen bonding [9], ion pairing [10,11] and aggregation levels [12], for instance, proved to be extremely important in the catalysts performance through the stabilization of the Lewis acidic metal centres that are the actual polymerization catalysts.

Among several types of support ligands extensively used in Group 4 metal olefin polymerization catalysts are nitrogen-based ligands as benzamidinates [13–15], amidos [16–18] and, more recently, phosphinimides [19,20] and ketimides [21]. Compounds of the type $Cp'Ti(N{=}C^tBu_2)Cl_2$, patented by Nova Chemicals [22], have proven to be extremely active catalysts in α-olefin homopolymerizations [23–26], and are capable of copolymerizing ethylene with polar [23] and apolar monomers [24,26]. Particularly noteworthy is the ethylene–styrene copolymerization that was obtained in a living manner by Nomura [26]. The cationic complexes $[TiCp'(N{=}CR_1R_2)Me]^+$, which are accepted as the active species in olefin polymerization catalysis, have been studied by Piers et al. [27,28].

We have recently reported that the titanium tris(ketimide) complex $Ti(N{=}C^tBu_2)_3Cl$ is a good ethylene polymerization catalysts when activated by MAO [29] and carried out reactivity studies relevant to the understanding of their behaviour as ethylene polymerization catalysts [30]. We present now the syntheses and characterization of mono- and bis-ketimide titanium complexes of general formula $Ti(N{=}C^tBu_2)_nX_{4-n}$ ($n = 1, 2$; $X = Cl$, $PhCH_2$) and reactivity studies that include ethylene polymerization.

2. Experimental

All manipulations, except stated otherwise, were carried out under nitrogen, using either standard Schlenk-line or dry-box techniques.

Solvents were pre-dried using 4 Å molecular sieves and refluxed over sodium-benzophenone (diethyl ether, tetrahydrofuran and toluene) or calcium hydride (dichloromethane, acetonitrile and *n*-hexane) under an atmosphere of nitrogen, and collected by distillation. Deuterated solvents were dried with molecular sieves and freeze–pump–thaw–degassed prior to use.

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^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR spectra were recorded in a Varian Unity 300, at 298 K unless stated otherwise. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and reported relative to tetramethylsilane (δ 0). ^{19}F and ^{11}B spectra were referenced externally to CF_3COOH (δ −76 ppm) and $BF_3{\cdot}Et_2O$, respectively. Peak assignments were aided by NOE experiments (one- and two-dimensional) and by one bond ^{13}C–^{1}H hetero–correlations, as appropriate. ^{1}H NMR and ^{13}C NMR polymer spectra were obtained on samples dissolved in either a mixture of 1,3,5-trichlorobenzene with 30% C_6D_6 at 110 °C (the spectra were referenced internally using hexamethyldisiloxane δ_H 0.058, δ_C 1.9 relative to tetramethylsilane, TMS) or $CDCl_3$ at room temperature.

High-resolution electron ionisation (EI) mass spectra were obtained by a Fourier transform ion cyclotron resonance mass spectrometer (Finnegan FT/MS 2001-DT spectrometer), equipped with a 3-T superconducting magnet. FAB/MS spectra were obtained in a TRIO 2000, VG Micromass Spectrometer at the University of Rouen in France. Elemental analyses were obtained from the Laboratório de Análises do IST (Fisons Instrument 1108).

$ClMgCH_2Ph$ (1.5 mol dm^{-3} in ether) was purchased from Aldrich and LiMe (1.8 M in ether) was purchased from Merk. Both were titrated by usual methods before use. MAO (5% Al in toluene) was purchased from Akzo Nobel and used as received. The compounds $LiN{=}C^tBu_2$ [31], $SiMe_3N{=}C^tBu_2$ [32], $Ti(N{=}C^tBu_2)_3Cl$, **3** [29], $Ti(N{=}C^tBu_2)_4$, **4** [29] and $B(C_6F_5)_3$ [33] were prepared according to literature methods.

2.1. *[Ti(N=C^{t}Bu$_2$)Cl$_3$]$_2$ (**1**)*

To a solution of $TiCl_4$ (0.273 g, 1.44 mmol) in toluene cooled to −80 °C, a solution of $SiMe_3N{=}C^tBu_2$ (0.613 g, 2.87 mmol) was added. The mixture, that turned immediately dark after the addition, was allowed to come slowly to room temperature. After 15 h, a bright green solid has precipitated out of solution. The mixture was then filtered, the solid was washed with hexane and the residue was dried in vacuum (0.404 g, 95% yield). ^{1}H NMR (C_6D_6, 300 MHz): 1.07 (s, 36H, $^tBu^{A+B}$). ^{13}C-{^{1}H} NMR (C_6D_6, 75 MHz): 208.6 (N=C^B), 51.1 ($C^A(CH_3)_3$), 42.2 ($C^B(CH_3)_3$), 30.0 ($C(C^AH_3)_3$), 28.8 ($C(C^BH_3)_3$). ^{1}H NMR (C_6D_5Br, 300 MHz): 1.79 (s, 18H, $^tBu^A$), 1.52 (s, 18H, $^tBu^B$). ^{13}C-{^{1}H} NMR (C_6D_5Br, 75 MHz): 208.2 (N=C^B), 51.6 ($C(C^AH_3)_3$), 42.3 ($C^B(CH_3)_3$), 30.0 ($C(C^AH_3)_3$), 28.0 ($C(C^BH_3)_3$). EI/FT ICR-MS: 292.99979 (100) ($[C_9H_{18}Cl_3N^{48}Ti]^-$). MS (FAB, *m/z*): 574 (M^+ − Me), 532 (M^+ − ^{t}Bu). Elem. Anal. Calcd. for $C_9H_{184}Cl_3Ti$: C, 36.71; H, 6.16; N, 4.76. Found: C, 37.01; H, 6.83; N, 4.69.

2.2. *[Ti(N=C^{t}Bu$_2$)$_2$Cl$_2$]$_2$ (**2**)*

To a suspension of **1** (0.518 g, 1.76 mmol) in toluene cooled to −80 °C, $LiN{=}C^tBu_2$ (0.259 g, 1.67 mmol) was added, also suspended in toluene. The mixture was allowed to reach room temperature and to stir at that temperature for 3 h. After solvent removal the residue was extracted with hexane. Cooling the solution to 4 °C afforded 0.218 g of a dark red crystalline solid (31% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.14 (s, 36H, ^{t}Bu). ^{13}C-{^{1}H} NMR (C_6D_6, 75 MHz): δ 209.1 (N=*C*), 47.9 ($C(CH_3)_3$), 30.3 ($C(CH_3)_3$). HR EI/FT ICR-MS: 398.17905 (100) ($[C_{18}H_{36}Cl_2N_2{}^{48}Ti]^-$). Elem. Anal. Calcd. for $C_{18}H_{36}Cl_2N_2Ti$: C, 54.14; H, 9.09; N, 7.02. Found: C, 53.66; H, 10.04; N, 6.59.

2.3. *Ti(N=C^{t}Bu$_2$)(CH$_2$Ph)$_3$ (**3**)*

1 (0.0916 g, 0.33 mmol) was dissolved in 40 mL of hexane and cooled to −50 °C. $ClMgCH_2Ph$ (1.5 M, 1.5 mmol) was added and the mixture was allowed to reach room temperature. The mixture was filtered and the solvent was removed. The residue was reextracted in hexane. Pumping off the solvent afforded 0.138 g of a dark red oil (91% yield). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.12 (t, $^3J_{HmHp}$ = 7.2 Hz, 6H, H_m), 6.96 (t, $^3J_{HmHp}$ = 7.2 Hz, 3H, H_p), 6.44 (d, $^3J_{HmHo}$ = 7.5 Hz, 6H, H_o), 2.67 (s, 6H, CH_2), 1.11 (s, 18H, ^{t}Bu). ^{13}C-{^{1}H} NMR (C_6D_6, 75 MHz): δ 143.7 (C_{ipso}), 129.3 (C_m), 128.8 (C_o), 123.6 (C_p), 87.5 (CH_2), 47.2 ($C(CH_3)_3$), 30.7 ($C(CH_3)_3$). HR EI/FT ICR-MS: 461.256196 (100) ($[C_{30}H_{39}N^{48}Ti]^-$). Elem. Anal. Calcd. for $C_{30}H_{39}NTi$: C, 78.07; H, 8.52; N, 3.03. Found: C, 71.98; H, 8.09; N, 3.26.

2.4. *Ti(N=C^{t}Bu$_2$)$_2$(CH$_2$Ph)$_2$ (**4**)*

The reaction was done in exactly the same way as was described above for **3**. Compound **4** was obtained as a red solid in 95% yield (0.502 g) from the reaction of **2** (0.416 g, 1.04 mmol) with $ClMgCH_2Ph$ (1.5 M, 3.12 mmol). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.15–7.06 (m, 6H, $H_o + H_p$), 6.90 (t, $^3J_{HH}$ = 6.8 Hz, 4H, H_m), 2.77 (s, 4H, CH_2), 1.14 (s, 36H, ^{t}Bu). ^{13}C-{^{1}H} NMR (C_6D_6, 75 MHz): δ 198.6 (*C*=N), 145.8 (C_{ipso}), 128.7 (C_o), 128.2 (C_p), 122.3 (C_m), 78.1 (CH_2), 46.1 ($C(CH_3)_3$), 30.7 ($C(CH_3)_3$). HR EI/FT ICR-MS: 510.33947 (100) ($[C_{32}H_{50}N_2{}^{48}Ti]^-$). Elem. Anal. Calcd. for $C_{32}H_{50}N_2Ti$: C, 75.27; H, 9.87; N, 5.49. Found: C, 72.10; H, 10.86; N, 4.75.

2.5. *[Ti(N=C^{t}Bu$_2$)(CH$_2$Ph)$_2$(μ-CH$_2$Ph)B(C$_6$F$_5$)$_3$] (**5**)*

Compound **5** (0.015 g, 0.03 mmol) was dissolved in 0.3 mL of toluene-d^8 and placed in a sealable NMR tube. The solution was degassed and frozen prior to the introduction of 0.3 mL of a solution of $B(C_6F_5)_3$ (0.017 g, 0.03 mmol) in toluene-d^8, that was immediately frozen. The tube was sealed under vacuum and was unfrozen in a bath at −80 °C, prior to its introduction in the NMR machine, where it was allowed to come to room temperature, as it was monitored. Reaction was complete instantly at −80 °C, in quantitative yield. ^{1}H NMR (C_7D_8, −30 °C, 300 MHz): δ 7.4–6.8 (m, 6H, $H_9 + H_{10}$), 6.55 (d, J = 7.8 Hz, 4H, H_8), 6.48 (m, 2H, H_3), 6.10 (t, $^3J_{H4H5}$ = 6.8 Hz, 1H, H_5), 5.95 (t, $^3J_{H4H5}$ = 6.8 Hz, 2H, H_4), 3.02 (br, s, 2H, BCH_2), 2.34 (dd, 4H, $^2J_{HH}$ = 10.7 Hz, Ti–CH_2), 1.02 (s, 18H, ^{t}Bu). ^{19}F NMR (C_7D_8, −30 °C, 282 MHz): δ −128.2 (s, 2F, F_o), −157.7 (br, 1F, F_p), −162.0 (br, 2F, F_m). ^{11}B NMR (C_7D_8, −30 °C, 96 MHz): δ −7.6 (s). ^{13}C-{^{1}H} NMR (C_7D_8, −40 °C,

75 MHz): δ 49.6 (Ti–CH_2), 38.5 ($C(CH_3)_3$), 29.8 (CH_3), 29.7 (BCH_2, br).

2.6. [Ti(N=C^{t}Bu$_2$)$_2$(CH$_2$Ph)(μ-CH$_2$Ph)B(C$_6$F$_5$)$_3$] (6)

The procedure is the same as described for **5**. ^{1}H NMR (C_7D_8, −30 °C, 300 MHz): δ 7.08 (d, $^3J_{H3H4}$ = 7.8 Hz, 2H, H_3), 6.88 (t, $^3J_{H5H4}$ = 6.8 Hz, 1H, H_5), 6.78 (m, 2H, H_4), 6.50 (d, $^3J_{H8H9}$ = 7.5 Hz, 2H, H_8), 5.86 (m, 2H, H_9), 5.62 (m, 1H, H_{10}), 3.30 (s, 2H, H_6), 2.46 (s, 2H, H_1), 0.99 (s, 36H, ^{t}Bu). ^{19}F NMR (C_7D_8, −30 °C, 282 MHz): δ −123.9 (s, 2F, F_o), −154.3 (t, $^3J_{FpFm}$ = 20.7 Hz, 1F, F_p), −158.2 (t, $^3J_{FpFm}$ = 18.3 Hz, 2F, F_m). ^{11}B NMR (C_7D_8, −30 °C, 96 MHz): δ −7.5 (s). ^{13}C-{^{1}H} NMR (C_7D_8, −40 °C, 75 MHz): δ 204.8 (N=*C*), 150.0 and 146.8 (d, $^1J_{CF}$ = 240 Hz, C_o–F), 138.8 and 135.2 (d, $^1J_{CF}$ = 240 Hz, C_m–F), 45.8 ($C(CH_3)_3$), 31.6 (BCH_2, br), 29.1 (CH_3).

3. General procedure for olefin polymerization

The polymerization apparatus and polymer work up were described in previous papers [34–36]. The polymerization mixture was quenched with acidic methanol (2% HCl) and the precipitated polymer was filtered, washed with methanol and dried in a vacuum oven at 60 °C during 3 days.

3.1. General procedures for X-ray crystallography

Pertinent details can be found in Table 1. Suitable crystals of complex **2** were mounted on a Mach3 Nonius equipped with Mo radiation (λ = 0.70169 Å). Data were collected at room temperature. Solution and refinement were made using SIR 97 [37] and SHELXL-97 [38] included in the package of programs WINGX-version 1.64.05 [39]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were inserted in idealized positions riding in the parent C atom. The molecular structures were done with ORTEP3 for Windows, [40] included in the software package.

Data for complex **2** was deposited in CCDC under the deposit number 612833 and can be obtained free of charge from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (tel: +44 1223 336408; fax: +44 1223 336033).

Table 1
Crystallographic data for **2**

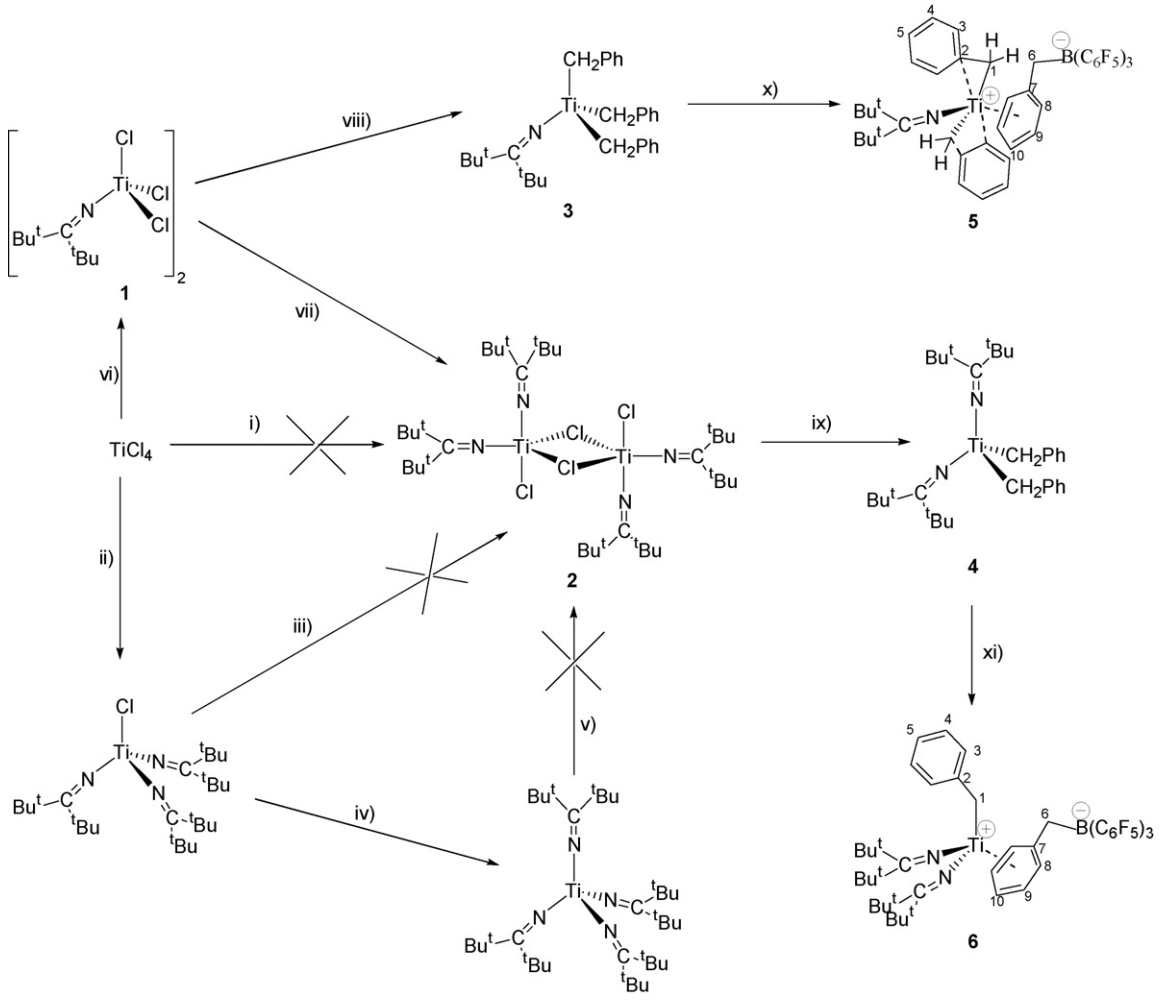
Empirical formula	$C_{36}H_{72}Cl_4N_4Ti_2$
Formula weight	798.58
Temperature (K)	293 (2)
Wavelength (Å)	0.70169
Crystal system	Triclinico
Space group	P-1
a (Å)	12.089 (4)
b (Å)	14.530 (6)
c (Å)	14.693 (3)
α (°)	65.65 (3)
β (°)	79.87 (2)
γ (°)	79.28 (3)
V (Å^3)	2296.0 (13)
Z	2
D_c (g cm^{-3})	1.155
Absorption coefficient	0.607
F(0 0 0)	856
Crystal size	0.44 × 0.10 × 0.02
Crystal morphology	Needle
Color	Red
θ range for data collection	1.70°–24.94°
Limiting indices	$-14 \le h \le 14$; $-17 \le k \le 15$; $-17 \le l \le 0$
Reflections collected/unique	8306/7966 [R_{int} = 0.0253]
Completeness to theta	99.0% (θ = 24.94°)
Refinement method	Full matrix least-squares on F^2
Data/restrains/parameters	7966/228/415
Goodness of fit on F^2	0.991
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0766, *wR*2 = 0.1811
R indices (all data)	*R*1 = 0.1242, *wR*2 = 0.2038
Extinction coefficient	0
Largest diff. peak and hole	0.738 and −0.971 e Å^{-3}

4. Results and discussion

4.1. Synthesis and characterization

The reactions and compounds discussed in this work are represented in Scheme 1.

The standard procedure to synthesize [Ti(N=C^{t}Bu$_2$)$_2$Cl$_2$] would be the reaction of $TiCl_4$ with two equivalents of LiN=C^{t}Bu$_2$ ((i) in Scheme 1) [41,42]. This reaction, however, did not lead to the target complex but to [Ti(N=C^{t}Bu$_2$)$_3$Cl] [29]. Although surprising, this result has analogy to reports on non-stoichiometric Group 4 metal halide metathesis reactions with lithium amides [43–45]. The electrophilic attack with TMSCl and the transmetallation reaction between $TiCl_4$ and Ti(N=C^{t}Bu$_2$)$_4$ [29] were thus explored as an alternative approach to [Ti(N=C^{t}Bu$_2$)$_2$Cl$_2$] but proved, once more, unsuccessful. The failure of the first reaction may reflect the unavailability of the nitrogen electron pairs in [Ti(N=C^{t}Bu$_2$)$_3$Cl]. The transmetallation reaction failure is probably related to the stereochemical protection that the four ketimide ligands provide to the metal centre in Ti(N=C^{t}Bu$_2$)$_4$. In accordance with this interpretation is the fact that a significant amount of Ti(N=C^{t}Bu$_2$)$_4$ is recovered at the end of the reaction. A third attempt to obtain [Ti(N=C^{t}Bu$_2$)$_2$Cl$_2$] was the reaction of $TiCl_4$ with two equivalents of a softer ketimide transfer reagent, Me_3SiN=C^{t}Bu$_2$ ((iii) in Scheme 1). Treatment of $TiCl_4$ with one or two equivalents of Me_3SiN=C^{t}Bu$_2$ afforded quantitatively [Ti(N=C^{t}Bu$_2$)Cl$_3$]$_2$, **1**, as a bright green solid. The ^{1}H and ^{13}C NMR spectra of **1** in the temperature range of −30 to 110 °C show two sets of signals for the ketimide ligand. This result suggests that **1** is a dimer where the metals are pentacoordinated by two bridging chloride ligands, two terminal chlorides and one ketimide ligand. The NMR data reflect thus the existence of two isomeric structures in solution, resulting from different arrangements of the ketimide ligand in the metal coordination sphere. This assumption is supported by the FAB/MS spectrum that shows one signal at *m*/*z* 574 corresponding to the dimer parent-ion minus one methyl group ($[M - Me]^+$). Further confirmation was attempted by high resolution mass spectrometry (HR EI/FT ICR-MS) but

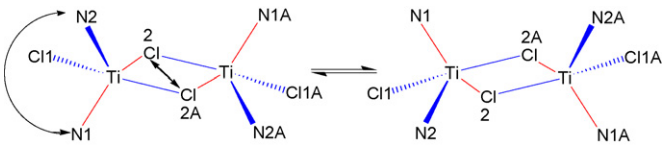


Scheme 1. (i) Two equiv. of LiN=C^{t}Bu$_2$; (ii) two equiv. of LiN=C^{t}Bu$_2$; (iii) TMSCl; (iv) 1 equiv. of LiN=C^{t}Bu$_2$; (v) TiCl$_4$; (vi) Me$_3$SiN=C^{t}Bu$_2$; (vii) one equiv. of LiN=C^{t}Bu$_2$; (viii) PhCH$_2$MgCl; (ix) PhCH$_2$MgCl; (x) B(C$_6$F$_5$)$_3$; (xi) B(C$_6$F$_5$)$_3$.

compound fragmentation gave origin to a peak at *m*/*z* 292.99979, corresponding to $[1/2M]^+$, with the correct isotopic pattern.

Complex **1** was used as a starting material for the successful preparation of [Ti(N=C^{t}Bu$_2$)$_2$Cl$_2$]. The reaction of **1** with one equivalent of LiN=C^{t}Bu$_2$ allowed the isolation of [Ti(N=C^{t}Bu$_2$)$_2$Cl$_2$]$_2$, **2**, in 31% yield-based on titanium ((iv) in Scheme 1). The relatively low yield obtained reveals the poor stoichiometric control of the reaction that also gives [Ti(N=C^{t}Bu$_2$)$_3$Cl] in an equimolar amount. The proton NMR spectrum of the reaction crude shows two resonances at δ 1.14 and 1.27 ppm that are assigned to the ^{t}Bu groups in **2** and [Ti(N=C^{t}Bu$_2$)$_3$Cl], respectively. The reaction outcome is therefore controlled by the amount of the lithium salt present and there is no kinetic preference for the first or the second chloride substitution. This result reveals that ketimide ligands offer poor steric shielding to the metal centre [29] and is consistent with the recurrent formation of small clusters as [{Ti(N=C^{t}Bu$_2$)$_2$(μ_2-F)}$_3$(μ_3-F)$_2$]PF$_6$ [30].

The formulation of **2** as a dimer is supported by the X-ray diffraction data presented below. In solution, the complex maintains the dimeric structure as attested by variable-temperature NMR studies that show the splitting of the proton ketimide singlet into two resonances at temperatures below 196 K (Eq. (1)). The Gibbs free energy of activation $\Delta G^{\ddagger}$ calculated on the basis of Eyring equation at the coalescence temperature is 40.3 ± 0.8 kJ mol^{-1} [46].



(1)

The molecular structure of **2** is depicted in Fig. 1 and in Table 2 relevant bond distances and angles are presented. The two titanium centres are pentacoordinated with one inversion centre located in the plane that contains the titanium and the bridging chloride ligands. The metals coordination geometry is distorted trigonal bipyramidal with the axial positions occupied by N2 and Cl2A that define an angle of 161.75 (15)°.

The angles defined by the Ti1–N2 bond and the Ti–X equatorial bonds (*X* = N1, Cl2, Cl1) range between 85.86 (14)° and 101.53 (17)°. The wider angle is defined by N2–Ti1–N1, as

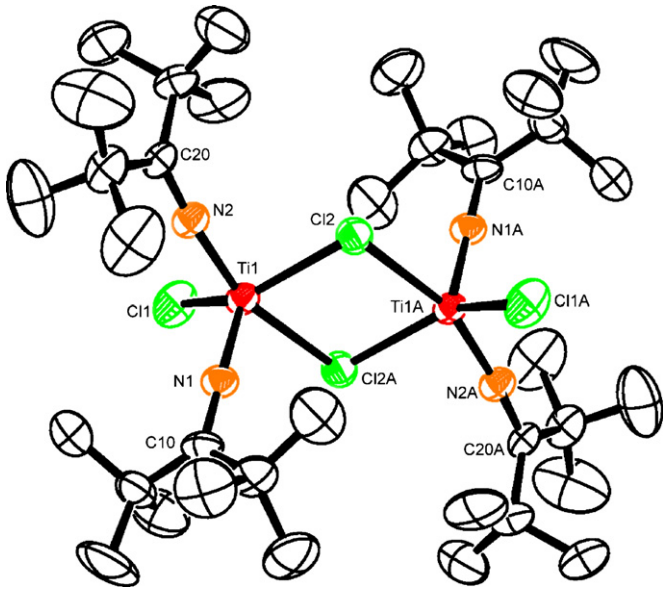


Fig. 1. Molecular structure of 2. Hydrogen atoms are omitted for clarity. Ellipsoids shown with 40% probability.

a result of the stereochemical requirements of the two bulky $^{t}Bu_2C{=}N$ ligands. The angle Cl2–Ti1–Cl2A (79.06 (5)°), inside the bridging $[Ti(\mu\text{-}Cl)]_2$ moiety, is much narrow than all the other angles around Ti1. The Ti1–N1 and Ti1–N2 bond lengths have values comparable to those reported for other Ti(IV) ketimide compounds and reflect the π character of the ketimide coordination [27,47,48]. The Ti–N–C angles are close to linearity as expected for sp nitrogen hybridization. The nitrogen π donation to the titanium causes the elongation of the Ti1–Cl2A bond that is in *trans* position when compared to the Ti1–Cl2 bond length. Although this difference, the bridging and terminal Ti–Cl distances are inside the usual values for Ti(IV) complexes [49].

Table 2
Selected bond lengths and angles for compound **2**

Bond lengths (Å)	
Ti1–Cl2	2.4453 (16)
Ti1–Cl2A	2.5076 (17)
Ti1–Cl1	2.2820 (17)
Ti1–N1	1.818 (4)
Ti1–N2	1.842 (4)
N1–C10	1.285 (6)
N2–C20	1.249 (6)
Angles (°)	
Cl2A–Ti1–N2	161.74 (13)
Cl1–Ti1–Cl2	140.52 (7)
Cl2–Ti1–N1	108.84 (14)
N1–Ti1–N2	101.53 (18)
N1–Ti1–Cl1	109.11 (15)
Cl2–Ti1–Cl2A	79.06 (5)
Cl2A–Ti1–N1	93.11 (13)
Cl2A–Ti1–Cl1	88.42 (6)
Cl2–Ti1–N2	85.86 (14)
N2–Ti1–Cl1	96.91 (14)
Ti1–N1–C10	172.0 (4)
Ti1–N2–C20	172.7 (4)
Ti1–Cl2–Ti1A	100.94 (5)

The reaction of **1** with $PhCH_2MgCl$ in diethylether led to the formation of $[Ti(N{=}C^{t}Bu_2)(CH_2Ph)_3]$, **3**, in 91% yield. The complex was identified by HR EI/FT ICR-MS that showed one signal at *m/z* 461.256196 (100%) with the correct isotopic pattern for $[M]^+$. As expected, the ^{1}H NMR spectrum of **3** displays three aromatic resonances due to the benzyl phenyl rings and two singlets for the methylenic (δ 2.67 ppm) and methyl (δ 1.11 ppm) groups of the benzyl and ketimide ligands, respectively.

The reaction of **2** with $PhCH_2MgCl$ in hexane allowed the synthesis of $[Ti(N{=}C^{t}Bu_2)_2(CH_2Ph)_2]$, **4**, in 95% yield. The proton and carbon NMR spectra show two magnetically equivalent benzyl ligands σ-bonded to the titanium. The imine C=N carbon is observed at δ 198.6 ppm. This value is shielded when compared to the same resonance in 2 (δ 209.1 ppm) as expected taking in account the higher electronegativity of the chloride ligand.

Addition of $B(C_6F_5)_3$ to toluene-d^8 solutions of **3** and **4** at −80 °C led to the immediate formation of $[Ti(N{=}C^{t}Bu_2)(CH_2Ph)_2(\mu\text{-}CH_2Ph)B(C_6F_5)_3]$, **5** and $[Ti(N{=}C^{t}Bu_2)_2(CH_2Ph)(\mu\text{-}CH_2Ph)B(C_6F_5)_3]$, **6**, respectively, in quantitative yields. The proton NMR spectra of **5** and **6** are consistent the formation of zwitterionic species where the abstracted benzyl groups are π-coordinated to the metal centres since the H_m and H_p resonances in **5** (δ 5.90 and 6.04 ppm) and **6** (δ 5.95 and 6.10 ppm) of the $[B(\eta\text{-}CH_2Ph)(C_6F_5)_3]^-$ moiety are shifted to higher fields than those of the σ-bonded benzyl ligand (δ 6.78 and 6.88 ppm in **3** and 7.40–6.80 ppm in **4**) and those of the free anion (δ 7.13 and 7.00 ppm) [50–57]. Also consistent with one benzyl η-coordinated are the ^{19}F NMR patterns observed for **5** and **6** that present Δδ values of 4.33 ppm for **5** and 3.90 for **6** ($\Delta\delta = \delta F_p - \delta F_m$) [50,52–54,58,59].

4.2. Ethylene polymerization studies

Complexes **1** and **2** activated by methylaluminoxane (MAO) were studied as catalysts in the polymerization of ethylene and the results compared to those obtained with complex $[Ti(N{=}C^{t}Bu_2)_3Cl]$ previously studied [29]. The activity values obtained under the best experimental conditions for each catalytic system are of the same order of magnitude, about 800 kg/(mol(Ti[E]) h) (Tables 3 and 4).

The optimum reaction temperature for system **1**/MAO is 19 °C and for **2**/MAO is 60 °C. Both temperatures are lower than the one found for the system $Ti(N{=}C^{t}Bu_2)_3Cl$/MAO (80 °C), as previously reported [29]. Thus, temperature activation follows the order $Ti(N{=}C^{t}Bu_2)_3Cl > [Ti(N{=}C^{t}Bu_2)_2Cl_2]_2 > [Ti(N{=}C^{t}Bu_2)Cl_3]_2$. At temperatures below 60 °C the system **1**/MAO is more active than **2**/MAO. Above 60 °C an inversion in the relative activities of the two systems occurs, with **2**/MAO being the most active catalyst system. These results point out that the polymerization reaction is governed by two different factors depending on the temperature range. At lower temperatures, the critical factor ruling the catalysts activity is the activation energy for the generation of the active species that is lower for **1** than for **2**. This conclusion is in agreement with the observation that the formation of **5** from **3** and $B(C_6F_5)_3$ occurs readily at −80 °C

Table 3
Ethylene polymerization studies (effect of the temperature)

Run no.	Catalyst	T (°C)	Yield (g)	Activity kg/(mol(Ti[E]) h)
PJ 110	$[Ti(N{=}C^tBu_2)Cl_3]_2$ **1**	0	0.2595	152.2
PJ 109		19	0.3234	217.1
PJ 111		38	0.2149	171.2
PJ 108		60	0.0891	92.9
PJ 112		80	0.0021	3.1
PJ 127	$[Ti(N{=}C^tBu_2)_2Cl_2]_2$ **2**	0	0.0268	15.4
PJ 129		20	0.0898	60.1
PJ 131		40	0.1059	85.2
PJ 126		61	0.7619	794.6
PJ 128		82	0.3334	525
PJ 65 [29]	$Ti(N{=}C^tBu_2)_3Cl$	80	0.3179	470

Experimental conditions: Al/Ti = 2000; P(E) = 2 atm; Cocatalyst: MAO; V = 50 mL toluene; [Ti] = 80 μM; t = 60 min.

Table 4
Ethylene polymerization studies (effect of the Al/Ti ratio)

Run no.	Catalyst	Al/Ti	[Ti] (μM)	T (°C)	Yield (g)	Activity kg/(mol(Ti[E]) h)
PJ 118	$[Ti(N{=}C^tBu_2)Cl_3]_2$ **1**	1000	80	19	1.0761	693.4
PJ 117		2000	80		0.8126	523.6
PJ 121		4000	80		0.6026	388.3
PJ 122		1000	40		0.6224	802
PJ 123		1000	160		1.6493	531.3
PJ 138	$[Ti(N{=}C^tBu_2)_2Cl_2]_2$ **2**	1000	80	60	0.1362	136.2
PJ 137		2000	80		0.4686	428.6
PJ 139		4000	80		0.258	258
PJ 140		1000	40		0.0786	157.2
PJ 141		1000	160		0.6295	314.8
PJ 8 [29]	$Ti(N{=}C^tBu_2)_3Cl$	1000	80	80	0.0961	276.6
PJ 4 [29]		2000	80		0.2394	702.2
PJ 9 [29]		4000	80		0.2628	756.5

Experimental conditions: $P(E)$ = 2 atm; Cocatalyst: MAO; V = 50 mL toluene; t = 60 min; PJ 8, PJ 4, PJ 9, t = 30 min.

whereas the complete conversion of **4** in **6** requires temperatures above −30 °C. The importance of temperature in the formation of the active species is the prevailing factor for the system $Ti(N{=}C^tBu_2)_3Cl$/MAO that, simultaneously to the metal alkylation and cation generation, requires the cleavage of one Ti–N bond [30]. In the upper temperature range, the higher activity of **2**/MAO may reflect that the bis-ketimide catalyst is more thermally robust than the mono-ketimide counterpart. The reactivity, in this temperature range, is thus dictated by the thermal stability of the catalyst.

The Al/Ti ratio also affects the activity although not very significantly since the activities are in the same order of magnitude. The best Al/Ti ratio for system **1**/MAO is 1000 and for **2**/MAO is 2000. Again if we consider the three catalytic systems, the trend is $[Ti(N{=}C^tBu_2)_3Cl] > [Ti(N{=}C^{t\text{-}}Bu_2)_2Cl_2]_2 > [Ti(N{=}C^tBu_2)Cl_3]_2$.

5. Conclusions

The study of complexes $[Ti(N{=}C^tBu_2)_nCl_{4-n}]$ (n = 1, 2, 3 [29]) reveals that ketimide ligands proved appropriate support ligands for Ti(IV) centres and display activity as ethylene polymerization catalysts. The activities displayed by all compounds are similar and close to 800 kg/(mol(Ti[E]) h). Compared to $[TiCp'(N{=}C^tBu_2)Cl_2]$ complexes, [29] compounds **1**, **2**, and $Ti(N{=}C^tBu_2)_3Cl$ are two to three orders of magnitude less active. This observation should be related not only to the electronic unsaturation of titanium in the cationic catalysts but also to stereochemical features. Indeed, although the ^{t}Bu groups are bulky they are located far from the metal centre and thus fail to offer an efficient steric protection. The relevance of this aspect is asserted by the lack of stoichiometric control in chloride metathesis reactions, as described in the synthesis of **2**, and by the formation dimers and small clusters [30].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2007.11.054.

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