Journal of Organometallic Chemistry 696 (2011) 2330-2337

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Studies on the active species in olefin polymerisation generated from phenoxo-amido titanium "*chiral-at-metal*" compounds

Giuseppe Alesso^b, Vanessa Tabernero^a, Marta E.G. Mosquera^{a,1}, Tomás Cuenca^{a,*}

^a Departamento de Química Inorgánica, Universidad de Alcalá, Edificio de Farmacia, Campus Universitario, 28871 Alcalá de Henares, Spain ^b Dipartimento di Chimica, Via Vienna 2, 07100 Sassari, Italy

ARTICLE INFO

Article history: Received 3 December 2010 Received in revised form 17 January 2011 Accepted 9 February 2011

Keywords: Titanium Phenoxo-amido Phenoxo-amino Asymmetric metal centre

ABSTRACT

Treatment of RHN-CH₂-(3,5-tBu₂C₆H₂-2-OH) (R = C₆H₅ **1a**, p-MeC₆H₄ **1b**, Cy **1c**; Cy = cyclohexyl) with 1 equiv of TiCp*Cl₃ (Cp* = η^5 -C₅Me₅) in the presence of 2.5 equiv of NEt₃ in pentane or hexane at room temperature gives the monocyclopentadienyl phenoxo-amido monochloro complexes [TiCp*{RN-CH₂-(3,5-tBu₂C₆H₂-2-O)]Cl] (R = C₆H₅ **2**, p-MeC₆H₄ **4**, Cy **5**). In a more polar solvent the phenoxo-amino complex [TiCp*{(C₆H₅)(H)N-CH₂-(3,5-tBu₂C₆H₂-2-O)]Cl₂] (**3**) is obtained from the reaction with **1a**. The reaction of TiCp*Cl₃ with tBu(H)N-CH₂-(3,5-tBu₂C₆H₂-2-OH) (**1d**) affords the complex [TiCp*{tBu (H)N-CH₂-(3,5-tBu₂C₆H₂-2-OH) (**1d**) affords the complex [TiCp*{tBu (Compounds were characterised by the usual analytical and spectroscopic methods and the molecular structures of **2** and **5** were determined by X-ray diffraction analysis from suitable single crystals.

Studies of catalytic activity for ethylene or propylene polymerisation using boron or aluminium reagents as cocatalysts were performed under different conditions. In general the trends observed for the phenoxo-amido precatalysts with the aluminium reagent as cocatalyst in the α -olefin polymerisation reactions might suggest a catalyst decomposition process through ligand abstraction by sMAO. The activity found for ethylene or propylene polymerisation when B(C₆F₅)₃ or [CPh₃][B(C₆F₅)₄] are used as cocatalysts is related to the strength of the cation-anion interactions.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of Ziegler–Natta catalysis, considerable effort has been devoted to catalyst modification in order to improve the olefin polymerisation process and to know more about its mechanistic aspects [1–11]. The more accepted mechanism was developed by Cossee–Arlman [12,13]. In accordance with this proposal, the minimum requirement for a catalyst precursor has been established as a transition metal complex containing an unreactive ancillary ligand system (generally a cyclopentadienyl type ligand) and at least two coordination sites which can be activated to provide a metal alkyl bond *cis* to a vacant coordination site for monomer binding. Descriptions of group 4 metal complexes

E-mail addresses: martaeg.mosquera@uah.es (M.E.G. Mosquera), tomas.cuenca@ uah.es (T. Cuenca). with these requirements have been extensive [4,14–19] but examples of precatalysts containing only one group that can be active for olefin polymerisation are scarce [20–22].

Ligands with nitrogen and oxygen as donor atoms are particularly interesting, due to their mode of complexation to an acidic metal centre [23–25]. Previously, we have reported the synthesis of a series of cyclopentadienyl titanium complexes containing chelating dialkoxo [26–28] and diamido [29,30] ligands and studied the nature of the catalytic species in the α -olefin polymerisation processes generated by the reaction of these complexes with aluminium and boron reagents as cocatalyst [31]. As a part of a broad research programme aimed at investigating the catalytic performance of compounds with these characteristics, combining a cyclopentadienyl group and a chelating ligand, we have also recently reported the synthesis and polymerisation studies of various phenoxo-amido group 4 metal complexes stabilised by an unsubstituted cyclopentadienyl ligand (η^5 -C₅H₅) [32].

In this paper we describe the synthesis and characterisation of a family of this type of compounds containing the permethylated cyclopentadienyl ring $[TiCp*{R'N-CH_2-(3,5-tBu_2C_6H_2-2-O)}CI]$





^{*} Corresponding author. Tel.: +34 918854655; fax: +34 918854683.

 $^{^{1}}$ Correspondence concerning the crystallography data should be addressed to this author.

⁰⁰²²⁻³²⁸X/\$ – see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jorganchem.2011.02.011



Scheme 1. Synthesis of the phenoxo-amido compounds.

 $(Cp^* = \eta^5 - C_5 Me_5)$ and a concise study of the active species generated when the precatalysts are treated with different boron or aluminium reagents as cocatalyst. The variety of synthesised ligands allows us to modify the electronic properties at the metal centre as well as the geometry of the complex. An analysis of these differences helps to elucidate the correlation between the properties of the metal and catalytic behaviour.

2. Results and discussion

2.1. Synthesis and characterisation of phenoxo-amido and phenoxo-amino compounds

We have previously provided a contribution to the synthesis and characterisation of new and somewhat unusual phenoxo-amido and phenoxo-amino titanium complexes stabilised by the presence of the unsubstituted cyclopentadienyl ligand (η^5 -C₅H₅) and containing asymmetric metal centres. These complexes are interesting from basic coordination chemistry perspectives because only a few derivatives of this type are known. Initial studies of their ethylene polymerisation performance under MAO-activation conditions have also been reported [32]. It is interesting to analyse how the greater bulkiness and electron donor capacity of the permethylated cyclopentadienyl ring causes lower acidity at the titanium centre and consequently influences the behaviour of the analogous derivatives.

As observed in the reactions with TiCpCl₃ [32], treatment of the phenol-amine compounds $RHN-CH_2-(3,5-tBu_2C_6H_2-2-OH)$ ($R = C_6H_5$ **1a**, 4-MeC₆H₄ **1b**, Cy **1c**, tBu **1d**, Cy = cyclohexyl) [32–34] in pentane or hexane with TiCp*Cl₃ (Cp* = η^5 -C₅Me₅) in the presence of NEt₃, under different reaction conditions, gives the corresponding monocyclopentadienyl phenoxo-amido monochloro complexes [TiCp*{RN-CH₂-(3,5-tBu₂C₆H₂-2-O)}Cl] ($R = C_6H_5$ (**2**), 4-MeC₆H₄ (**4**), Cy (**5**)) (Scheme 1) or the monocyclopentadienyl phenoxo-amino dichloro derivatives [TiCp*{(C₆H₅)(H)N-CH₂-(3,5-tBu₂C₆H₂-2-O)} Cl₂] (**3**) (Scheme 2) and [TiCp*{tBu(H)N-CH₂-(3,5-tBu₂C₆H₂-2-O)}



Scheme 3. Synthesis of the phenoxo-amino compound 6.

Cl₂] (**6**) (Scheme 3). The formation of these compounds can be interpreted as a result of Ti–Cl bond aminolysis and alcoholysis reactions. The two processes are not simultaneous and, depending on the reaction conditions, the alcoholysis reaction is favoured over the aminolysis process with the N–H phenol-amine group remaining unreacted to yield the phenoxo-amino derivatives. Formation of mononuclear phenoxo-amido derivatives, rather than alternative dinuclear complexes containing a bridging ligand, is favoured in these reactions due to the thermodynamic stability imposed by the six-membered ring exhibited by these species and the inherent favourable entropy.

Compounds **2–6** are air-sensitive but thermally stable in solution and in the solid state and can be stored unaltered for weeks if strictly inert atmospheric conditions are maintained. They are soluble in aromatic and chlorinated solvents but poorly soluble in aliphatic hydrocarbons. All of these compounds were fully characterised by NMR spectroscopy and elemental analysis. The analytical composition fits well with the proposed formulations. In addition, the X-ray molecular structures of **2** and **5** are reported.

For compounds **2**, **4** and **5** spectroscopic data are consistent with "*chiral-at-metal*" coordination geometry in solution. The ¹H NMR spectra (CDCl₃ or C₆D₆ at room temperature) show the expected singlet assigned to the Cp* ring protons, two signals for the *tert*-butyl groups, two doublets (⁴*J* \approx 2.5 Hz) for the two protons of the phenylene ring, and the expected resonances for the N–R substituent protons. The methylene protons show the expected diastereotopic character (²*J* \approx 15–16 Hz in C₆D₆) corresponding to asymmetric metal centre derivatives. The NMR spectroscopic data (C₆D₆ at room temperature) for **6** are in agreement with a C_s-symmetry. A broad signal for the N*H* proton, and the expected resonances for the cyclopentadienyl, *tert*-butyl and phenyl protons are observed in the ¹H NMR spectrum (see Experimental Section).

The NMR spectroscopic analysis (C_6D_6 at room temperature) reveals that **3** is a mixture of two stereoisomers (**3a** and **3b**, Scheme 2) due to axial or equatorial coordination of the amine nitrogen atom in a trigonal bipyramidal geometry around the titanium centre with C_1 - and C_s -symmetry for **3a** and **3b**, respectively, and the nitrogen atom is coordinated to the metal centre [32]. The NH resonances for both isomers appear considerably



Scheme 2. Synthesis of the phenoxo-amino compound 3. Fluxional behaviour in solution.

shifted downfield (δ 3.08 for **3a** and δ 3.66 for **3b**) with respect to that found for the free amine **1a** (δ 2.82). The isomer **3a** shows an ABX spin system (resolves in an AB system) for the CH₂NH fragment with a broad signal for the NH proton at δ 3.08 and doublets of doublets for the methylene protons at δ 4.16 and 4.44, with a coupling constant value of $J_{AB} = 16.8$ Hz. The isomer **3b**, with the amino group in the axial position, shows an A₂X spin system for the CH₂NH fragment with a triplet for the NH proton at δ 3.66 and a doublet for the methylene protons at δ 4.52 (J_{Ax} of 6.0 Hz). Similar behaviour has been observed for analogous cyclopentadienyl titanium derivatives [35-37]. It is interesting to note how the more electron donating capacity of the Cp* ring causes a high-field shift for the NH proton and less acidity at the titanium centre compared with a similar derivative containing the unsubstituted cyclopentadienyl ring [32], and consequently how it influences the strength of the amino group coordination.

Attempts to synthesise alkyl complexes from the analogous chloro derivatives containing the unsubstituted cyclopentadienyl ring were always unsuccessful and repeated efforts to obtain the alkyl compounds as pure samples on a preparative scale remain unfruitful [32]. By contrast, reaction of the chloro compound [TiCp* $\{(C_6H_5)N-CH_2-(3,5-tBu_2C_6H_2-2-0)\}Cl\}$ (2) or $[TiCp^*\{(p-MeC_6H_4)\}$ $N-CH_2-(3,5-tBu_2C_6H_2-2-O)$ (4) with LiMe or MgClMe at low temperature in ether or hexane affords the methyl derivatives $[TiCp*{(C_6H_5)N-CH_2-(3,5-tBu_2C_6H_2-2-O)}Me]$ (7) or $[TiCp*{(p-1)}Me]$ MeC₆H₄)N-CH₂-(3,5-tBu₂C₆H₂-2-O)}Me] (8) (Scheme 4). Reactions to obtain similar benzyl derivatives using MgClBz as alkylating reagent or alternatively the synthesis of the alkyl derivatives by treatment of TiCp*R₃ (R = Me, CH₂Ph) with phenol-amines were unsuccessful. This behaviour is indicative of the crucial role played by the Cp* ligand, where its bulkiness and higher electron donor ability has a decisive affect in these reactions. The ¹H and ${}^{13}C{}^{1}H{}$ NMR spectra (C_6D_6 , room temperature) for the methyl compounds 7 and 8 show patterns for the proton and carbon resonances similar to those described for the starting chloro compounds. Furthermore, the spectra show the expected signals assigned to the methyl ligand attached to titanium.

Suitable crystals for X-ray diffraction of compounds **2** and **5** were obtained by cooling a hexane solution to -10 °C. The molecular structures of [TiCp*{C₆H₅N-CH₂-(3,5-tBu₂C₆H₂-2-O)}Cl] (**2**) (Fig. 1(a)) and [TiCp*{CyN-CH₂-(3,5-tBu₂C₆H₂-2-O}Cl] (**5**) (Fig. 1 (b)), show mononuclear dispositions with the titanium atom in a tetrahedral environment, similar to that found for analogous TiCpL₃ compounds [38]. In both complexes, the metal is an asymmetric centre and the racemic mixture of the two possible enantiomers appears in the unit cell. Compound **5** crystallized with one molecule of hexane for two titanium molecules. Table 1 summarizes selected bond distances and angles.

The angles around the nitrogen atom (*ca.* 360°) are consistent with sp² hybridisation (355.97° for **2** and 359.4 for **5**). The Ti–N bonds of 1.929(3) Å in **2** and 1.877(3) Å in **5** are consistent with an appreciable multiple bond character and suggest the presence of



Fig. 1. Molecular structures of **2** (a) and **5** (b), (30% probability) showing the labelling scheme (hydrogen atoms have been omitted for clarity).

 $p\pi$ -d π interactions [39–44]. The Ti–O bonds (1.843(2) Å (2) and 1.866(2) Å (**5**)) are longer that similar distances (1.801 Å average) found for diphenoxo complexes with or without a cyclopentadienyl ligand [26,27]. The "Ti-O-C_{Ph}-C_{Ph}-C_{methylene}-N" appears as a sixmembered ring with a boat conformation, where the sp³ methylene carbon and the oxygen atom are located out of the plane defined by the rest of the atoms. The C–C distances within the cyclopentadienyl ring, Ti-Cg(centroid) distance and Ti-Cl bond length are within the range for monocyclopentadienyl and dicyclopentadienyl titanium complexes [40,42]. It is interesting to highlight how the substituent attached to the nitrogen atom (Ph for compound 2 and Cy for compound 5) influences its donor capacity. Thus, in 5 the nitrogen bears an alkyl substituent, which is more electron donating and consequently Ti-N distances are shorter and the angles around the nitrogen atoms are closer to ideal sp² hybridisation than in 2.

2.2. Olefin polymerisation studies

We are interested in the polymerisation behaviour of group 4 monocyclopentadienyl diamido [31] or dialkoxo [26,27] metal complexes. Using sMAO (solid methylalumoxane) and $B(C_6F_5)_3$ or [CPh₃][B(C₆F₅)₄] as cocatalysts, the chloro compound [TiCp*{(C₆H₅) N–CH₂-(3,5-tBu₂C₆H₂-2-O)}Cl] (**2**) and the methyl derivative [TiCp*{(C₆H₅)N–CH₂-(3,5-tBu₂C₆H₂-2-O)}Me] (**7**) were studied as ethylene and propylene polymerisation precatalyst systems under various conditions. The observed results show averages of two or, in some cases, more polymerisation runs, which showed good reproducibility.

For the chloro complex **2** the results are summarized in Table 2 for ethylene polymerisation and in Table 3 for propylene polymerisation. When activated with sMAO, the chloro compound **2** shows moderate activities for ethylene polymerisation (Table 2) and poor activity for propylene polymerisation (Table 3). The increase in activity with increasing Al supports the suggestion that



Scheme 4. Synthesis of the methyl derivatives and the corresponding cationic species.

Table 1 Selected bond lengths (Å) and angles (°) for compounds 2 and $5 \cdot 0.5C_{e}H_{14}$

	U	()	() I		•
Bond	2	$5 \cdot 0.5 C_6 H_{14}$	Angle	2	$5.0.5C_{6}H_{14}$
Ti-O	1.843(2)	1.866(2)	C(31)-N(1)-C(20)	116.3(3)	116.1(3)
Ti-Cl	2.3024(10)	2.2911(12)	C(31)-N(1)-Ti(1)	124.1(2)	127.3(2)
Ti-N	1.929(3)	1.877(3)	C(20)-N(1)-Ti(1)	115.57(19)	116.0(2)
Ti-Cg	2.0491(18)	2.0637			

the active species is formed after ligand abstraction. No ethylene polymerisation was found when the reaction was carried out at 50 °C with 5 atm of monomer and a Ti/Al molar ratio of 1/10. Ethylene polymerisation activities increase slightly when the Al/Ti ratio increases (Table 2; entries 1-3) and consequently the Ti/Al molar ratio 1/100 was chosen as "standard" conditions. Similar activities were observed at 20 °C and 50 °C, although the activity decreases with time more markedly at 20 °C. This feature has been explained as a consequence of monomer diffusion problems [45]. The methyl compound 7, activated with boron reagents and without the presence of aluminium compounds as scavengers, remained inactive for ethylene and propylene polymerisations. The observed activity is high at 25 °C when TIBA is used as a scavenger (Table 4). The methyl complex 7 activated with $[CPh_3][B(C_6F_5)_4]$ shows higher ethylene and propylene polymerisation activities than those observed following activation with $B(C_6F_5)_3$ (Table 4). The PE polymer samples obtained show melting point values close to 130 °C, characteristic of high density polyethylene, and remarkable differences in the ΔH enthalpy values and the degree of crystallinity (α). The ¹H NMR analysis of the polypropylene showed an atactic stereochemistry.

2.3. Reaction with Lewis acids

In order to get a better knowledge of the nature of the active species and the chemical behaviour of these precatalyst systems in the α -olefin polymerisation processes, the reactions of the methyl complexes **7** and **8** with Lewis acids B(C₆F₅)₃ and [CPh₃][B(C₆F₅)₄] were monitored by ¹H NMR spectroscopy using a stoichiometric 1:1 Ti/B ratio. Likewise, the reactions of the methyl complex **7** and the chloro derivative **2** with trimethylalumium (TMA) and sMAO were examined. All the procedures were carried out in NMR tubes, fitted with Teflon valves to prevent water and oxygen ingress, using deuterated benzene (C₆D₆) as the reaction solvent at room temperature, and when possible analytically pure samples were isolated on a preparative scale.

Addition of C_6D_6 to an equimolecular amount of $B(C_6F_5)_3$ and the chloro derivative **2** affords the unaltered starting compounds, suggesting that in these systems the Ti–N and Ti–O bonds remain unreacted upon treatment with boron reagents. After addition of C_6D_6 to a mixture of $B(C_6F_5)_3$ and the corresponding neutral methyl derivatives **7** or **8** in 1:1 M ratio at room temperature in an NMR

 Table 2

 Polymerisation of ethylene with compound 2 as precatalyst and sMAO as cocatalyst.

Run	Time (min)	T (°C)	Ti/Al	Activity ^a
1	15	50	1/100	12
2	15	50	1/300	19
3	15	50	1/500	36
4	30	50	1/100	16
5	60	50	1/100	9
6	15	20	1/100	11
7	30	20	1/100	7
8	60	20	1/100	4

Reaction conditions: 10^{-4} mol Ti, P = 5 atm, volume 50 mL. ^a Activity = KgPE/mol Ti.h.atm.

Table 3

Polymerisation of propylene with compound ${\bf 2}$ as precatalyst and sMAO as cocatalyst.

Run	Time (min)	T (°C)	Activity ^a
1	15	50	8
2	60	50	2
3	60	20	8
4	60	-10	10

Reaction conditions: 10^{-4} mol Ti, Ti/Al = 1/100, P = 5atm except for run 4: 3.5 atm, volume 50 mL.

^a Activity = KgPE/mol Ti.h.atm.

tube inside the glovebox, the samples were quickly introduced into the NMR equipment and the spectra recorded at 25 °C over a period of time. After 1 h at room temperature, the formation of the ionic titanium species $[TiCp^{*}{(C_{6}H_{5})N-CH_{2}-(3,5-tBu_{2}C_{6}H_{2}-2-O)}][MeB$ $(C_6F_5)_3$ (9) and $[TiCp^*{(p-MeC_6H_4)N-CH_2-(3,5-tBu_2C_6H_2-2-0)}]$ [MeB(C₆F₅)₃] (**10**) (Scheme 4) were detected. Complexes **9** and **10** can be isolated as analytically pure samples when the reactions are carried out in toluene on a preparative scale. They are partially soluble in C₆D₆ and stable in solution at room temperature over long periods of time (days). NMR spectroscopic studies demonstrate the expected abstraction of the methyl group by the Lewis acid boron reagents. ¹H and ¹³C{¹H} NMR spectra show downfield shifted resonances, compared with the neutral compounds, as a consequence of the high Lewis acidity of titanium metal after formation of the cation (see Experimental Section). Interaction of the methylborate anion with the cationic metal centre can be deduced from the downfield shift of the methyl group (δ 1.13 and 1.12 for compounds **9** and **10** respectively) in the ¹H NMR spectrum, compared to that observed in the neutral titanium precursor (δ 0.96 and 0.95 for compounds **7** and **8** respectively) and the $\Delta\delta(m, p-F)$ value of ~ 4.7 ppm deduced from the ¹⁹F NMR spectrum. The partial solubility of these compounds in benzene is also consistent with anionic coordination to the titanium cationic centre.

In order to avoid a strong cation—anion interaction a noncoordinating trytil borate reagent, in place of $B(C_6F_5)_3$, was employed. The reaction of **7** or **8** with $[CPh_3][B(C_6F_5)_4]$ in C_6D_6 at 25 °C was spectroscopically studied by NMR. The formation of Ph₃CMe as a by-product of the reaction [46] was immediately detected, allowing us to deduce that abstraction of the methyl group initially attached to titanium occurred. The ¹⁹F NMR spectrum exhibits undisturbed $[B(C_6F_5)_4]^-$ anion resonances. However, a complicated set of resonances in the ¹H NMR spectra of the cation fragment precludes signal assignment and substance identification. Therefore, we suggest that initially separated ions were formed, but because there is no stabilization conferred by anion coordination, a further decomposition process is induced.

These results permit us to conclude that the Lewis acid $B(C_6F_5)_3$ reacts with the neutral complexes through the abstraction of the alkyl group, to give highly stable cationic species, retaining unreacted Ti–O and Ti–N bonds with the bidentate phenoxo-amido

Table 4

Olefin polymerisation with compound **7** as precatalyst and different boron reagents as cocatalyst in the presence of TIBA as scavenger.

Run	Monomer (atm)	cocat.	<i>T</i> (°C)	Time (min)	Activity ^a
1	Ethylene (2)	$B(C_{6}F_{5})_{3}$	25	10	292
2	Ethylene (2)	$[CPh_3][B(C_6F_5)_4]$	25	5	775
3	Propylene (5)	$B(C_{6}F_{5})_{3}$	25	40	2
4	Propylene (5)	$[CPh_3][B(C_6F_5)_4]$	25	40	116

Reaction conditions: 2.10^{-5} mol of Ti, 2.10^{-5} mol of Cocatalyst, volume 100 mL, TIBA/Ti = 50/1.

^a Activity = KgPol/mol Ti.h.atm.

ligand bonded to the titanium centre. Formation of such a stable species exhibiting strong interactions with the anionic unit prevents coordination of the olefin and consequently these systems show low activity in ethylene and propylene polymerisation. With the [CPh₃] [B(C₆F₅)₄] reagent, we initially assumed similar reactivity. However, the anionic unit [B(C₆F₅)₄]⁻ is a less coordinated anion than [MeB (C₆F₅)₃]⁻ and in the absence of an olefin, these [B(C₆F₅)₄]⁻ anionic systems show a lack of stability with fast and immediate decomposition in solution, although in the presence of an olefin a clear polymerisation reaction is observed.

During the olefin polymerisation process, aluminium compounds are normally used as cocatalysts (MAO) to generate the active species or as scavenger reagents (TIBA). MAO initially produces alkylation of the halo groups in the precursor and subsequently the abstraction of one of the alkyl groups generated to give cationic alkyl species, which are considered as the active species in the polymerisation reaction. Considering that polymerisation studies were made with MAO and given our interest in the identification of the nature of the active species in olefin polymerisation, we studied the reactions of compounds **2** and **7** with TMA or sMAO.

A solution of the monochloro compound **2** was treated with sMAO in a 1:20 M ratio in toluene at -78 °C. Spectroscopic analysis by ¹H NMR revealed the presence of the methyl complex 2, indicating the alkylation of the Ti–Cl bond and the selective formation of the methyl derivative 7 (Scheme 5). The NMR spectra also showed the presence of signals assignable to secondary unidentified products. Similarly, treatment of a solution of the monochloro compound **2** in hexane with one equiv of TMA at -78 °C afforded the same mixture of the methyl compound 7 and the analogous NMR spectroscopic pattern corresponding to the unidentified species. The intensity of the signals assignable to the secondary unidentified products increases when an excess of TMA is used as reagent, along with the disappearance of the signals assignable to compound **7**. The methyl derivative **7** reacts directly with sMAO in 1:20 M ratio, at room temperature in C_6D_6 and alternatively with TMA to give this same mixture of secondary unidentified species. These observations accord with the alkylating capacity of the sMAO or the TMA to give the methyl derivative. Transmetallation reactions of the phenoxo-amido ligand from titanium to aluminium should explain the formation of these secondary products [47,48]. Consequently, the ligand transfer processes in the reaction with aluminium reagents are associated with the activity of the chloro complex 2 for ethylene and propylene polymerisations.

In general, the different results in polymerisation activity depending on the nature of the cocatalyst can be attributed to the ability of aluminium derivatives to abstract the chelate ligand and consequently affect the Ti–N or Ti–O bonds providing the alkyl group necessary to achieve polymerisation in a Ziegler–Natta manner. This possibility is unavailable when the perfluoroborane compound is used. The activity shown by methyl complex **7** when aluminium and boron compounds are simultaneously in the reaction medium (Table 4) confirms this suggestion.



Scheme 5. Methylation reactions of 2 with sMAO or AlMe3.

3. Concluding remarks

Here we report the synthesis and characterisation of new and unusual phenoxo-amido and phenoxo-amino titanium complexes stabilised by the permethylated cyclopentadienyl ligand and containing asymmetric metal centres. The results of the studies on ethylene and propylene polymerisation by using these precatalyst systems in the presence of different cocatalysts suggest the formation of catalytic species with variable natures.

4. Experimental section

4.1. General considerations

All manipulations and reactions of air- and/or moisture sensitive compounds were carried out under argon (Air Liquid N45, O₂: 1 ppm; H₂O: 3 ppm) using Schlenk and high-vacuum line techniques or in a dry argon atmosphere MBraun glovebox model MB150B-G. Deuterated solvents were firstly degassed by several freeze-thaw cycles, held at room temperature over fresh activated 4 Å molecular sieves and then stored at room temperature over freshly activated 4 Å molecular sieves. Compounds TiCp*Cl₃, TiCp*Me₃ and TiCp*Bz₃ were prepared by a known procedure [49]. All reactants for the preparation of the phenoxo-amine derivatives were purchased and used as received from Aldrich, except tertbutylamine and N-tert-butyl-methylamine (Aldrich) which were purified under argon according to literature procedures [50]. MgClMe was used as 3 M solution in THF and MgClBz as 2 M solution in THF (Aldrich). Solid AlMe₃-free methylalumoxane (sMAO) was obtained from commercial methylalumoxane (MAO) (CROMPTON, 10 wt. % solution in toluene) by drying under reduced pressure at 50 °C to remove the uncoordinated AlMe₃ and used after washing with *n*-hexane and complete drying. The white solid obtained was stored in dry box before use to prepare the samples. Calculated quantities of the desired compound and solid MAO were taken, in the dry box, to provide the samples with the desired Ti/Al ratio. The NMR samples of air- and/or moisture sensitive compounds were prepared under argon at room temperature in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. NMR spectra were recorded at 400.13 (¹H), 376.00 (¹⁹F) and 100.60 (¹³C) MHz on a Bruker AV400. Chemical shifts (δ) are given in ppm using CDCl₃ or C₆D₆ as solvent. ¹H and ¹³C resonances were measured relative to solvent peaks considering TMS $\delta = 0$ ppm, while ¹⁹F was measured relative to external CFCl₃. Elemental analyses were obtained on a Perkin-Elmer Series II 2400 CHNS/O analyser. The thermal properties of the samples were studied, after recrystallization, in a Perkin Elmer DSC 6 instrument calibrated by measuring the melting point of indium. From the second heating curve was obtained the melting point (Tm) and the ΔH_m .

4.2. Polymerisation procedure

For ethylene or propylene polymerisation the typical procedure was as follows. The desired amount of the selected precatalyst was weighted in the dry-box and in a sealed glass vial put into a high pressure glass reaction vessel (Büchi). Then a solution of toluene (50 mL) containing sMAO (in the desired Al:Ti ratio) was injected via *cannula* and the mixture stirred for 15 m. Subsequently, the polymerisation temperature was adjusted and the argon was replaced by the monomer by degassing the solution under vacuum and refilling with the olefin. This procedure was repeated and the solution was finally saturated with the olefin over 15 m and pressurized at 2 or 5 atm for 1 h before cracking the vial. After the polymerisation time was reached, the monomer gas was vented and the reaction was quenched with 10 mL of a 5% solution of HCl/

CH₃OH. The resultant suspension was then poured in a large excess of this solvent mixture and the resultant polyethylene was separated by filtration, washed several times (HCl/CH₃OH) and dried under *vacuum* overnight to constant weight.

4.3. $[TiCp^*{(C_6H_5)N-CH_2-(3,5-tBu_2C_6H_2-2-0)}Cl]$ (2)

A solution of 1 mmol of **1a** (311.5 mg) and 2.5 mmol (0.35 mL) of NEt₃ in 50 mL of pentane was added under vigorous stirring to 1 mmol of TiCp*Cl₃ (289.5 mg). After 12 h the solution turned brown with abundant [NHEt₃]Cl as a white precipitate. The solution was filtered off and concentrated until a brown precipitate started to appear. The suspension was maintained at $-40 \,^{\circ}$ C for 12 h, when the liquid phase was filtered off and the solid dried under vacuum. Yield 72% (384.2 mg, 0.72 mmol).

¹H NMR (CDCl₃): δ 1.16 (s, 9H, *tBu*), 1.27 (s, 9H, *tBu*), 1.90 (s, 15H, C₅*Me*₅), 4.04 and 5.18 (AB system, $J_{H-H} = 14.7$ Hz, 2H, CH₂), 6.90–7.25 (m, 7H, *Ph*N and *Ph*O). ¹H NMR (C₆D₆): δ 1.26 (s, 9H, *tBu*), 1.57 (s, 9H, *tBu*), 1.85 (s, 15H, C₅*Me*₅), 4.01 and 5.10 (AB system, $J_{H-H} = 16.8$ Hz, 2H, CH₂), 6.80–6.90 and 7.05–7.10 (m, 5H, *Ph*N), 7.02 (d, $J_{H-H} = 2.4$ Hz, 1H, *o*-H, *Ph*O), 7.47 (d, $J_{H-H} = 2.4$ Hz, 1H, *m*-H, *Ph*O). Anal. Calcd. for C₃₁H₄₂ClNOTi (527.60 g/mol): C 70.52; H 8.02; N 2.65. Found: C 70.65; H 8.16; N 2.34.

4.4. $[TiCp^*{(C_6H_5)(H)N-CH_2-(3,5-tBu_2C_6H_2-2-O)}Cl_2]$ (3)

A solution of **1a** (311.5 mg, 1 mmol) and NEt₃ (0.35 mL, 2.5 mmol) in toluene (50 mL) was added under vigorous stirring to TiCp*Cl₃ (289.5 mg, 1 mmol). After 12 h the solution appeared red with the formation of [NHEt₃]Cl as a white precipitate. The solution was filtered off and concentrated to a volume of 10 mL and maintained at -40 °C for 12 h to give a solid, which was recrystallised from toluene at -30 °C and characterised as a mixture of **3a:3b** (336.1 mg, 0.59 mmol, 59% yield).

¹H NMR (300 MHz, C_6D_6) of stereoisomer **3a**: δ 1.22 (s, 9 H, *tBu*), 1.42 (s, 9 H, *tBu*), 1.96 (s, 15H, C_5Me_5), 3.08 (s broad, 1H, NH), 4.16 and 4.44 (dd, $J_{AB} = 16.8$ Hz, AB of an ABX spin system, 2H, CH_2), 6.40–7.20 (m, 7H, arom.). ¹H NMR (300 MHz, C_6D_6) of stereoisomer **3b**: δ 1.24 (s, 9H, *tBu*), 1.56 (s, 9 H, *tBu*), 3.66 (pt, $J_{A-x} = 6.0$ Hz, X of an A₂X spin system, 1H, NH), 4.52 (pd, $J_{A-x} = 6.7$ Hz, A of an A₂X spin system, 2H, CH_2), 6.62 (d, $J_{H-H} = 7.8$ Hz, 2H, *o*-H, PhO), 6.74 (d, $J_{H-H} = 7.2$ Hz, 2H, *o*-H, PhO), 6.85–7.53 (m, 4H, Ph), 7.46 (1 H, d, $J_{H-H} = 2.4$ Hz, PhO). Anal. Calcd. for $C_{31}H_{43}Cl_2$ NOTi (564.08 g/mol): C 66.00; H 7.62; N 2.48. Found: C 65.98; H 7.53; N 2.44.

4.5. $[TiCp^*{(4-MeC_6H_4)N-CH_2-(3,5-tBu_2C_6H_2-2-O)}Cl]$ (4)

A solution of 1 mmol of **1b** (325.5 mg) and 2.5 mmol (0.35 mL) of NEt₃ in 50 mL of pentane was added under vigorous stirring to 1 mmol of TiCp*Cl₃ (289.5 mg). After 12 h, the solution appeared brown with abundant [NHEt₃]Cl as a white precipitate. The solution was filtered off and concentrated to give a brown solid. The suspension was maintained at $-40 \,^{\circ}$ C for 12 h, when the liquid phase was filtered off and the solid dried under vacuum. Yield 67% (364.1 mg, 0.67 mmol). ¹H NMR (C₆D₆): δ 1.24 (s, 9H, *tBu*), 1.52 (s, 9H, *tBu*), 1.86 (s, 15H, C₅*Me*₅), 2.12 (s, 3H, Me), 3.99 and 5.13 (AB system, *J*_{H-H} = 15.0 Hz, 2H, *CH*₂), 6.89–6.96 (AB system, *J*_{H-H} = 15.0 Hz, 4H, *Ph*N), 7.03 (d, 1H, *J*_{H-H} = 2.4 Hz, PhO), 7.47 (d, 1H, *J*_{H-H} = 2.4 Hz, 1H, PhO). Anal. Calcd. for C₃₂H₄₄ClNOTi (542.0 g/mol): C 70.91; H 8.18; N 2.58; Experimental: C 70.85; H 8.36; N 2.46.

4.6. [TiCp*{CyN-CH₂-(3,5-tBu₂C₆H₂-2-0)}Cl] (5)

A solution of 1 mmol of 1c (317.3 mg) and 2.5 mmol (0.35 mL) of NEt₃ in 50 mL of pentane was added under vigorous stirring to 1 mmol

of TiCp*Cl₃ (289.5 mg). After 12 h the solution appeared red and with [NHEt₃]Cl as a white precipitate. The solution was filtered off and evaporated. Yield 89% (473.2 mg, 0.89 mmol). ¹H NMR (C₆D₆): δ 0.73–1.62 (m, 10H, cyclohexyl), 1.33 (s, 9H, *tBu*), 1.52 (s, 9H, *tBu*), 2.04 (s, 15H, C₅*Me*₅), 3.58 and 4.84 (AB system, *J*_{H-H} = 16.2 Hz, 2H, *CH*₂), 3.67 (pt, 1H, cyclohexyl), 7.09 (d, *J*_{H-H} = 2.4 Hz, 1H, *Ph*O), 7.38 (d, *J*_{H-H} = 2.4 Hz, 1H, *Ph*O). Anal. Calcd. for C₃₁H₄₈ClNOTi (5343.63 g/ mol): C 69.72; H 9.00; N 2.62. Found: C 68.82; H 8.54; N 2.81.

4.7. $[TiCp^*{tBu(H)N-CH_2-(3,5-tBu_2C_6H_2-2-0)}Cl_2]$ (6)

The procedure is similar to that described for **2**. A solution of 1 mmol of **1d** (291.5 mg) and 2.5 mmol (0.35 mL) of NEt₃ in 50 mL of pentane was added under vigorous stirring to 1 mmol of TiCp*Cl₃ (289.5 mg). Yield 62% (339.6 mg, 0.62 mmol). ¹H NMR (C_6D_6): δ 1.19 (s broad, 9H, *tBu*), 1.38 (s broad, 9H, *tBu*), 1.56 (s broad, 9H, *tBu*), 1.91 (s, 15H, C₅*Me*₅), 3.96 (br, 2H, *CH*₂), 7.42 (d, $J_{H-H} = 2.2$ Hz, 1H, PhO), 7.88 (br, 1H, NH), the Ph signals appear overlapped with the solvent resonances and are not observed. Anal. Calcd. C₂₉H₄₇Cl₂NOTi (544.5 g/mol): C 63.97; H 8.63; N 2.57. Found: C 63.15; H 9.17; N 3.18.

4.8. $[TiCp^*{(C_6H_5)N-CH_2-(3,5-tBu_2C_6H_2-2-0)}Me]$ (7)

1.2 mmol of MgClMe (3-M solution in THF) was added under vigorous stirring to a suspension of 1 mmol of 2 (528.0 mg) cooled at -78 °C in 50 hexane. After 12 h the solution appeared orange brown with abundant MgCl₂ as a white precipitate. The solution was filtered off and concentrated until a light brown precipitate started to appear. The suspension was maintained at -40 °C for 12 h, when the liquid phase was filtered off and the solid dried under vacuum. Yield 72% (364.5 mg, 0.72 mmol). ¹H NMR (CDCl₃): δ 0.73 (s, 3H, Me-Ti), 1.27 (s, 9H, tBu), 1.32 (s, 9H, tBu), 1.90 (s, 15H, C_5Me_5), 4.19 and 5.07 (AB system, $J_{H-H} = 15.0$ Hz, 2H, CH₂), 6.67 (d, $J_{H-H} = 7.4$ Hz, 2H, m-H PhN), 6.87 (t, $J_{H-H} = 7.4$ Hz, 1H, p-H PhN), 7.10–7.23 (m, 4H, arom.). ¹H NMR (C_6D_6): δ 0.96 (s, 3H, Me–Ti), 1.32 (s, 9H, tBu), 1.54 (s, 9H, tBu), 1.77 (s, 15H, C₅Me₅), 4.18 and 5.04 (AB system, J_{H-H} = 15.0 Hz, 2H, CH₂), 6.70 (d, J_{H-H} = 7.5 Hz, 2H, m-H *PhN*), 6.85 (t, J_{H-H} = 7.4 Hz, 1H, *p*-H *PhN*), 7.09 (d, J_{H-H} = 8.4 Hz, 2H, o-H PhN), 7.20 (d, J_{H-H} = 2.4 Hz, 1H, m-H, PhO), 7.50 (d, $J_{\rm H-H} = 2.4$ Hz, 1H, m-H, PhO). ¹³C NMR (C₆D₆): δ 11.8 (C₅Me₅), 30.6 (tBu), 32.3 (tBu), 35.8 (Cipso, tBu), 38.8 (Cipso, tBu), 51.9 (Me-Ti), 58.6 (CH₂), 119.6 (C_{ipso}, C₅Me₅), 122.1-141.9 (arom.), 152.8 (C_{ipso}, PhO), 161.1 (Cipso, PhN). Anal. Calcd. for C₃₂H₄₅NOTi (507.20 g/mol): C 75.72; H 8.87; N 2.76. Found: C 75.75; H 8.81; N 3.00.

4.9. $[TiCp^*{(4-MeC_6H_4)N-CH_2-(3,5-tBu_2C_6H_2-2-0)}Me]$ (8)

1.2 mmol of MgClMe (3-M solution in THF) was added under vigorous stirring to a suspension of 1 mmol of **4** (542.0 mg) cooled at -78 °C in 50 mL of hexane. After 12 h the solution appeared orange-brown with abundant MgCl₂ as a white precipitate. The solution was filtered off and concentrated until a light brown precipitate started to appear. The suspension was maintained at -40 °C for 12 h and then the liquid phase was filtered off and the solid dried under *vacuum*. Yield 69% (357.9 mg, 0.69 mmol). ¹H NMR (C₆D₆): δ 0.95 (s, 3H, *Me*–Ti), 1.31 (s, 9H, *tBu*), 1.55 (s, 9H, *tBu*), 1.80 (15H, s; C₅*Me*₅), 2.16 (s, 3H, *Me*–Ph), 4.20 and 5.10 (AB system, *J*_{H–H} = 15.0 Hz, 2H, *CH*₂), 6.67 (d, *J*_{H–H} = 7.4 Hz, 2H, *m*-H PhN), 6.93 (t, *J*_{H–H} = 7.5 Hz, 2H, *o*-H PhN), 7.19 (d, *J*_{H–H} = 2.4 Hz, 1H, *m*-H, PhO). Anal. Calcd. for C₃₃H₄₇NOTi (521.6 g/mol): C 76.04; H 9.09; N 2.70. Found: C 76.30; H 8.93; N 2.67.

4.10. $[TiCp^*{(C_6H_5)N-CH_2-(3,5-tBu_2C_6H_2-2-O)}][MeB(C_6F_5)_3]$ (9)

30 mL of toluene was added to a solid mixture of B(C₆F₅)₃ (1 mmol, 512.0 mg) and of **7** (1 mmol, 507.3 mg) at -78 °C. The reaction evolved over 12 h. The solution turned brown and a dark oil precipitated. The liquid phase was removed by filtration and the oil dried under *vacuum* to produce a dark solid. Yield 83% (846.3 mg 0.83 mmol). ¹H NMR (C₆D₆): δ 1.13 (br, 3H, B–*Me*–Ti), 1.28 (s, 9H, *tBu*), 1.30 (s, 9H, *tBu*), 1.57 (s, 15H, C₅*Me*₅), 3.80 and 4.81 (AB system, *J*_{H–H} = 16.2 Hz, 2H, C*H*₂), 6.40 (d, *J*_{H–H} = 7.8 Hz, 2H, *m*-*H* PhN), 6.85 (t, *J*_{H–H} = 7.8 Hz, 1H, *p*-*H* PhN), 6.96 and 7.40 (d, *J*_{H–H} = 2.4 Hz, 2H, *m*-*H*, PhO), 7.09 (t, *J*_{H–H} = 8.1 Hz, 2H, *o*-*H* PhN). ¹⁹F NMR (C₆D₆): δ –132.67 (s, *o*-F C₆F₅), -160.35 (s, *p*-F C₆F₅), -165.03 (s, *m*-F C₆F₅). Anal. Calcd. for C₅₀H₄₅BF₁₅NOTi (1019.6 g/mol): C 58.90; H 4.45; N 1.37. Found: C 57.94; H 5.16; N 1.46.

4.11. $[TiCp^*{(4-MeC_6H_4)N-CH_2-(3,5-tBu_2C_6H_2-2-O)}]$ $[MeB(C_6F_5)_3]$ (**10**)

The procedure is similar to that described for **9** using 1 mmol (512.0 mg) of B(C₆F₅)₃ and 1 mmol (521.6 mg) of **8**. Yield 75% (775.0 mg 0.75 mmol). ¹H NMR (C₆D₆): δ 1.12 (br, 3H, B–*Me*–Ti), 1.28 (s, 9H, *tBu*), 1.30 (s, 9H, *tBu*), 1.59 (s, 15H, C₅*Me*₅), 2.07 (s, 3H, *Me*–Ph), 3.83 and 4.83 (AB system, *J*_{H–H} = 16.2 Hz, 2H, *CH*₂), 6.38 (d, *J*_{H–H} = 8.4 Hz, 2H, *m*-H PhN), 6.96 (t, *J*_{H–H} = 8.4 Hz, 2H, *o*-H PhN), 6.98 and 7.42 (d, *J*_{H–H} = 2.4 Hz, 2H, *m*-H, PhO). ¹⁹F NMR (C₆D₆): δ –132.60 (s, *o*-F C₆F₅), -160.42 (s, *p*-F C₆F₅), -165.07 (s, *m*-F C₆F₅). Anal. Calcd. for C₅₁H₄₇BF₁₅NOTi (1033.3 g/mol): C 59.26; H 4.58; N 1.36. Found: C 58.61; H 3.76; N 1.33.

4.12. Reaction between $[TiCp^*{(C_6H_5)N-CH_2-(3,5-tBu_2C_6H_2-2-O)} CI]$ (2) and AlMe₃

1 mmol of AlMe₃ (0.5 mL of 2 M hexane solution) was added under vigorous stirring to a solution of 1 mmol of 2 (528.2 mg)

Table 5

Crystal Data and Structure Refinement Details for 5.0.5C₆H₁₄ and 2.

	2	5 · 0.5C ₆ H ₁₄
Formula	C ₃₁ H ₄₂ CINOTi	C34H55CINOTi
FW	528.01	577.14
Color/habit	Dark red/prism	Dark red/prism
Cryst dimensions (mm ³)	$0.31 \times 0.23 \times 0.20$	$0.50\times0.31\times0.28$
Cryst syst	Monoclinic	Triclinic
Space group	P21/c	P-1
<i>a</i> , Å	13.6121(14)	8.691(5)
<i>b</i> , Å	9.4673(6)	13.078(5)
<i>c</i> , Å	22.931(2)	15.321(5)
α, (deg)	90	87.510(5)
β, (deg)	102.422(10)	76.474(5)
γ, (deg)	90	78.855(5)
<i>V</i> , Å ³	2885.9(4)	1661.2(13)
Ζ	4	2
Т, К	150	150
$ ho_{ m calcd}$, g cm ⁻³	1.215	1.154
μ , mm ⁻¹	0.412	0.363
F(000)	1128	626
θ range, deg	3.01-27.50	3.07-25.00
No. of rflns collected	20,800	11,244
No. of indep $rflns/R_{int}$	6615/0.2029	5832/0.0519
No. of obsd rflns $(I > 2\sigma(I))$	4089	4243
No. of data/restraints/params	6615/0/317	5832/0/346
$R1/wR2 (I > 2\sigma(I))^{a}$	0.0703/0.1529	0.0614/0.1562
R1/wR2 (all data) ^a	0.1216/0.1794	0.0913/0.1678
Extinction coefficient	0.0028(9)	0.005(2)
GOF (on F^2) ^a	1.025	1.057
Largest diff peak/hole (e Å ⁻³)	0.510 and -0.625	+0.993/-0.532

 $\overline{[A_{1}]_{a} R_{1}} = \Sigma(||F_{0}| - |F_{c}||) / \Sigma|F_{0}|; \ wR2 = \{\Sigma[w(F_{0}^{2} - F_{c}^{2})^{2}] / \Sigma[w(F_{0}^{2})^{2}]\}^{1/2}; \ GOF = \{\Sigma[w(F_{0}^{2} - F_{c}^{2})^{2}] / (n-p)\}^{1/2}.$

at -78 °C in 50 mL of hexane. After 8 h when the reaction mixture had reached the room temperature, the solution was dried under *vacuum*. In the solid obtained, a mixture of the methyl compound **7** and unidentified species was spectroscopically observed.

4.13. Reaction between $[TiCp^*{(C_6H_5)N-CH_2-(3,5-tBu_2C_6H_2-2-O)}]$ Me] (7) and AlMe₃

1 mmol of AlMe₃ (0.5 mL of 2 M hexane solution) was added under vigorous stirring to a solution of 1 mmol of **7** (507.4 mg) at -78 °C in 50 mL of hexane. After 8 h the reaction mixture had reached the room temperature, the solution was dried under *vacuum*. In the obtained solid a mixture of unidentified species was spectroscopically observed.

4.14. X-ray crystal structure determinations of compounds **2** and $5 \cdot 0.5C_6H_{14}$

Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in Table 5. Suitable single crystals of 2 and 5.0.5C₆H₁₄ for the X-ray diffraction study were selected. Data collection was performed at 150(2) K, with the crystals covered with perfluorinated ether oil. The crystals were mounted on a Bruker-Nonius Kappa CCD single crystal diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Multiscan [51] absorption correction procedures were applied to the data. The structures were solved, using the WINGX package [52], by direct methods (SHELXS-97) and refined using full-matrix least-squares against F² (SHELXL-97) [53,54]. For compound **2**, all non-hydrogen atoms were anisotropically refined and the hydrogen atoms were geometrically placed and left riding on their parent atoms. In 5 the carbon atoms C38, C39 and C40 from a tBu group were disordered in two positions, the disorder was treated and the atoms left isotropic. The remaining non-hydrogen atoms were anisotropically refined including the disordered molecule of hexane that crystallized with every two molecules of 5. The hydrogen atoms were geometrically placed and left riding on their parent atoms except for the hydrogen on C31 that was found on the Fourier map and refined.

Acknowledgement

Financial support for this research by Dirección General de Investigación Científica y Técnica (Project MAT2010-14965), Comunidad Autónoma de Madrid: (Project S-0505-PPQ/0328-02) and by European Commission (Contract Nr. HPRN-CT2000-00004) is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 802062 and 802063 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

References

- [1] A.T. Rappé, W.M. Skiff, C.J. Casewit, Chem. Rev. 100 (2000) 1435-1456.
- [2] G.G. Hlatky, Coord. Chem. Rev. 199 (2000) 235-329.
- [3] H.G. Alt, A. Koppl, Chem. Rev. 100 (2000) 1205–1221.
- [4] P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1–29.
 [5] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Edit. Engl. 34 (1995) 1143–1170.
- [6] M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255–270.
- 7] V. Busico, Dalton Trans. (2009) 8794–8802.
- [8] W. Kaminsky, A. Funck, H. Hahnsen, Dalton Trans. (2009) 8803-8810.

- [9] K. Nomura, Dalton Trans. (2009) 8811-8823.
- [10] G. Stojcevic, M.C. Baird, Dalton Trans. (2009) 8864-8877.
- [11] A. Poater, L. Cavallo, Dalton Trans. (2009) 8878-8883.
- [12] E.J. Arlman, P. Cossee, J. Catal. 3 (1964) 99-104.
- [13] P. Cossee, J. Catal. 3 (1964) 80-88.
- [14] S.W. Ewart, M.J. Sarsfield, D. Jeremic, T.L. Tremblay, E.F. Williams, M.C. Baird, Organometallics 17 (1998) 1502-1510.
- [15] W. Kaminsky, M. Arndt, Polymer Synthesis/Polymer Catalysis, vol. 127, Springer-Verlag, Berlin 33, 1997, 143–187.
- [16] G. Guerra, P. Longo, L. Cavallo, P. Corradini, L. Resconi, J. Am. Chem. Soc. 119 (1997) 4394–4403.
- [17] A.M. Thayer, Chem. Eng. News 73 (1995) 15-20.
- [18] K.B. Sinclair, R.B. Wilson, Chem. Ind. (1994) 857-862.
- [19] V.K. Gupta, S. Satish, I.S. Bhardwaj, J. Macromol. Sci.-Rev. Macromol. Chem. Phys. C34 (1994) 439–514.
- [20] M.C. Baird, Chem. Rev. 100 (2000) 1471-1478.
- [21] J. Cano, P. Royo, M. Lanfranchi, M.A. Pellinghelli, A. Tiripicchio, Angew. Chem. Int. Edit. 40 (2001) 2495–2497.
- [22] J.Z. Jin, D.R. Wilson, E.Y.X. Chen, Chem. Commun. (2002) 708-709.
- [23] M.L. Gao, Y.F. Gu, C. Wang, X.L. Yao, X.L. Sun, C.F. Li, C.T. Qian, B. Liu, Z. Ma, Y. Tang, Z.W. Xie, S.Z. Bu, Y. Gao, J. Mol. Catal. A-Chem. 292 (2008) 62–66.
- [24] A.Q. Jia, G.X. Jin, Organometallics 28 (2009) 1872-1877.
- [25] P. Elo, A. Parssinen, S. Rautiainen, M. Nieger, M. Leskela, T. Repo, J. Organomet. Chem. 695 (2010) 11–17.
 [26] M. González-Maupoey, T. Cuenca, L.M. Frutos, O. Castaño, E. Herdtweck,
- Organometallics 22 (2003) 2694–2704.
- [27] M. González-Maupoey, T. Cuenca, Organometallics 25 (2006) 4358-4365.
- [28] M. González-Maupoey, T. Cuenca, L.M. Frutos, O. Castaño, E. Herdtweck, B. Rieger, Eur. J. Inorg. Chem. (2007) 147–161.
- [29] V. Tabernero, T. Cuenca, E. Herdtweck, Eur. J. Inorg. Chem. (2004) 3154–3162.
 [30] V. Tabernero, C. Maestre, G. Jiménez, T. Cuenca, C.R. de Arellano, Organome-
- tallics 25 (2006) 1723–1727. [31] V. Tabernero, T. Cuenca, Eur. J. Inorg. Chem. (2005) 338–346.
- [32] G. Alesso, M. Sanz, M.E.G. Mosquera, T. Cuenca, Eur. J. Inorg. Chem. (2008) 4638-4649.
- [33] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 123 (2001) 6847–6856.

- [34] D.C.H. Oakes, B.S. Kimberley, V.C. Gibson, D.J. Jones, A.J.P. White, D.J. Williams, Chem. Commun. (2004) 2174–2175.
- [35] M.C. Maestre, V. Tabernero, M.E.G. Mosquera, G. Jiménez, T. Cuenca, Organometallics 24 (2005) 5853–5857.
- [36] M.C. Maestre, C. Paniagua, E. Herdtweck, M.E.G. Mosquera, G. Jiménez, T. Cuenca, Organometallics 26 (2007) 4243–4251.
- [37] M.C. Maestre, M.E.G. Mosquera, H. Jacobsen, G. Jiménez, T. Cuenca, Organometallics 27 (2008) 839–849.
- [38] A. Van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008–3021.
- [39] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc. Dalton Trans. (1989) S1–S83.
- [40] R.M. Pupi, J.N. Coalter, J.L. Petersen, J. Organomet. Chem. 497 (1995) 17–25.
- [41] M.F. Lappert, P.P. Power, A.R. Sanger, R.C. Srivastava, Metal and Metalloide Amides. Ellis Horwood, John Wiley and Sons, New York, 1980.
- [42] D.M. Giolando, K. Kirschbaum, LJ. Graves, U. Bolle, Inorg. Chem. 31 (1992) 3887–3890.
 [43] M.H. Chisholm, I.H. Huang, I.C. Huffman, W.F. Streib, D. Tiedtke, Polyhedron.
- [43] M.H. Chisholm, J.H. Huang, J.C. Huffman, W.E. Streib, D. Tiedtke, Polyhedron 16 (1997) 2941–2949.
- [44] S. Fokken, T.P. Spaniol, J. Okuda, F.G. Sernetz, R. Mulhaupt, Organometallics 16 (1997) 4240–4242.
- [45] H. Sinn, W. Kaminsky, H.J. Vollmer, R. Woldt, Angew. Chem. Int. Edit. Engl. 19 (1980) 390–392.
- [46] M. Bochman, S.J. Lancaster, Organometallics 12 (1993) 633–640.
 [47] A.V. Firth, J.C. Stewart, A.J. Hoskin, D.W. Stephan, J. Organomet. Chem. 591
- (1999) 185–193.
 [48] E.A. Ison, K.A. Abboud, I. Ghiviriga, J.M. Boncella, Organometallics 23 (2004)
- 929–931. (A) M Mara M A Balliaghalli, D Boug D Comerce A Tisisischie I, Cham Cas
- [49] M. Mena, M.A. Pellinghelli, P. Royo, R. Serrano, A. Tiripicchio, J. Chem. Soc. Chem. Commun. (1986) 1118–1119.
- [50] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, third ed. Pergamon Press, Oxford, 1988.
- [51] R.H. Blessing, Acta. Crystallogr. A51 (1995) 33-38 Sortav.
- [52] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837-938.
- [53] G.M. Sheldrick, SHELXL-97. Universität Göttingen, Göttingen (Germany), 1998.
- [54] G.M. Sheldrick, Acta Crystallogr. Sect. A 64 (2008) 112-122.