

Reactivity of cationic α -diimine cyclopentadienyl nickel complexes towards AlEt_2Cl : Synthesis, characterisation and ethylene polymerisation

Clara S. B. Gomes,[†] Alejandro F. G. Ribeiro,[†] Anabela C. Fernandes,[†] Artur Bento,[†] M. Rosário Ribeiro,[†] Gabriele Kociok-Köhn,[‡] Sofia I. Pascu,[‡] M. Teresa Duarte,[†] Pedro T. Gomes*,[†]

[†]Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal; e-mail: pedro.t.gomes@tecnico.ulisboa.pt

[‡]Chemistry Department, University of Bath, Claverton Down, Bath, UK

Abstract:

The electronically saturated and air-stable complexes $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-BIAN})][\text{PF}_6]$ (**1**) and $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-DAD})][\text{PF}_6]$ (**2**) were found to behave as efficient catalyst precursors for the polymerisation of ethylene under mild reaction conditions (temperature and pressure), when activated with excesses of AlEt_2Cl (DEAC), and exhibiting activities in the range 4×10^4 to 22×10^4 g PE/(mol Ni·h·bar). Compound **2** was synthesised and fully characterised as reported hereby for the first time, and exhibits a catalytic activity of *ca.* 30×10^4 g PE/(mol Ni·h·bar) in the polymerisation of ethylene. The reactivity of these complexes towards DEAC was found to lead to the formation of diamagnetic cationic Ni(II) complexes (**4** and **3**, respectively) containing the same initial cation $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\alpha\text{-diimine})]^+$ and a $[\text{AlEtCl}_3]^-$ anion, whereby diamine = BIAN (**1** and **4**) and DAD (**2** and **3**). In the corresponding reaction of complex $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-BIAN})][\text{PF}_6]$ (**1**), an unusual paramagnetic complex incorporating a cationic trinuclear α -diimine Ni cluster (**5**), containing five bridging Cl ligands and a $[\text{AlCl}_4]^-$ anion, was also isolated and fully characterised, in which the cyclopentadienyl ligand was absent. The intermediates **3** and **5** catalysed efficiently the polymerisation of ethylene when the DEAC co-catalyst was used in slight excess. The polyethylene produced (*ca.* 10×10^4 to 30×10^4 g PE/(mol Ni·h·bar), respectively) showed branching numbers ranging from 7 to 75 branches/1000 carbon atoms according to ^1H NMR spectroscopy analysis. These findings are surprising given that the new 18-electron nickel precursors show remarkable properties towards ethylene polymerisation catalysis when activated with a small amount of aluminium activator under mild conditions, and also that

some unusual intermediates responsible for the observed activity were isolated and characterised by X-ray crystallography.

Introduction

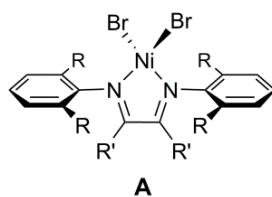
Cationic complexes of late-transition metals with multidentate ligands have been found to catalyse several new homo- and copolymerisation reactions of olefins.¹

Alpha-diimines are versatile bidentate chelating ligands, widely employed as ancillary ligands in the field of coordination/organometallic chemistry, and these have been prepared by the condensation of α -diketones and primary amines under acid catalysis.

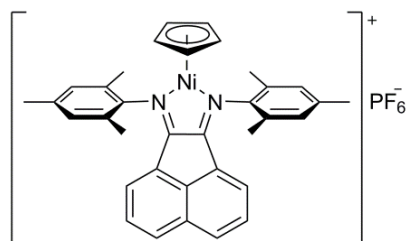
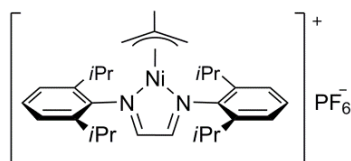
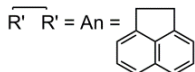
The field of late-transition metal polymerisation catalysis beyond metallocenes was impacted upon by the seminal work of Brookhart *et al.*, who reported new Ni(II) and Pd(II) catalyst systems bearing bulky α -diimine ligands of the types *N,N*-diaryl-1,4-diazabuta-1,3-diene (aryl-DAD) or bis(arylimino)acenaphthene (aryl-BIAN) (**A**).² Designing bidentate neutral *N,N*-chelating ligands containing sterically demanding groups has been crucial for the blockage of the axial coordination sites of the metal towards the incoming monomer and reduction of chain transfer, which made them highly active, affording polyethylenes with high molecular weights and relatively narrow molecular weight distributions. Moreover, these systems led to highly branched products (*ca.* 100 branches/1000 carbon atoms) in a controllable manner, especially those prepared with the Pd(II) catalysts.³ On the other hand, the need for a large excess of an aluminium cocatalyst, such as the expensive methyl aluminoxane (MAO), was a major drawback.

The high versatility exhibited by these late-transition α -diimine metal complexes led to the development of a lively area of investigation around these catalyst precursors, giving rise to several important contributions that helped to highlight these systems as alternatives to early-transition metal catalysts.^{1b-d,4} One of such contributions was reported by Souza *et al.* who synthesised a 16-electron cationic nickel(II) complex containing simultaneously a 2-methyl-allyl and a α -diimine ligand (**B**).^{4f} This complex behaved as an efficient catalyst for the polymerisation of ethylene, when activated with MAO or diethyl aluminium chloride (DEAC), AlEt₂Cl, leading to products with different properties, ranging from high density polyethylene (HDPE) to low density polyethylene (LDPE).

We have been interested in the chemistry of nickel(II) complexes bearing either aryl-BIAN⁵ or cyclopentadienyl (η -C₅H₅)⁶ ligands. In the case of late-transition η^5 -cyclopentadienyl-metal complexes, this ligand can undergo η^5 to η^1 ring-slippage processes, upon coordination of further ligands to the metal centre, acting as a reacting hydrocarbyl fragment.⁷



M = Ni, Pd; R = Me, *i*Pr; R' = H, Me;



Recently, we reported the synthesis of a new cationic cyclopentadienyl nickel(II) complex, $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-BIAN})][\text{PF}_6]$ (**1**) (Mes= mesityl = 2,4,6-Me₃-C₆H₂; Mes-BIAN= bis(mesitylimino)acenaphthene), *via* two alternative routes.⁸ Although electronically saturated, complex **1** was tested in the polymerisation of ethylene in the presence of the cocatalyst methylaluminoxane (MAO), revealing to be an efficient catalyst precursor for the polymerisation of ethylene under mild reaction conditions (low temperature and pressure).⁸

These results prompted us to evaluate the performance of complexes of the type $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\alpha\text{-diimine})][\text{PF}_6]$ in the presence of the well-defined cocatalyst AlEt₂Cl (DEAC). In this work, we report their application as efficient catalyst precursors for the polymerisation of ethylene and also their reactivity towards DEAC, in order to get possible insights into the precatalyst transformation. All the newly synthesised and isolated compounds in this study were fully characterised by multinuclear nuclear magnetic resonance (NMR) spectroscopy and X-ray diffraction, when possible.

Results and discussion

Polymerisation of ethylene catalysed by Ni(II) precatalysts **1** and **2** activated by DEAC

In the present work, complex **1** was tested in the polymerisation of ethylene, in the presence of the cocatalyst DEAC, showing to be an efficient catalyst precursor. The results obtained are summarised in Table 1. It has already been shown that complex **1** is inactive towards the polymerisation of ethylene in the absence of a co-catalyst and when reactions were conducted at low pressures.⁸ This inactivity may be attributed to its electronic saturation (18-electron count) and also possibly to the fact that the Cp-Ni⁺ bond is much stronger than that of a Ni⁺-ethylene bond. Therefore, a ring-slippage from η^5 to η^1 is unlikely to occur. However, in the presence of an aluminium cocatalyst such as DEAC, as previously described for MAO,⁸ this complex revealed to be an efficient catalyst precursor for the polymerisation of ethylene (Table 1, entries 1–14).

Nevertheless, the activity is highly dependent upon the nature of the alkyl aluminium employed. Under the same experimental conditions, for a reaction time of 1 h, DEAC revealed to be a much better cocatalyst than MAO (Table 1, entries 10 and 14, respectively), the DEAC system showing even a considerable higher catalytic activity at a reaction time of 0.5 h (Table 1, entries 8 and 14). We decided then to investigate the behaviour of the catalyst system when low ratios of [Al]/[Ni] were employed (Table 1, entries 1–7; Fig. 1). This cocatalyst, even used at low concentrations, such as [DEAC]/[**1**] = 3 (Table 1, entry 3), afforded moderate polymerisation activities, but showed to be inactive at ratios lower than 3 (Table 1, entries 1 and 2). At ratios *ca.* [DEAC]/[**1**] \geq 4 (Table 1, entries 4–8 and 10), the activity became practically independent of the amount of DEAC added to the reaction (Fig. 1). Conversely, when MAO was used, precatalyst **1** was inactive for a ratio of [Al]/[Ni]=10, showing similar activities for ratios of 100 and 1000.⁸

The substantial differences observed in the nature of the polyethylene samples obtained with systems **1**/MAO and **1**/DEAC, in terms of molecular weight and branching number, are reflected in their macroscopic properties, such as melting temperature and crystallinity. With DEAC, the polyethylene molecular weights are lower and the branching numbers are higher, which resulted in the decrease of the melting point and crystallinity (Fig. 2 and Table 1, entries 10 and 14). A further analysis to Table 1 shows that an increase in the amount of DEAC, using [DEAC]/[**1**] ratios in the range 3 to 100 (entries 3–8), generally decreases the melting temperature and the crystallinity of the polyethylenes, which suggests a decrease in the molecular weight of the samples.

Table 1. Catalytic performance of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-BIAN})][\text{PF}_6]$ (**1**) and $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-Me}_2\text{DAD})][\text{PF}_6]$ (**2**) activated by DEAC in the polymerisation of ethylene.^a

$\text{=} \xrightarrow[\text{t = 30 min}]{\text{Cat. / n AlEt}_2\text{Cl}} \text{branched polyethylene}$											
Entry	Cat.	[Al]/[Ni]	<i>T</i> (°C)	Polymer mass (g)	Activity×10 ⁻⁴ (g PE/(mol Ni·h·bar))	<i>M_n</i> ×10 ^{-3^b (g mol⁻¹)}	<i>D</i> ^c	<i>N</i> ^d	<i>T_m</i> ^e (°C)	ΔH_m^f (J g ⁻¹)	Cryst. ^g (%)
1 ^h	1	1	22	0	0	–	–	–	–	–	–
2 ^h	1	2	22	0	0	–	–	–	–	–	–
3	1	3	22	0.43	4.3				112.9	205.8	72.0
4	1	4	22	1.71	17.1				106.1	145.6	50.7
5	1	6	22	1.84	18.4				105.7	137.1	47.9
6	1	8	22	1.91	19.1				101.3	127.1	44.4
7	1	10	22	1.75	17.5						
8	1	100	22	1.91	19.1				94.8	132.4	46.3
9 ^h	1	100	0	0.85	4.3	494	2.11	7	122.1	203.8	71.4
10 ^h	1	100	22	4.12	20.6	31	2.11	60	62.8	98.8	34.5
11 ^h	1	100	30	4.44	22.2	33	2.09	64	32.7	43.0	15.0
12 ^h	1	100	40	4.28	21.4	26	1.98	70	32.4	28.0	9.7
13 ^h	1	100	50	2.74	13.7	18	1.81	75	30.4	18.2	6.3
14 ^{h,i}	1	100	22	1.27	6.4	320	2.68	15	117.8	197.4	69.0
15 ^h	2	100	22	6.12	30.6	35	2.09	35	95.1	15.8	5.5

^a Precatalysts **1** or **2**: 10 μmol; t: 0.5 h; V_{ODCB}: 50 mL (ODCB = *o*-dichlorobenzene); P_{ethylene} (absolute): 2 bar. ^b Determined by GPC/SEC. ^c *D* = *M_w*/*M_n*, dispersity index (determined by GPC/SEC). ^d Number of branches/1000 carbons (determined by ¹H NMR; ref. 9). ^e Melting temperature (determined by DSC). ^f Enthalpy of fusion. ^g Crystallinity % = ($\Delta H_m/285.9$)×100 (ref. 10). ^h t: 1 h. ⁱ cocatalyst: MAO; V_{PhCl}: 50 mL (PhCl = chlorobenzene).

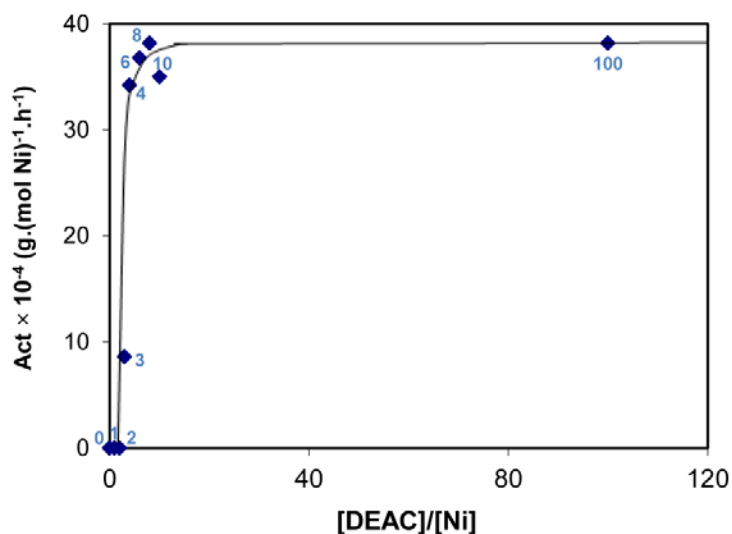


Fig. 1 Variation of the activity of the catalyst system **1**/DEAC in the polymerisation of ethylene, with the ratio [DEAC]/[Ni] (numbers in blue), at 22 °C, in ODCB.

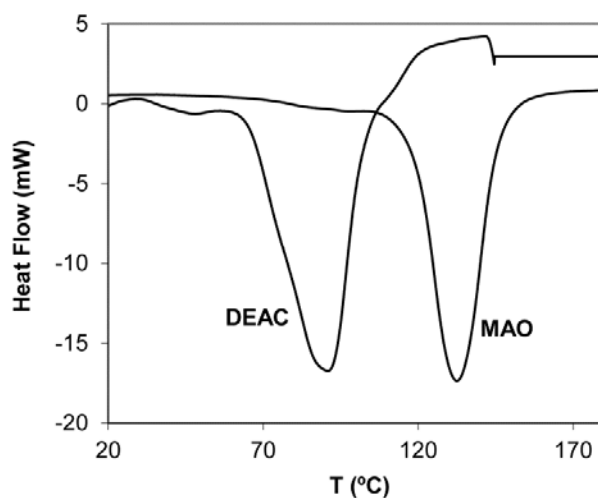


Fig. 2 DSC thermograms of the polyethylenes obtained with the catalyst systems **1**/DEAC and **1**/MAO (Table 1, entries 10 and 14, respectively).

The catalytic activity of the system **1**/DEAC and the physical properties of the polyethylenes obtained are considerably influenced by the reaction temperature, which was varied in the range 0–50 °C. The catalytic activity increases with the reaction temperature from 0 to 22 °C (Table 1, entries 9 and 10; Fig. 3), going through a plateau in the range 22–40 °C and then decreasing at 50 °C (Table 1, entries 11–13; Fig. 3), which can be attributed to a partial deactivation of the

catalyst. The increase in the reaction temperature caused a significant decrease in the polyethylenes number-average molecular weight (M_n), since the β -hydrogen elimination reaction, and therefore the chain-transfer step, is favoured. In fact, the highest molecular weight is obtained when the polymerisation reaction was performed at 0 °C (Table 1, entry 9; Fig. 3). The increase in the reaction temperature also causes a substantial increase in the branching number, leading to the consequent decrease in the polyethylene melting temperature and crystallinity.

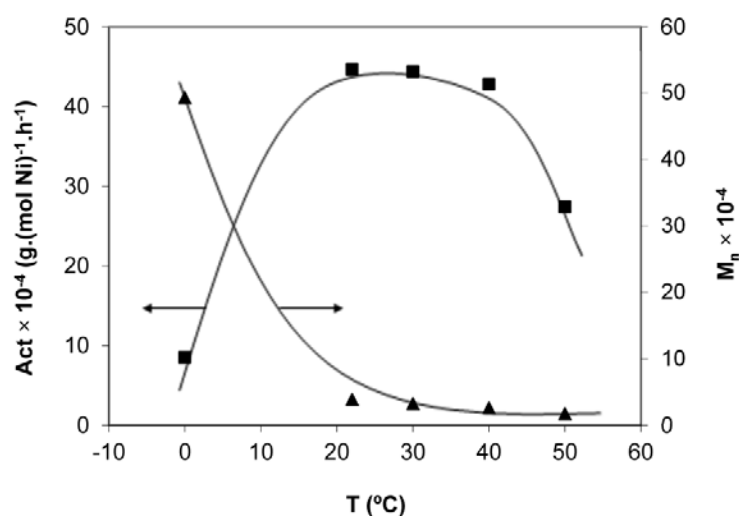
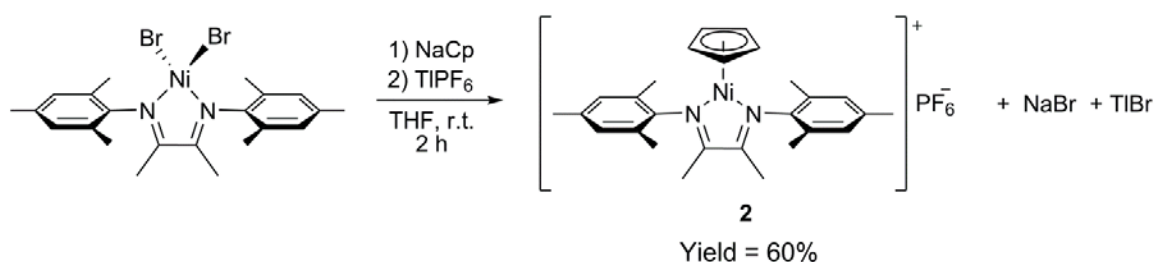


Fig. 3 Influence of the reaction temperature on the catalytic activity (squares) and on the M_n (triangles) of the polyethylenes obtained with the catalyst system **1**/DEAC.

A new complex of the type $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\alpha\text{-diimine})][\text{PF}_6]$ was also prepared by reacting $[\text{NiBr}_2(\text{Mes-Me}_2\text{DAD})]$ ($\text{Mes-Me}_2\text{DAD} = N,N\text{-bis(mesityl)-2,3-dimethyl-1,4-diazabuta-1,3-diene}$) with NaCp, followed by treatment with $\text{Ti}[\text{PF}_6]$ (Scheme 1), in THF, at room temperature. The resulting complex, $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-Me}_2\text{DAD})][\text{PF}_6]$ (**2**), was obtained as a dark violet microcrystalline solid, in 60% yield. Complex **2** is stable in air, being very soluble in solvents such as dichloromethane and chloroform, soluble in *o*-dichlorobenzene (ODCB), and moderately soluble in chlorobenzene.



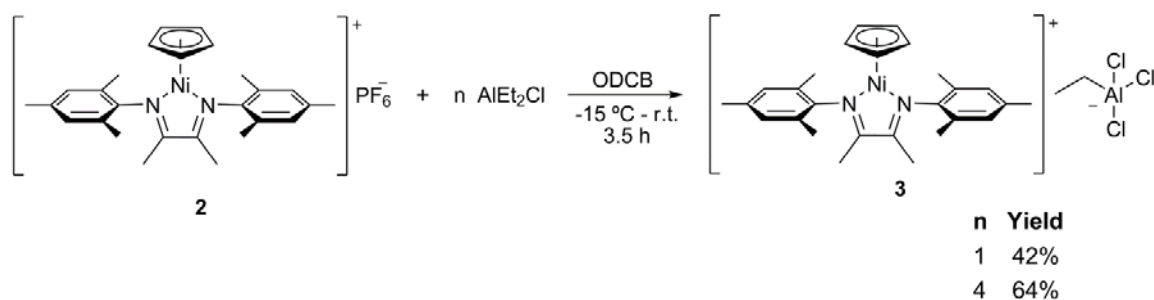
Scheme 1 Synthesis of complex **2**.

Complex **2** was also tested in the polymerisation of ethylene, upon activation with DEAC, revealing to be considerably more active than precatalyst **1** (Table 1, entries 15 and 8 or 10), giving rise to polyethylenes with similar M_n values but with a degree of branching approximately half of that obtained with **1**.

Studies on the reactivity of Ni(II) complexes **1** and **2** towards DEAC

To understand the interaction of these $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\alpha\text{-diimine})][\text{PF}_6]$ complexes with alkyl aluminium activators, both **1** and **2** were reacted with 1 equivalent or a moderate excess (4 equivalents) of DEAC, in the absence of ethylene.

In the first attempted experiment, complex **2** and DEAC were used in an equimolar ratio ($[\text{DEAC}]/[\mathbf{2}] = 1$). Complex **2**, which was only partially soluble in ODCB, was cooled to $-15\text{ }^\circ\text{C}$, followed by the dropwise addition of a solution containing one molar equivalent of DEAC in the same solvent (Scheme 2). After warming up to room temperature, a violet suspension of unreacted complex **2** was observed, which was separated by filtration. After evaporation of the solvent to dryness and washings of the residue with *n*-hexane, diethyl ether and toluene, the reaction products were extracted with ODCB affording a carmine pink solution, from which complex **3** was isolated as a dark violet solid, in 42% yield.



Scheme 2 Formation of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-DAB})][\text{AlEtCl}_3]$ (**3**).

The ^1H NMR spectrum of **3** (ESI, Fig. S1), in CD_2Cl_2 at room temperature, exhibited resonances identical to those of the cationic moiety of complex **2**, at the same chemical shifts (δ). However, the spectrum also revealed the existence of two additional resonances, a triplet at *ca.* 0.95 ppm and a doublet at *ca.* -0.05 ppm, corresponding to an ethyl group connected to a metal centre. The $^{27}\text{Al}\{^1\text{H}\}$ NMR spectrum was also determined (ESI, Fig. S2), showing the presence of this element in the structure of **3** at δ 129.8 (in CD_2Cl_2) or 128.6 (in $\text{C}_6\text{D}_5\text{Br}$).

The same reaction performed at a ratio of $[\text{DEAC}]/[\mathbf{2}] = 4$ also gave rise to compound **3**, now with an improved (with respect to the reaction performed at a $([\text{DEAC}]/[\mathbf{2}] = 1)$ overall yield of 64%. However, the employment of a higher ratio of $[\text{DEAC}]/[\mathbf{2}] = 10$ led to full conversion of complex **2** into an uncharacterised black paramagnetic oil, which, after a work-up similar to that used in the previous reactions, did not afford crystals suitable for X-ray diffraction.

The molecular structure of complex **3** was established by single-crystal X-ray diffraction, confirming the cationic moiety is identical to that of reagent **2**, but a different anion, $[\text{AlEtCl}_3]^-$, is present instead of $[\text{PF}_6]^-$. The asymmetric unit of complex **3** contains two independent molecules, and 1.75 molecules of disordered *o*-dichlorobenzene molecules (one ODCB site refining with occupation of 75% and the second ODCB molecule was refined as disordered over two sites, with probability of 60 and 40%, respectively). Its molecular structure is depicted in Fig. 4, selected bond distances (\AA) and angles ($^\circ$) and other relevant structural parameters being listed in Table S1 in ESI.

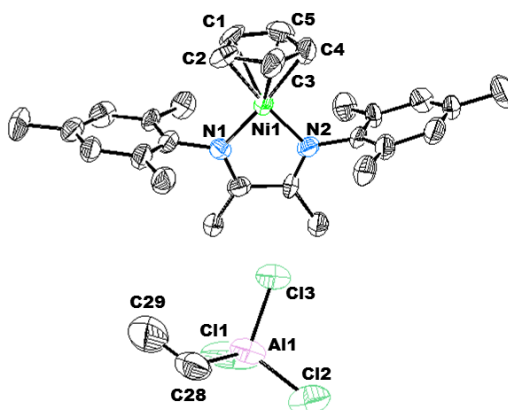


Fig. 4 Molecular structure of complex **3** (molecule A of the asymmetric unit) using 50% probability level ellipsoids. Hydrogen atoms and disordered *o*-dichlorobenzene molecules were omitted for clarity.

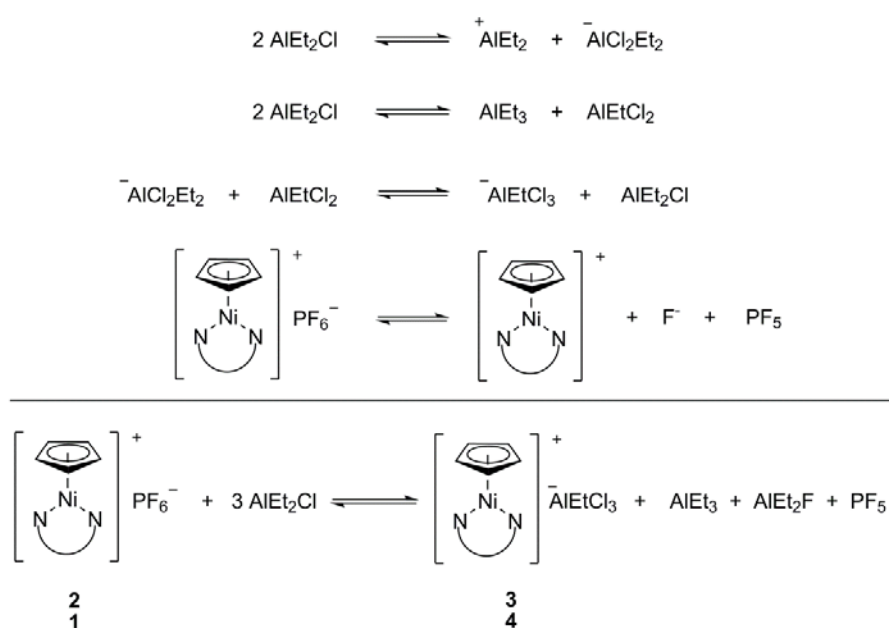
The geometry around the nickel centre is trigonal, where the sum of the three internal angles about Ni is 360°, considering the Cp centroid as one of the ligands. The Cp ligand is coordinated to the metal centre with η^5 hapticity, being almost perpendicular to plane (N1-Ni1-N2), as can be observed by the estimated values of the dihedral angles χ , which are reasonably close to 90° (92.1(6) in molecule 1, and 91.4(5)° in molecule 2) and nearly parallel to the plane defined by the mesityl rings (Table S1 in ESI). Consistent with these observations, complex **3** exhibits a formal count of 18 valence electrons.

The analysis of selected parameters shown in Tables S1 and S2 in ESI reveals that the bond distances within the Cp ligand are not homogeneous, and, as a consequence, some of the internal angles of the five-membered ring deviate from 108°, although their sum is very close to the value of a regular pentagon (540°). However, in both molecules A and B of complex **3**, the Cp ring internal bonds do not exhibit a clear trend to localisation, as in the previously reported structure of complex **1**.⁸ In fact, the Cp rings of complex **3** do not display neither the *ene-allyl* nor the *diene* types of distortion described by Andersen *et al.*,¹¹ rather tending to be essentially delocalised (see Table S2 in ESI). The Cp atom C4 (molecule 1) or C32 (molecule 2) are “on” the respective nickel planes (N-Ni-N) (see Distances A in Table S1 in ESI), which can be seen as a pseudo-square planes, and the distances Ni1–C4 (molecule 1) or Ni2–C32 (molecule 2) are the shortest of all Ni–C_{Cp} bonds. As suggested by Andersen *et al.*,¹¹ a structure with a carbon atom “on” (less than 0.10 Å) the Ni pseudo-square plane, exhibiting a stronger interaction with the metal centre through that atom, should have a diene distortion in the Cp ring, which in this case is not clearly verified. Interestingly, both $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\alpha\text{-diimine})]^+$ cations are interacting in the unit cell through a π - π stacking interaction of the Cp rings, which are close (distance between centroids of 3.569(12) Å) and parallel (dihedral angle of 1.9(8) Å) to each other.

Comparing these observations with those obtained previously for complex **1**,⁸ it is possible to conclude that the structure of the cation is almost unaltered in what the bond distances and angles involving the Ni atom and the type of coordination observed for the Cp ring are concerned. The $[\text{AlEtCl}_3]^-$ counter-anion shows a tetrahedral geometry around the Al centre, with all bond distances and angles within the expected values for similar species.¹² The formation of a $[\text{AlEtCl}_3]^-$ anion was also observed by Gambarotta *et al.*, in a reaction of a Cr(III) complex containing a pyridine-based pincer PNP-type of ligand with a small excess of DEAC.¹³ The crystal structure of compound **3** also revealed a very disordered ODCB molecule per Ni atom, which is consistent with the results obtained in the elemental analysis.

Alkylaluminium compounds are generally associated in dimers. According to Robinson *et al.*,¹⁴ these dimers can dissociate or disproportionate via three different modes (ESI, Fig. S4): (a) the symmetric bridge cleavage of the dihalo-bridged alkylaluminium dimer (mode **I** in Fig. S4), affording two DEAC monomers; (b) the asymmetric bridge cleavage of mixed chloro-alkyl-bridged dimers, resulting in the $[\text{AlEt}_2]^+$ and $[\text{AlCl}_2\text{Et}_2]^-$ species (mode **II** in Fig. S4); and (c) the asymmetric cleavage of the mixed chloro-ethyl-bridged dimers, leading to the formation of species AlEt_3 and AlEtCl_2 (mode **III** in Fig. S4). The latter two types of cleavage are much less frequent than the first one.

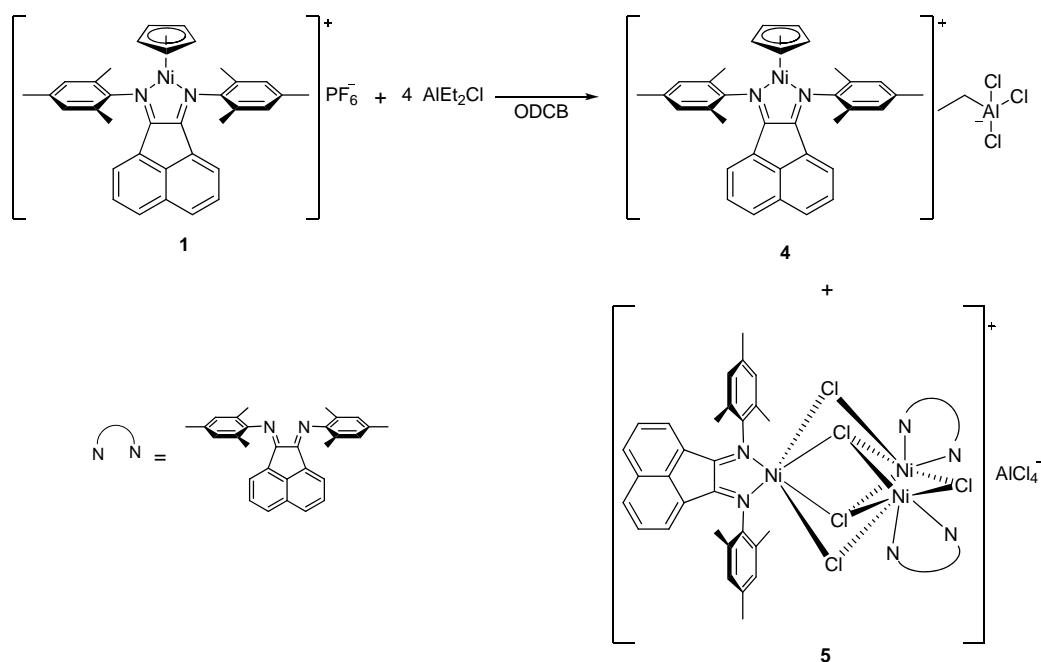
In agreement with the alkylaluminium dimer cleavages mentioned above, we propose a possible pathway for the formation of complex **3** (Scheme 3). Owing to the dissociation/disproportionation equilibria discussed above, all the aluminium species can exist in solution, allowing the reaction between $[\text{AlCl}_2\text{Et}_2]^-$ and AlEtCl_2 , which give rise to the anion $[\text{AlEtCl}_3]^-$ and AlEt_2Cl . On the other side, the $[\text{PF}_6]^-$ anion may partially dissociate giving rise to PF_5 and F^- . The sum of these four equilibria (Scheme 3) leads to a possible overall reaction where the cationic compound $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-Me}_2\text{DAD})][\text{PF}_6]$ (**2**) requires 3 equivalents of DEAC to give rise to the same cationic complex with a different anion $[\text{AlEtCl}_3]^-$ (complex **3**), possibly along with other compounds such as AlEt_3 , AlEt_2F and PF_5 (Scheme 3, bottom), or further combinations among them.



Scheme 3 Possible equilibria involved in the formation of complexes **3** and **4**.

The stoichiometry 1:3 found in this proposed mechanism is in agreement with the increase of the reaction yield when 4 equivalents of DEAC were used, and also with the partial recovery of the starting material **2**, in the case of the ratio $[\text{DEAC}]/[\mathbf{2}] = 1$.

We have also performed the reaction of complex **1** with 4 equivalents of DEAC, under the same reaction conditions used for the preparation of **3** (Scheme 4). The reaction products were initially extracted with diethyl ether, followed by toluene and finally ODCB. The ^1H NMR spectra showed that the Et_2O and toluene extracts contained the diamagnetic complex **4**, analogous to complex **3**, whereas the ODCB extract contained a compound displaying paramagnetic nature (complex **5**, Scheme 4). Compound **4** was obtained as a dark green microcrystalline solid and compound **5** as black crystals, in 66 and 16% yield, respectively. The black crystals were suitable enough for X-ray diffraction, enabling the determination of the molecular structure of complex **5**, which is depicted in Fig. 5, with selected bond distances (\AA) and angles ($^\circ$) listed in Table S3 (ESI).



Scheme 4 Formation of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-BIAN})][\text{AlEtCl}_3]$ (**4**) and $[\{\text{Ni}(\text{Mes-BIAN})\}_3(\mu\text{-Cl})_5][\text{AlCl}_4]$ (**5**) from the reaction of complex **1** with 4 equivalents of DEAC.

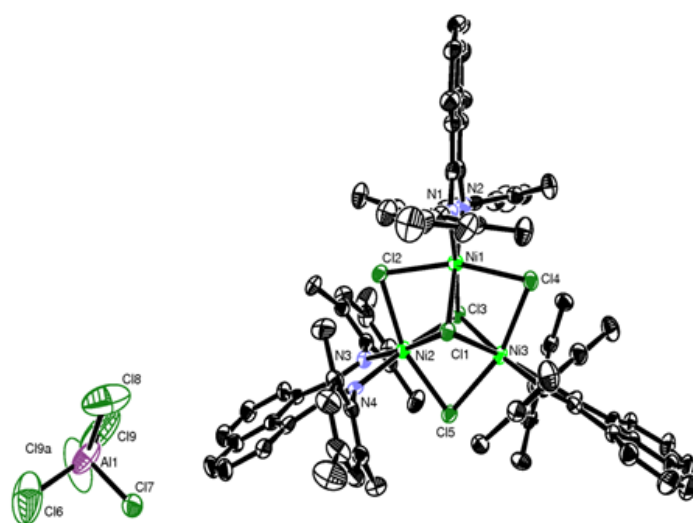


Fig. 5 Molecular structure of complex **5** using 50% probability level ellipsoids. Hydrogen atoms were omitted for clarity.

Compound **5** is a cationic cluster containing three [Ni(Mes-BIAN)] moieties linked by five chlorine bridging atoms, and the counteranion [AlCl₄]⁻. The geometries around each nickel centre are octahedral with some degree of distortion (Cl-Ni-Cl is *ca.* 160 °), probably due to steric effects. Upon formation of the cluster, the α -diimine bite angles became smaller than that observed for the precursor complex **1** (*ca.* 81 vs. 85°).⁸ On the other hand, the anion [AlCl₄]⁻ has a distorted tetrahedral geometry around the Al atom. One of the Cl atoms is disordered over two positions (Cl9 and Cl9a) with 65 and 35% probability, respectively.

Moreover, within the bulk of the dark green microcrystalline solid of compound **4**, it was also possible to identify very few crystals of a different species, compound **6**, whose molecular structure was unambiguously established by X-ray diffraction, and is depicted in Fig. 6. Selected bond distances and angles for **6** are summarised in Table S4 in ESI.

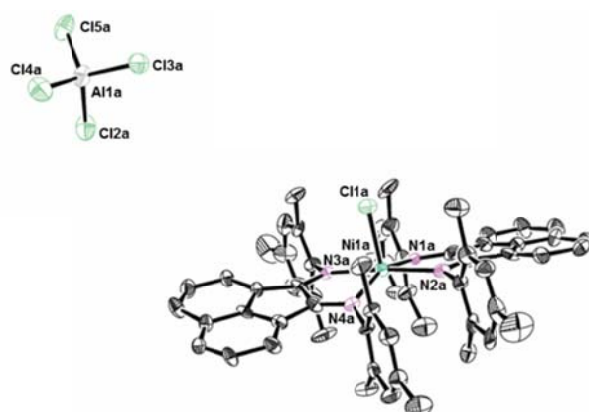
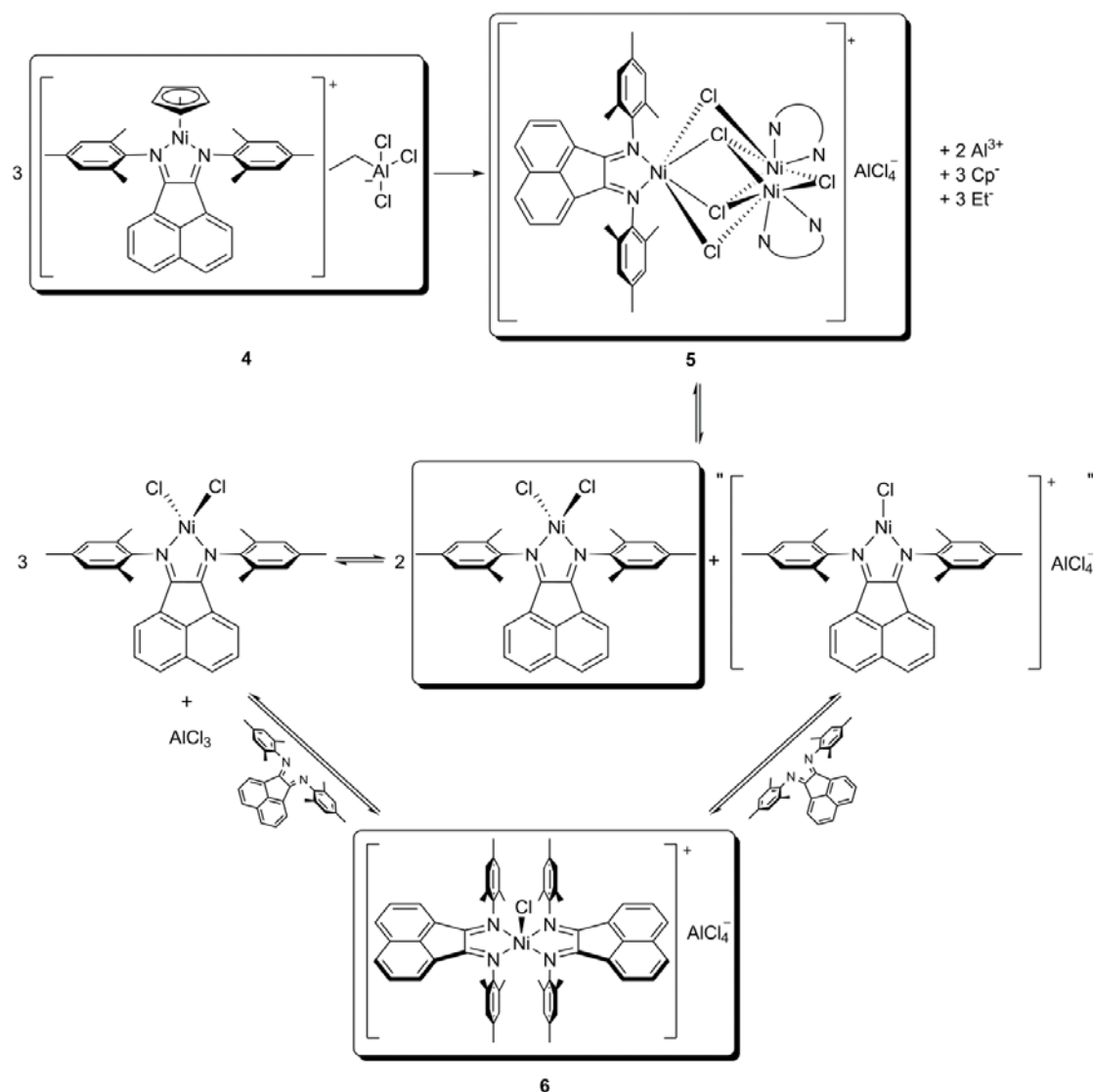


Fig. 6 Molecular structure of complex **6** (molecule A of the asymmetric unit) using 50% probability level ellipsoids. Hydrogen atoms and three CH₂Cl₂ molecules were omitted for clarity.

The asymmetric unit of complex **6** contains two independent molecules and three dichloromethane solvent molecules. The geometry around the cationic nickel centre is that of a distorted square pyramid (τ parameter¹⁵ of 0.311 and 0.252, for molecule A and B, respectively; see Table S4 in ESI), composed by two Mes-BIAN chelating ligands and a chlorine atom. The dihedral angle between the planes containing the atoms of each of the Mes-BIAN ligands is of 18.33° and 16.87°, for molecules A and B, respectively. The mesityl rings are nearly perpendicular to the BIAN backbones with dihedral angles of 87.86°, 85.93°, 88.63°, 88.77° (molecule A) and 86.52°, 85.15°, 87.30°, and 87.18° (molecule B). In addition, these mesityl rings of adjacent BIAN backbones are nearly parallel to each other, showing dihedral angles of 2.74° and 6.14° (molecule A) and 1.39° and 6.40° (molecule B), respectively. This arrangement occurs through the establishment of additional π -bonds between the adjacent mesityl rings, with distances between centroids of 3.558 Å and 3.582 Å (molecule A), and 3.497 Å and 3.555 Å (molecule B). On the other hand, the anion [AlCl₄]⁻ displays a tetrahedral geometry around the Al centre.

The formation of complex **4** can be envisaged as a process similar to that proposed for the formation of compound **3** (Scheme 3). On the other hand, the formation of cluster **5** could be seen as a further reaction occurring between three molecules of **4**, after losing the Cp⁻ ligand, which very likely occurs by acidic abstraction performed by the aluminium species present in solution, and the concomitant halogenation reactions of the Ni centres.

Complex **5** should be formed along with species Al^{3+} , Cp^- and Et^- (Scheme 5), which are possibly combined in compounds containing AlCp^{2+} moieties or AlEt_3 . It is very likely that, in solution, compound **5** is involved in a dissociative equilibrium with two equivalents of $[\text{NiCl}_2(\text{Mes-BIAN})]$ and one equivalent of a “ $[\text{NiCl}(\text{Mes-BIAN})][\text{AlCl}_4]$ ” species, which may rearrange and give rise to an additional equivalent of $[\text{NiCl}_2(\text{Mes-BIAN})]$ and AlCl_3 .



Scheme 5. Possible pathways for the formation for complexes **5** and **6**, from a reaction involving three molecules of **4**.

On the other hand, compound **6** is a nickel complex with a formal 20-electron count, containing two Mes-BIAN bidentate ligands, which was likely formed by the addition of residual free Mes-BIAN ligand to the “[NiCl(Mes-BIAN)][AlCl₄]” species existing in solution. The Ni halide adducts containing two α -diimine ligands are reported to exhibit good catalytic activities in the polymerisation of olefins.^{5d-f,16}

Therefore, all the species resulting from the treatment of cationic cyclopentadienyl nickel(II) complexes **1** and **2** with a large excess of AlEt₂Cl may give rise to Brookhart-type catalyst precursors [NiCl₂(α -diimine)] for the polymerisation of ethylene.

Polymerisation of ethylene catalysed by Ni(II) intermediates **3 and **5** activated by DEAC**

As discussed above, complex **1**, when activated with DEAC, is an efficient catalyst precursor for the polymerisation of ethylene for ratios [DEAC]/[catalyst] \geq 3, and the use of ratios [DEAC]/[catalyst] \geq 4 made the catalytic activity virtually independent of the amount of DEAC used (Table 1).

Because they are possible intermediates in the transformation of complexes **1** and **2** into the catalytic active species, complexes **3** and **5**, which resulted from the reaction of **2** and **1**, respectively, with small excesses of DEAC, were also tested in the polymerisation of ethylene. The reactions were carried out in ODCB solutions, at 22 °C, with and without the addition of the cocatalyst (DEAC). Both complexes showed to be inert towards ethylene polymerisation in the absence of cocatalyst. Nevertheless, these compounds revealed to be efficient catalyst precursors when DEAC was employed (Table 2).

In a preliminary experiment, in order to determine whether complex **3** was active in the polymerisation of ethylene, a ratio [DEAC]/[**3**] = 1000 was used, leading to the formation of 0.123 g of polyethylene (Table 2, entry 1), which corresponded to an activity of 12.3×10^4 g/(mol Ni·h·bar). Therefore, taking this result into account and also those obtained for complex **1**/DEAC (see Table 1 and discussion above), we examined the influence of the [Al]/[Ni] ratio in the catalytic activity of the system. We have used ratios [DEAC]/[**3**] ranging from 1 to 4 in order to determine the minimum amount of DEAC needed to make complex **3** active towards ethylene polymerisation. These tests showed that complex **3** was able to promote the polymerisation of ethylene using a minimum ratio [Al]/[Ni] = 2 (Table 2, entry 3). This ratio corresponds to a minimum overall ratio [DEAC]/[**2**] = 5 (since a stoichiometry [DEAC]/[**2**] = 3 is required for the formation of complex **3** – see Scheme 3), which is higher than the minimum ratio observed for

complex **1** to become catalytically active ([DEAC]/[**1**] = 3). The fact that no activity was observed for a ratio of [DEAC]/[**3**] = 1 (Table 2, entry 2), which corresponds formally to a ratio of [DEAC]/[**2**] = 4, may explain the non-isolation of a Ni species analogous to **5** in the stoichiometric reactions of complex **2** with DEAC described in the previous subsection, in which the Cp ligand was abstracted. However, we may postulate the formation of such an analogous intermediate for the catalyst system **2**/DEAC for ratios [DEAC]/[**2**] \geq 5, on the basis of the structural similarities of both precatalysts **1** and **2**.

For complex **5** only two runs were performed, one in the absence of DEAC and the other one in the presence of 4 equivalents of this cocatalyst. In the latter case (Table 2, entry 6), a large amount of polyethylene was obtained (4.536 g), corresponding to a moderate-high catalytic activity of 29.8×10^4 g/(mol Ni · h · bar).¹⁷

Table 2. Catalytic performance of [Ni(η^5 -C₅H₅)(Mes-Me₂DAD)][AlEtCl₃] (**3**) and [Ni(Mes-BIAN)₃(μ -Cl)₅][AlEtCl₃] (**5**) activated by DEAC in the polymerisation of ethylene.

Entry	Cat.	[Al]/[Ni]	Polymer mass (g)	Cat. / n AlEt ₂ Cl		branched polyethylene							
				ODCB	t = 1 h	Act $\times 10^{-4}$ (g PE/(mol Ni · h · bar))	$M_n \times 10^{-3}^d$ (g/mol)	M_w/M_n^d (\bar{D})	$[\eta]^d$ (dl/g)	N^e	T_m^f (°C)	ΔH_m^f (J/g)	Cryst. ^h (%)
1 ^a	3	1000	0.123			12.3	90.5	3.2	3.43	18	112.5	125.1	43.1
2 ^b	3	1	0			0	–	–	–	–	–	–	–
3 ^b	3	2	0.064			0.39	55.2	2.9	2.09	21	99.8	100.8	34.8
4 ^b	3	3	0.869			5.3	73.7	3.2	2.83	24	104.1	114.3	39.4
5 ^b	3	4	1.579			9.7	69.4	3.2	2.53	30	100.0	109.7	37.8
6 ^c	5	4	4.536			29.8	22.1	2.1	0.68	67	112.6 / 20.2 ^g	21.2	7.3

^a Precatalyst **3**: 0.5 μ mol; t: 1 h; V_{ODCB}: 50 mL; P_{ethylene} (absolute): 2 bar; T=22 °C. ^b Precatalyst **3**: 8.13 μ mol; t: 1 h; V_{ODCB}: 50 mL; P_{ethylene} (absolute): 2 bar; T=22 °C. ^c Precatalyst **5**: 7.62 μ mol; t: 1 h; V_{ODCB}: 50 mL; P_{ethylene} (absolute): 2 bar; T=22 °C. ^d Determined by GPC/SEC coupled to viscometry ([η] is the intrinsic viscosity). ^e Number of branches/1000 carbons (determined by ¹H NMR; ref. 9). ^f Determined by DSC; scans performed from -30 to 170 °C, scan rate: 10 °C/min and the second heating cycle was recorded; the peak value of the melting endotherm (ideally taken as the temperature at which the largest and most perfect crystals are melting) is frequently assigned as the melting temperature, *i.e.* T_m \equiv T_{max}. ^g Two melting ranges are observed, the corresponding maxima being indicated. ^h Crystalline fraction calculated as the ratio between the ΔH_m of the sample and that of a perfectly crystalline PE material (290 J/g; refs. 9, 10).

The four polyethylene samples prepared using precatalyst **3** (entries 1 and 3–5, Table 2) are white solids, whereas for complex **5** a rubbery material (entry 6) was obtained. All samples were characterised by NMR spectroscopy, differential scanning calorimetry (DSC) and gel permeation chromatography/size exclusion chromatography (GPC/SEC) (Table 2).

The branching degree (N) of these samples, *i.e.* the total number of branches per 1000 carbon atoms, was determined by ^1H NMR.⁹ These values range from typical low density polyethylene (LDPE) to very low density polyethylene (VLDPE), varying from 18 to 67 branches per 1000 carbon atoms. Similar branched polyethylenes were also obtained using Brookhart's^{2,3d,18} and Souza's^{4f-4h} α -diimine complexes. The results obtained (Table 2) show an increase in the branching degree in the order: entries 1 < 5 << 6. The branching number calculated for entry 6, produced with the catalyst system **5**/DEAC (Table 2), is close of that obtained for the precursor system **1**/DEAC (Table 1).

We have also determined the type and distribution of branches in selected polyethylene samples (Table 2, entries 1, 5 and 6). Fig. S5 in ESI presents the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the polyethylene of entry 6 (Table 2), showing the observed chemical shifts and the assignment of each type of branch. For this sample, the majority of the branches present in the polymer are methyl groups, following the order: methyl > long > butyl > propyl > amyl \approx ethyl.

The differences observed in the branching number of these polyethylene samples (Table 2, entries 1 and 3–6) are reflected in the macroscopic thermal properties, such as the melting point (T_m), enthalpy of fusion (ΔH_m) and crystallinity. These properties were determined by DSC (Table 2 and Fig. S6 in the ESI). For samples of entries 1, 4 and 5, which have an increasing branching number ($18 < 24 < 30$, as determined by ^1H NMR), a decrease of T_m , ΔH_m and crystallinity is observed with an increasing branching number.

All these polyethylene samples were analysed by GPC/SEC, showing that, at 22 °C, both precatalysts **3** and **5** give rise to polyethylene having monomodal distributions with dispersities ($\mathbb{D} = M_w/M_n$) ranging from 2.9 to 3.2 for **3**, and 2.1 for **5** (Table 2). For the PE samples prepared using catalyst precursor **3**, the M_n varies between 55200 and 90500 g/mol, following the order: entries 3 < 5 \approx 4 < 1, *i.e.*, the M_n increases with the increase of the ratio $[\text{Al}]/[\text{Ni}]$ used. The lowest number-average molecular weight (22100 g/mol) corresponds to the PE of entry 6 (catalyst system **5**/DEAC), though exhibiting a narrower dispersity ($M_w/M_n = 2.1$).

may generate an active species (**A**, Scheme 6) similar to that proposed by Brookhart^{2,3,18} and de Souza ($[\text{NiMe}(\alpha\text{-diimine})]^+$).^{4f} Therefore, we suggest that, under the conditions tested hereby, the catalyst systems **3**/DEAC or **5**/DEAC operate via a mechanism analogous to that suggested by Brookhart,^{1-3,18} (Scheme 6) except in the initiation step (transformation of catalyst precursor **3** or **5** into the active species). The initiation reaction, which we propose to be the acidic abstraction of the Cp ligand of the Ni precursor and its replacement by alkyl groups of the DEAC cocatalyst in the presence of ethylene. This sequence generates the cationic alkyl complex **A** (catalyst resting state), followed by the three usual main processes: (1) chain propagation by migratory insertion of ethylene into the growing polymer chain, (2) metal migration along the polymer chain (“chain walking”), and (3) chain transfer by β -hydride elimination. These steps are common to all the other α -diimine nickel catalyst precursors, being well described and extensively discussed in the literature.^{1-3,4f-4h,18,19}

Conclusions

Complexes $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-BIAN})][\text{PF}_6]$ (**1**) and $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-DAD})][\text{PF}_6]$ (**2**), although electronically saturated, showed to be efficient catalyst precursors for the polymerisation of ethylene when activated with DEAC, even at very low ratios of $[\text{Al}]/[\text{Ni}]$. When $[\text{DEAC}]/[\text{Ni}] \geq 4$ was employed, the activity was practically independent of the amount of DEAC added to the reaction. The effect of the reaction temperature in the polymerisation of ethylene was also studied, revealing an increase of the catalytic activity with the reaction temperature from 0 to 22 °C, going through a maximum and decreasing until 50 °C, leading though to a decrease in the polyethylene average molecular weight, melting temperature and crystallinity, and to an increase in the branching number.

The reaction of complex $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-DAD})][\text{PF}_6]$ **2** with AlEt_2Cl gives rise to complex **3**, containing the same cation and an AlEtCl_3^- anion. The analogous reaction of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-BIAN})][\text{PF}_6]$ **1** with DEAC afforded two different species, the diamagnetic complex **4** (analogous to **3**), and a paramagnetic cationic trinuclear α -diimine Ni cluster **5** containing five bridging Cl ligands and a $[\text{AlCl}_4]^-$ anion, in which the cyclopentadienyl ring is absent, which is structurally reminiscent of a typical Brookhart’s catalyst precursor. Complexes **3** and **5** were tested in the polymerisation of ethylene with and without the addition of DEAC. Both complexes were inactive *per se*, but showed to be efficient catalytic precursors, when slight excesses of

DEAC were added. The PEs obtained are monomodal branched polymers (18–67 branches/1000 C), with melting points in the range 99–112 °C.

Experimental section

General Considerations. All experiments dealing with air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk techniques. Nitrogen gas was supplied in cylinders by Air Liquide and purified by passage through 4 Å molecular sieves. Unless otherwise stated, all reagents were purchased from commercial suppliers (e.g., Acrös, Aldrich, Alfa Aesar) and used without further purification. All solvents to be used under inert atmosphere were thoroughly deoxygenated and dehydrated before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium (for diethyl ether, and tetrahydrofuran (THF)), calcium hydride (for dichloromethane, chlorobenzene and *o*-dichlorobenzene), Na/K alloy (toluene for the polymerisation reactions). Solvents and solutions were transferred using a positive pressure of nitrogen through stainless steel cannulae and mixtures were filtered in a similar way using modified cannulae that could be fitted with glass fibre filter disks. Ethylene was supplied by Air Liquide, and was dried by passage through 4 Å molecular sieves. Solutions of cocatalyst diethyl aluminium chloride (DEAC) in pentane or toluene (Aldrich) were used.

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian Unity 300 (¹H, 299.995 MHz; ¹³C, 75.4296 MHz; ²⁷Al 78.158 MHz) spectrometer, at room temperature. Deuterated solvents were dried by storage over 4Å molecular sieves and degassed by the freeze-pump-thaw method. Spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane ($\delta=0$). All chemical shifts are quoted in δ (ppm) and coupling constants (*J*) given in Hz. Multiplicities were abbreviated as follows: singlet (s), doublet (d), triplet (t), septet (sept) and multiplet (m). The samples were prepared in J. Young NMR tubes. Polymer samples were prepared in a mixture of 1,2,4-trichlorobenzene and C₆D₆ (75:25 v/v) and recorded at 120 °C.

The elemental analyses were obtained from the Instituto Superior Técnico elemental analysis services.

The molecular weights of the polyethylenes listed in Table 1 were determined by Gel Permeation Chromatography/Size Exclusion Chromatography (GPC/SEC), on a GPC Waters 150

CV chromatograph. The solvent used as eluent was filtered through 0.50 μm membranes from Fluoropore (Millipore), and degassed by ultrasound for 45 min. A mixture of *o*-dichlorobenzene (ODCB) and the radical stabilizer BHT (0.01%) was used as eluent, at a flow rate of 1.0 mL min⁻¹, and the temperature was thermostated at 135, 135 and 60 °C, respectively, in the injector, column and pump compartments. The polymer solutions in ODCB were filtered automatically inside the heated injector compartment, using appropriate filters (Waters). The permeation of the polymers was performed with two Waters Styragel HT linear columns. The molecular weights were calibrated relative to polystyrene standards (TSK Tosoh Co.). The acquisition and data processing were performed with the program Millennium32 (version 3.05.01).

Molecular weight distributions of the polyethylene samples listed in Table 2 were analysed at Smithers Rapra Technology, Shrewsbury, UK, using a Polymer Laboratories GPC220 Instrument gel permeation chromatography apparatus, equipped with PLgel guard plus 2 mixed bed-B columns (30 cm, 10 μm), using 1,2,4-trichlorobenzene with anti-oxidant as a solvent and a flow-rate of 1.0 mL/min (nominal) at 160°C (nominal). Differential refractometer and differential pressure viscometer online detectors were used, the GPC/SEC system being calibrated with polystyrene standards. The resulting calibration curve was corrected to polyethylene values by the application of the corresponding viscometric Mark-Howink-Sakurada parameters.

The thermal analyses of polyethylene samples were performed by Differential Scanning Calorimetry (DSC) using a Setaram DSC 121 calorimeter (the samples were heated between 20 and 300 °C at 10 °C min⁻¹. The temperature of the maximum of the peak(s) was registered as the melting temperature and the area under the peak(s) was associated to the melting enthalpy of each polymer sample. During the experiments the sample holder was continuously purged with argon.) or using a TA Instruments DSC2920 with MDSC[®] option, connected to a liquid N₂ cooling system and calibrated with standards (the sample weights were *ca.* 6-11 mg in all the experiments. A temperature range from -30 to 175 °C has been studied and the heating and cooling rates used were 10 °C min⁻¹. The second heating cycle was recorded.).

The NaCp (Cp= C₅H₅)²⁰ and the α -diimine *N,N*-bis(mesityl)-2,3-dimethyl-1,4-diazabutadiene (Mes-DAD) and bis(mesitylimino)acenaphthene (Mes-BIAN)²¹ ligand precursors, the complexes [NiBr₂(DME)] (DME= 1,2-dimethoxyethane),²² [NiBr₂(Mes-BIAN)],²¹ [NiBr₂(Mes-DAD)₂],²¹ and [Ni(η^5 -C₅H₅)(Mes-BIAN)][PF₆] (**1**)⁸ were prepared according to literature procedures.

X-ray diffraction. Crystals of air- and/or moisture-sensitive compounds were selected under an inert atmosphere, covered with polyfluoroether oil, and mounted on a nylon loop. Since crystals of **3** were extremely small and weakly diffracting, synchrotron radiation was used to collect diffraction data on this compound. Data was collected using a Bruker SMART CCD diffractometer, at 150 K. Crystallographic data for compounds **5** and **6** were collected using graphite monochromated Mo-K α radiation ($\lambda=0.71073\text{\AA}$) on a Bruker AXS-KAPPA APEX II diffractometer equipped with an Oxford Cryosystem open-flow nitrogen cryostat, at 150 K. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all observed reflections. Absorption corrections were applied using SADABS.²³ For all the complexes, structure solution and refinement were performed using direct methods with the programs SHELXTL v6.12,²⁴ SIR2004,²⁵ and SIR2011²⁶ included in the package of programs WINGX-Version 2014.1²⁷ and SHELXL.²⁴ All hydrogen atoms were inserted in idealised positions and allowed to refine riding in the parent carbon atoms, with C–H distances of 0.95 Å, 0.98 Å and 0.99 Å for aromatic, methyl and methylene H atoms, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Both structures refined to a perfect convergence, even the crystals being of poor quality, presenting high R_{int} and relatively low ratio of observed/unique reflections. Crystal **3** showed the presence of disordered *o*-dichlorobenzene molecules, which refined with 75% occupation over the first site, and the other with probabilities of 60 and 40% per site, respectively. This model was further improved from an original refinement which also showed the presence of *ca.* disordered 1.75 ODCB solvent molecules using the PLATON/SQUEEZE²⁸ routine. Crystal **6** also showed the presence of disordered solvent molecules but, in this case, a good disorder model was not possible to achieve, PLATON/SQUEEZE²⁸ routine being applied. Figures of the molecular structures were generated using ORTEP-3²⁹ or Mercury 1.4.2³⁰ (Table S2 in ESI). The most relevant crystallographic data for each compound and experimental details are presented in Tables S1–S5 in ESI. Data was deposited in CCDC under the deposit numbers 1546750 for **3**, 1546751 for **5**, and 1546752 for **6**.

Synthetic and Catalytic Procedures and Product Characterisation.

Synthesis of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5(\text{Mes-DAD}))][\text{PF}_6]$ (2**).** A solution of NaCp (0.18 g, 1.98 mmol) in THF (20 mL) was added to a suspension of $[\text{NiBr}_2(\text{Mes-DAD})]$ (1.07 g, 1.98 mmol) in the same solvent (60 mL), at room temperature. The mixture was stirred overnight, leading to a violet

solution and a white precipitate (NaBr). The solution was filtered to another Schlenk tube, and $\text{Ti}[\text{PF}_6]$ (0.69 g, 1.98 mmol) was added and then stirred for 2 h. All volatiles were evaporated under vacuum and the resulting violet residue was washed with *n*-hexane, extracted with dichloromethane, and filtered through Celite[®] until extracts were colourless. The solution was concentrated (to *ca.* 50%) and double-layered with Et_2O (1:3). A dark violet microcrystalline solid of **2** precipitated, which were further washed with Et_2O and dried under vacuum. Yield: 0.70 g, 60%.

^1H NMR (300 MHz, CD_2Cl_2): δ 6.91 (s, 4H, H_{meta} mesityl), 4.89 (s, 5H, C_5H_5), 2.27 (s, 6H, Me_{para} mesityl), 2.20 (s, 12H, Me_{ortho} mesityl), 2.05 (s, 6H, $-\text{N}=\text{CCH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.43 MHz, CD_2Cl_2): δ 167.1 ($-\text{N}=\text{CCH}_3$), 147.0 (C_{ipso} mesityl), 138.7 (C_{ortho} mesityl), 130.1 (C_{meta} mesityl), 127.7 (C_{para} de mesityl), 95.8 (C_5H_5), 21.0 (Me_{para} mesityl), 18.4 ($-\text{N}=\text{CCH}_3$), 17.7 (Me_{ortho} mesityl); $^{31}\text{P}\{^1\text{H}\}$ NMR (121.44 MHz, CD_2Cl_2): δ -143.7 (sept, $^1J_{\text{PF}}=712$ Hz, $[\text{PF}_6^-]$); Anal. Calcd. for $\text{C}_{27}\text{H}_{33}\text{F}_6\text{N}_2\text{PNi}$: C, 55.0; N, 4.75; H, 5.64. Found: C, 54.27; N, 4.47; H, 5.54.

$[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-DAB})][\text{AlEtCl}_3]$ (**3**). A solution of AlEt_2Cl (DEAC) (0.4 mL, 3.09 mmol) in *o*-dichlorobenzene (ODCB) (15 mL) was added dropwise to a suspension of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{Mes-DAB})][\text{PF}_6]$ **2** (0.45 g, 0.77 mmol) in the same solvent (40 mL), previously cooled to -15 °C. The mixture was stirred in the cold bath and allowed to warm to room temperature (*ca.* 1.5 h). The cold bath was removed, and then stirred for another 2 h. The solvent was removed by trap-to-trap distillation, and the resulting residue was washed with *n*-hexane. The reaction product was initially extracted with diethyl ether, followed by toluene, and finally ODCB. All solutions were carmine pink, and ^1H NMR showed that all represented the same product, Et_2O and toluene being poor solvents. The solutions were combined, concentrated under vacuum (*ca.* 50%), double layered with *n*-hexane (1:3) and stored at $+4$ °C, yielding dark red-violet crystals of **3** (0.30 g, 64% yield) suitable for X-ray diffraction.

^1H NMR (300 MHz, CD_2Cl_2): δ 7.86-7.45 (m, 1H, $\text{C}_6\text{H}_4\text{Cl}_2$), 7.26-7.22 (m, 1H, $\text{C}_6\text{H}_4\text{Cl}_2$), 7.01 (s, 4H, Ph- H_{meta}), 4.99 (s, 5H, C_5H_5), 2.32 (s, 6H, Ph *p*- CH_3), 2.22 (s, 12H, Ph *o*- CH_3), 2.04 (s, 6H, $\text{N}=\text{CCH}_3$), 0.97 (t, 3H, $^3J_{\text{HH}}=8.0$ Hz, $\text{CH}_3\text{CH}_2\text{AlCl}_3$), -0.05 (q, 2H, $^3J_{\text{HH}}=8.0$ Hz, $\text{CH}_3\text{CH}_2\text{AlCl}_3$). ^1H NMR (300 MHz, $\text{C}_6\text{D}_5\text{Br}$): δ 7.62-7.58 (m, 1H, $\text{C}_6\text{H}_4\text{Cl}_2$), 7.31-7.28 (m, 1H, $\text{C}_6\text{H}_4\text{Cl}_2$), 7.17 (s, 4H, Ph- H_{meta}), 5.06 (s, 5H, C_5H_5), 2.62 (s, 6H, Ph *p*- CH_3), 2.57 (s, 12H, Ph *o*- CH_3), 2.40 (s, 6H, $\text{N}=\text{CCH}_3$), 1.93 (t, 3H, $^3J_{\text{HH}}=8.0$ Hz, $\text{CH}_3\text{CH}_2\text{AlCl}_3$), 1.01 (q, 2H, $^3J_{\text{HH}}=8.0$ Hz, $\text{CH}_3\text{CH}_2\text{AlCl}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_2Cl_2) δ 167.0 ($\text{N}=\text{CCH}_3$), 147.3 (Ph- C_{ipso}), 139.0

(Ph-C_{ortho}), 130.3 (Ph-C_{meta}), 127.8 (Ph-C_{para}), 96.2 (C₅H₅), 21.2 (Ph *p*-CH₃), 19.3 (CH₃CH₂AlCl₃), 19.1 (N=CCH₃), 18.2 (Ph *o*-CH₃), 9.2 (CH₃CH₂AlCl₃). ¹³C{¹H} NMR (75 MHz, C₆D₅Br) δ 166.6 (N=CCH₃), 145.3 (Ph-C_{ipso}), 136.6 (Ph-C_{ortho}), 129.3 (Ph-C_{meta}), 126.4 (Ph-C_{para}), 93.8 (C₅H₅), 19.9 (Ph *o*-CH₃), 17.9 (*br*, N=CCH₃, Ph *p*-CH₃ and CH₃CH₂AlCl₃), 8.7 (CH₃CH₂AlCl₃). ²⁷Al{¹H} NMR (78 MHz, CD₂Cl₂): δ 129.8 (*br*, Δν_{1/2}= 655 Hz, [AlEtCl₃]). ²⁷Al{¹H} NMR (78 MHz, C₆D₅Br): δ 128.6 (*br*, Δν_{1/2}= 2773 Hz, [AlEtCl₃]). Anal. Calcd. for C₂₉H₃₈AlCl₃N₂Ni·C₆H₄Cl₂: C, 55.78; H, 5.62; N, 3.72. Found: C, 55.35; H, 5.76; N, 3.75.

Synthesis of [Ni(η⁵-C₅H₅)(Mes-BIAN)][AlEtCl₃] (4) and isolation of [Ni₃(Mes-BIAN)₃Cl₅][AlCl₄] (5).

A solution of AlEt₂Cl (DEAC) (0.4 mL, 3.16 mmol) in *o*-dichlorobenzene (ODCB) (15 mL) was added dropwise to a suspension of [Ni(η⁵-C₅H₅)(Mes-BIAN)][PF₆] **1** (0.50 g, 0.79 mmol) in the same solvent (40 mL), previously cooled to -15 °C. The mixture was stirred in the cold bath and allowed to warm to room temperature (*ca.* 1.5 h). The cold bath was removed, and then stirred for another 2 h. The solvent was removed by trap-to-trap distillation, and the resulting residue was washed with *n*-hexane. The reaction products were initially extracted with diethyl ether, followed by toluene and finally ODCB. ¹H NMR showed that Et₂O and toluene solutions extracted the same diamagnetic product, whereas that extracted by ODCB had a paramagnetic nature. The solutions were concentrated under vacuum (*ca.* 50%) and double layered with *n*-hexane (1:3). Storage at -20 °C (Et₂O and toluene) or +4 °C (ODCB) yielded, respectively, a dark green microcrystalline solid of **4** (0.25 g, 66%) and black crystals of **5** (0.08 g, 16%), the latter suitable for X-ray diffraction.

Data for **4**: ¹H NMR (300 MHz, CD₂Cl₂): δ 8.14 (d, 2H, ³J_{HH}= 8.2 Hz, H5'), 7.53 (t, 2H, ³J_{HH}= 7.8 Hz, H4'), 7.13 (s, 4H, Ph-H_{meta}), 6.71 (d, 2H, ³J_{HH}= 7.1 Hz, H3'), 5.21 (s, 5H, C₅H₅), 2.43 (s, 6H, Ph *p*-CH₃), 2.35 (s, 12H, Ph *o*-CH₃), 0.98 (t, 3H, *J*=7.8 Hz, CH₃CH₂AlCl₃), -0.04 (q, 2H, *J*=7.8 Hz, CH₃CH₂AlCl₃). ¹H NMR (300 MHz, C₆D₅Br): δ 8.12 (*br*, H5'), 7.52 (t, 2H, ³J_{HH}= 7.4 Hz, H4'), 7.37 (s, 4H, Ph-H_{meta}), 7.08 (*br*, H3'), 5.27 (*br*, 5H, C₅H₅), 2.72 (*br*, 18H, Ph *p*-CH₃ and Ph *o*-CH₃), 1.57 (t, 3H, *J*=7.2 Hz, CH₃CH₂AlCl₃), 1.07 (q, 2H, *J*=7.2 Hz, CH₃CH₂AlCl₃). ¹³C{¹H} NMR (75 MHz, C₆D₅Br) δ 163.9 (N=CCH₃), Ph-C_{ipso} (absent), 138.7 (Ph-C_{ortho}), 135.2 (C7'), 134.9 (C6'), 127.5 (Ph-C_{meta}), 122.5 (Ph-C_{para}), 121.7 (*br*, C3', C4' and C5') 93.2 (C₅H₅), 21.1 (CH₃CH₂AlCl₃), 20.9 (Ph *o*-CH₃), 17.4 (Ph *p*-CH₃), 9.8 (CH₃CH₂AlCl₃). ²⁷Al{¹H} NMR (78 MHz, CD₂Cl₂): δ 130.9 (*br*, Δν_{1/2}= 742 Hz, [AlEtCl₃]).

Data for **5**: ^1H NMR (400 MHz, $\text{C}_6\text{D}_5\text{Br}$): δ 33.86 (s, 1H), 27.01 (*br*, 2H), 25.45 (s, 1H), 24.01 (s, 5H), 19.74 (*br*, 8H), 18.77 (*br*, 5H), 15.49 (s, 2H), 5.44 (s, 2H), 2.03 (s, 1H), 1.17 (s, 1H).

General procedure for the polymerisation tests with ethylene. Polymerisations were carried out in 250 mL crown capped pressure bottles sealed with neoprene septa and pump filled with nitrogen atmosphere (the bottles were previously dried in the oven at 140 °C for several days), and with magnetic stirring (600 rpm). To each polymerisation bottle, 50 mL of freshly distilled solvent were added, which were subsequently thermostated in ice (0 °C), water or oil baths. After removal of the N_2 atmosphere by vacuum, the solvent was saturated with ethylene at a relative pressure of 1 bar, which was maintained throughout the polymerisation reactions. Then, the appropriate amount of DEAC cocatalyst was added via a glass syringe at the defined Al/Ni ratio. Solutions were then brought to the desired temperature and allowed to equilibrate for 15 min. The polymerisation reactions were initiated by the addition of a solution of the desired amount of catalyst in 1 mL of ODCB via a glass syringe. The polymerisations were terminated after 0.5 or 1 h by quenching the mixture with 150 mL of an acidic methanol (1% HCl) solution. The polymers obtained were then filtered, washed several times with methanol and dried in a vacuum oven at 60 °C for 3 days.

AUTHOR INFORMATION

Corresponding author

*E-mail for P.T.G.: pedro.t.gomes@tecnico.ulisboa.pt

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