Studies of the Nature of the Catalytic Species in the α-Olefin Polymerisation Processes Generated by the Reaction of Diamido(cyclopentadienyl)titanium Complexes with Aluminium Reagents as Cocatalysts

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The reaction of the diamido(chloro)cyclopentadienyltitanium compounds $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Cl$ [Cp^{Rx} = $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5(CH_3)_5$, $\eta^5\text{-}C_5H_4(SiMe_3)$; R′ = CH_2tBu, Pr] with the Grignard reagent MgClR (R = Me, CH_2Ph) affords the monomethyl and monobenzyl derivatives $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]R$. Upon addition of methylaluminoxane (MAO), the chloro- and alkyltitanium complexes show low activity towards the polymerisation of ethylene and styrene. However, no methylation was observed during the treatment of trimethylaluminium with the chloro compounds $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Cl$. Instead, these reactions give the dinuclear aluminium complexes $Al_2[1,2\text{-}C_6H_4(NR')_2]Me_4$ (R′ = CH_2tBu, Pr) through transmetallation of the diamido ligand, suggesting a deactivation process of the catalysts in the olefin polymerisation reactions. In an additional effort to model the catalytic species, stoichiometric reactions between the methyl derivatives $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Me$ and solid methylaluminoxane (MAO) were studied by NMR spectroscopy. Monitoring of these reactions revealed the formation of zwitterionic species depending on the nature of the solvent.
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Introduction

In recent years, one of the achievements in transition metal organometallic chemistry has been the development of Ziegler–Natta catalysis for the polymerisation of ethylene and α-olefins and the research in this field has resulted in a good understanding of the mechanism of the olefin polymerisation process.[1–6] According to this, the minimum requirement for a catalyst precursor has been established as the existence of an unreactive ancillary ligand system (generally the cyclopentadienyl ligand) with 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 with these features used as catalysts for olefin polymerisation have been extensive.[4,7–12] However, examples of precatalysts containing only one such group which can be active for olefin polymerisation are scarce.[13–15]

Over the past few years a growing interest in developing organometallic compound alternatives to classical group 4 cyclopentadienyl complexes has emerged. Some of the more significant recent developments have occurred with early and late transition metal systems. High-performance compounds bearing a chelate ligand such as diimino(pyridino)[16,17] (Fe and Co), imino(phenoxo)[13,18] (Ni), diamido[19,20] (Ti) and iminobis(phenoxo)[21–23] ligands(Zr) are examples which have provided excellent activity for α-olefin polymerisation and in some cases for promoting copolymerisation of an α-olefin with polar monomers[24] as well as living polymerisation.[25–27]

As part of our investigations directed at obtaining a new class of organometallic compounds combining cyclopentadienyl and diamido ligands, we recently published the synthesis of diamido(chloro)cyclopentadienyltitanium compounds $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Cl$ [Cp^{Rx} = $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5(CH_3)_5$, $\eta^5\text{-}C_5H_4(SiMe_3)$; R′ = CH_2tBu, Pr] and as assessment of their behaviour as precatalysts for α-olefin polymerisation. As a continuation of this field, we report herein the synthesis of alkyl derivatives $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]R$ and their activation with solid MAO to give active species in ethylene and styrene polymerisation reactions. To identify the nature of the catalytic species in the olefin polymerisation processes arising from the interaction of this class of precursor of organometallic complexes (with only one alkyl group bonded to the metal centre) with aluminium compounds as cocatalysts, the reactions of the chloro compounds $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Cl$ with trimethylaluminium (TMA) and the methyl compounds $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Me$ with solid methylaluminoxane (MAO) were tested. The objective of the present work was to gain a direct insight into the role of these species in polymerisation activity.

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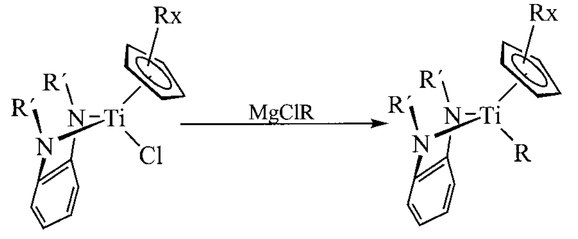
Results and Discussion

Synthesis of Dialkyl Derivatives

The reaction of 1 equiv. of MgClR (R = Me, 3 M solution in THF; R = CH_2Ph, 2 M solution in THF) with a solution of $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Cl$ [Cp^{Rx} = $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5(CH_3)_5$, $\eta^5\text{-}C_5H_4(SiMe_3)$; R′ = CH_2tBu, Pr] in hexane at −78 °C proceeds with substitution of the chloro ligand by the alkyl group affording the methyl and benzyl derivatives $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]R$ (**1**−**12**) (Scheme 1, Table 1). The methyl (**1** and **2**) and the benzyl (**7** and **8**) compounds were isolated, after purification, as red and dark solids respectively, while the complexes **3**−**6** and **9**−**12** exist as red or dark oils which are difficult to handle and recrystallise due to their very high solubility in all common solvents. For compound **8**, the alkylation of the Ti−Cl bond in hexane is not totally effective due to steric hindrance at the titanium centre and a mixture of the chloro and the benzyl compounds is obtained. However, the reaction between $Ti(\eta^5\text{-}C_5Me_5)[1,2\text{-}C_6H_4(NCH_2tBu)_2]Cl$ and MgClBz in a polar solvent proceeds with the formation of the pure benzyl complex **8**.



Scheme 1

Table 1. Amido- and titanium-alkyl groups in compounds **1**−**12**

Cp^{Rx}	R′	R	
$\eta^5\text{-}C_5H_5$	CH_2tBu	Me	(**1**)
		CH_2Bz	(**7**)
	Pr	Me	(**4**)
		CH_2Bz	(**10**)
$\eta^5\text{-}C_5Me_5$	CH_2tBu	Me	(**2**)
		CH_2Bz	(**8**)
	Pr	Me	(**5**)
		CH_2Bz	(**11**)
$\eta^5\text{-}C_5H_4(SiMe_3)$	CH_2tBu	Me	(**3**)
		CH_2Bz	(**9**)
	Pr	Me	(**6**)
		CH_2Bz	(**12**)

Complexes **1**−**12** are soluble in aromatic hydrocarbons, dichloromethane, chloroform, diethyl ether and alkanes (hexane and pentane). They are air- and moisture-sensitive in solution as well as in the solid state, although they can be stored unchanged for weeks under an inert gas. The complexes were characterised by the usual analytical and spectroscopic methods. In some cases, the ^1H NMR spectra of the $TiCp^{Rx}[1,2\text{-}C_6H_4(NPr)_2]R$ compounds in deuterated chlorinated solvents could not be obtained since the corresponding chloro compounds are formed in these solvents. In contrast, the $TiCp^{Rx}[1,2\text{-}C_6H_4(NCH_2tBu)_2]R$ derivatives can be dissolved in chlorinated solutions for long periods without transformation into the corresponding chloro compounds since the neopentyl substituent affords greater steric protection for the metal centre than the propyl substituent.

The NMR spectra of these compounds show patterns for the proton and carbon resonances similar to those described for the analogous chloro compounds.[28] The ^1H resonances (C_6D_6, room temperature) of the cyclopentadienyl protons appear at δ = 6.01−6.15 for the Cp and δ = 1.45−1.71 for the C_5Me_5 ligands. The $C_5H_4(SiMe_3)$ ring protons give AA′BB′ spin systems at δ = 6.13−6.53. The methyl protons of the $SiMe_3$ group exhibit one singlet located at δ = 0.17−0.31. The spectra for the propyl compounds show sets of multiplets and triplet resonances for the $N\text{-}CH_2{-}CH_2{-}CH_3$ fragment protons, while the expected signals for the neopentyl ligand protons can be observed in the spectra of the corresponding derivatives. The phenyl protons of the diamido ligands appear as two multiplets in the usual range. Furthermore, the ^1H NMR spectra show the expected signals assignable to the methyl and the benzyl ligands attached to titanium. Similar structural features to those described from ^1H NMR spectroscopy can be deduced from the $^{13}C\{^1H\}$ NMR spectra (C_6D_6, room temperature). These spectroscopic data are in agreement with C_s symmetry and are consistent with the presence of a mirror plane containing the Ti and C_α atoms of the alkyl groups bisecting the N−Ti−N angle of the chelate diamido ligand.

In this type of complex, the diamido ligand can adopt different coordination modes and has two possible conformation modes (*supine* or *prone*) relative to the cyclopentadienyl ring. A Nuclear Overhauser Enhancement (NOE) study of the benzyl complex **7** containing the Cp ligand enabled us to distinguish between these two possible dispositions. Irradiation of the Cp resonance resulted in a significant NOE enhancement in the methylene signals of the neopentyl group, while no NOE enhancements in the phenyl signals were observed. These observations suggest that the neopentyl group is located close to the Cp ring with the diamido ligand adopting a *supine* conformation, in accordance with the chemical shifts observed for the cyclopentadienyl ring protons in the ^1H NMR spectrum which are not influenced by phenylene magnetic anisotropy.[29] Similar results were obtained for the corresponding chloro derivatives which is consistent with the disposition found in the solid state using X-ray crystallography.[28]

Polymerisation Reactions

Given our interest in the polymerisation chemistry of group 4 diamido(cyclopentadienyl)-[15,30,31] or dialkoxometal complexes,[32] we undertook a study of α-olefin polymerisation processes of the alkyldiamido(cyclopentadienyl) compounds $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]R$ with methylaluminoxane (MAO) as a cocatalyst. The reaction conditions and the results are summarised in Table 2 and 3. The results show the averages of two or more polymerisation runs which showed good reproducibility between them.

Table 2. Polymerisation studies of ethylene with TiCp^{Rx}[1,2-$C_6H_4(NR')_2$]R in the presence of MAO as cocatalyst

Entry	Catalyst[a]	Activity[b]	ΔH_m (J g^{-1})[c]	T_m °C)[c]
1	1	8.0	59	130
2	2	4.3	45	126
3	3	1.6	52	122
4	4	47	55	130
5	7	3.0	24	133
6	8	7.5	45	129
7	10	51	28	135

[a] Reaction conditions: temperature = 25 °C, 10 mg of precatalyst, molar ratio Al/Ti = 400, 50 mL of toluene, 5 atm of ethylene pressure, 15 min. [b] g PE/mmol Ti h atm. [c] Determined by DSC.

Table 2. Polymerisation studies of styrene with TiCp^{Rx}[1,2-$C_6H_4(NR')_2$]R in the presence of MAO as a cocatalyst

Entry	Catalyst[a]	Activity[b]	T_m(°C)
1	**1**	25	252
2	**2**	35	250
3	**3**	15	260
4	**4**	18	248
5	**7**	15	256
6	**8**	10	246
7	**10**	13	257

[a] Reaction conditions: temperature = 50 °C, 10 mg of precatalyst, molar ratio Al/Ti = 400, 50 mL of toluene, 5 mL styrene, 15 min. [b] g PS/mmol Ti h. [c] Determined by DSC.

When activated with MAO, low activities for ethylene homopolymerisation were obtained with the neopentyl compounds **1**−**3** and **7**−**8** (Entries 1−3 and 5−6), while moderate activities with the propyl complexes **4** and **10** (Entries 4 and 7) were observed (Table 2). These activity values show a pronounced dependence on the steric requirements of the diamido ligand with the higher activity observed for the smaller substituent on the nitrogen atom of the amido ligand. Similar control of steric crowding at the metal centre has been observed in bulky amidinato complexes.[33,34] The activities exhibited for these complexes are of the same order of magnitude as those described for similar diamido(cyclopentadienyl)titanium compounds,[35−37] although they are smaller than those reported for noncyclopentadienyl diamido complexes.[17,38,39] Polymer samples show melting point values (T_m measured by DSC) typical of high-density polyethylene.

The TiCp^{Rx}[1,2-$C_6H_4(NR')_2$]R precatalysts were tested for styrene polymerisation upon activation with MAO but poor catalytic activities were found (Table 3). The observed activity values are markedly lower than those obtained with the well-known $CpTiCl_3$ used as a reference point.[40] The PS samples obtained are in the range typical for syndiotactic polymers (NMR spectroscopy), as expected for cyclopentadienyltitanium precatalysts,[41−46] with low molecular weights (as deduced from their T_m analyses).

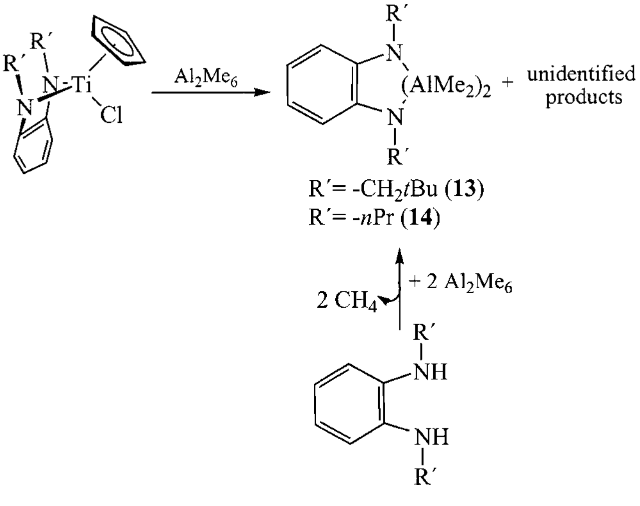
$B(C_6F_5)_3$ was also used as a cocatalyst in our polymerisation experiments but, unfortunately, no catalytic activity was observed even after using TIBA as scavenger in the reaction mixture. In the catalyst systems obtained by combining **1** or **2** with $B(C_6F_5)_3$, the colour of the solutions were different from those obtained in the reaction with solid MAO as a cocatalyst, suggesting that different species are formed. While **1** and solid MAO mixtures result in a green solution, a red colour was observed using $B(C_6F_5)_3$ as a cocatalyst. These results can be attributed to the ability of aluminium derivatives to abstract the diamido ligand providing the alkyl group requirement for polymerisation in a Ziegler−Natta manner, whereas this possibility is unavailable in the perfluoroborane compound.

The low activity trend observed for the TiCp^{Rx}[1,2-$C_6H_4(NR')_2$]R precatalysts in the α-olefin polymerisation reactions might be due to a catalyst decomposition process through ligand abstraction by MAO which may cause partial or complete loss of the ligand thus resulting in one or more inactive species for α-olefin polymerisation.[47] In an effort to model the nature of the catalytic species generated in these catalyst systems, the reactions of the cyclopentadienyldiamido, monochloro and monoalkyltitanium derivatives with trimethylaluminium (TMA) and solid methylaluminoxane MAO were examined.

Reactions of TiCp^{Rx}[1,2-$C_6H_4(NR')_2$]Cl with TMA

Attempts to obtain methyltitanium derivatives under the conditions described above from the Ti(η^5-C_5H_5)[1,2-$C_6H_4(NR)_2$]Cl starting compound using alkylating aluminium reagents such as TMA were unsuccessful. The methylated products was not observed but evolution of the starting material by ligand transfer from titanium to aluminium occurred.

Treatment of a red-brown solution of the monochloro compound Ti(η^5-C_5H_5)[1,2-$C_6H_4(NCH_2tBu)_2$]Cl in hexane at −78 °C with one equivalent of TMA resulted in the im-

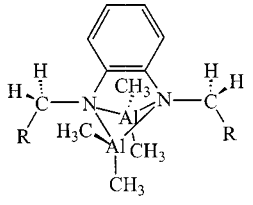


Scheme 2

mediate formation of a yellow solution but the expected monomethyl titanium complex **1** was not observed (monitoring by NMR spectroscopy). Concentration of the solution enabled isolation of the amidoalane compound $Al_2[1,2\text{-}C_6H_4(NCH_2t\text{Bu})_2]Me_4$ (**13**) and a mixture of unidentified and intractable titanium species. Similarly, when the reaction was carried out in a Ti:Al molar ratio of 1:100, formation of the amidoalane was observed along with a more complicated final mixture of products. In an analogous reaction, treatment of $Ti(\eta^5\text{-}C_5H_5)[1,2\text{-}C_6H_4(NPr)_2]Cl$ with TMA (in a Ti:Al molar ratio 1:1 and 1:100) afforded the amidoalane compound $Al_2[1,2\text{-}C_6H_4(NnPr)_2]Me_4$ (**14**) (Scheme 2).

These aluminium compounds can be synthesised as pure substances through a direct route by treating $1,2\text{-}C_6H_4(NHR')_2$ ($R' = CH_2t\text{Bu}$, Pr) with 2 equiv. of TMA in toluene with partial precipitation of the aluminium compounds occurring in 1 h (Scheme 2). Reactions between amines and aluminium compounds are well known[48−50] and in the first step, an adduct of the type N−Al is probably formed which then eliminates methane generating the amidoaluminium compound.

Compound **13** was characterised by elemental analysis, while the elemental analysis values found for **14** were inaccurate due to the presence of small amounts of impurities which could not be removed although both aluminium compounds were also characterised by spectroscopic methods. The ^{1}H NMR spectra (C_6D_6, room temperature) show two different types of methyl groups with each signal corresponding to six protons (see Exp. Sect.). The proposed structural dispositions (Figure 1) are similar to those described for analogous compounds[18,51,52] in which two "$AlMe_2$" moieties are symmetrically chelated by a diamido ligand. They exhibit two aluminium centres with tetrahedral geometry and two nitrogen atoms forming a four membered butterfly shaped metallacycle. Methyl groups are positioned in two different chemical environments with two being located towards the phenyl group and the other being orientated in the opposite direction.



R′= -*t*Bu (**13**)
R′= -Et (**14**)

Figure 1. Proposed structural disposition for compounds **13** and **14**

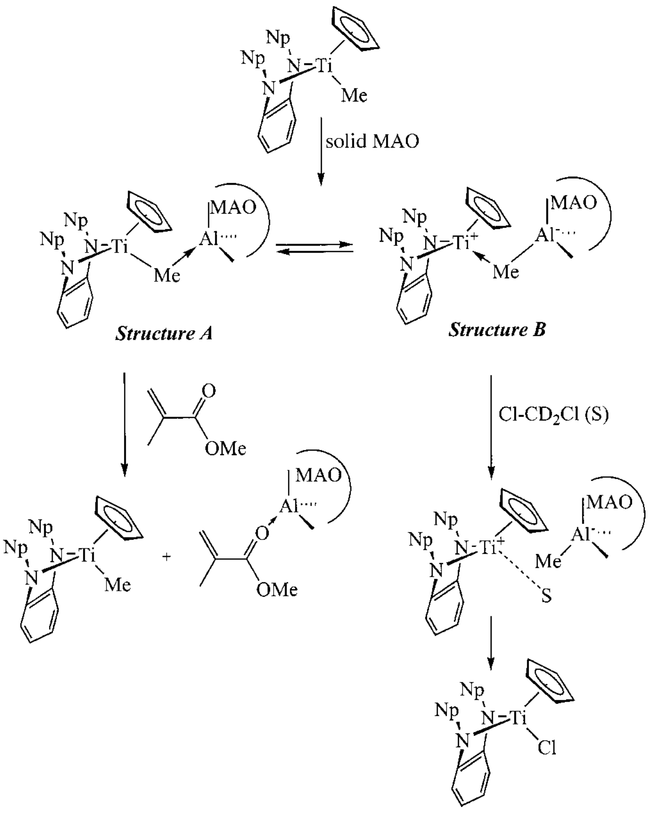
Such reactions starting from monocyclopentadienyl diamido titanium compounds forming aluminium derivatives therefore indicate that transmetallation reactions offer a facile reaction pathway in early transition metal complexes. Similar transmetallation reactions have been proposed for group 4[53] and more recently for group 6[54] complexes bearing diamido ligands. We believe that the resistance of the monocyclopentadienyl diamido chloro titanium complexes to form the alkylated product in the reaction with aluminium reagents and the ligand transfer processes are associated with the low activity of the chloro complexes $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Cl$ for ethylene and styrene polymerisations. These results provide an insight into the nature of the catalytic species generated during the olefin polymerisation processes through interaction of the precatalyst based on titanium complexes with the aluminium reagents as cocatalysts.

Reaction between $Ti(\eta^5\text{-}C_5H_5)[1,2\text{-}C_6H_4(NCH_2t\text{Bu})_2]Me$ (1) and Solid MAO

In order to obtain a better understanding of the nature of the active species and the chemical behaviour of the $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]R$ precatalyst systems in the ethylene and styrene polymerisation processes, the reaction of **1** with solid MAO was carried out using a stoichiometric 1:1 Ti/Al ratio and studied by ^{1}H NMR spectroscopy. Solid MAO was selected to avoid the inexorable presence of free TMA in commercial MAO[55] since this compound causes transmetallation which could be a crucial factor in the evolution of the reaction.

The ^{1}H NMR spectrum recorded immediately after mixing the reagents in CD_2Cl_2 at room temperature shows a broadening of Ti-Me resonance accompanied by a downfield shift with respect to the initial situation.[56] In the ^{1}H NMR spectrum of **1**, the methyl group protons appear at $\delta = -1.5$. After the reaction with MAO, this resonance overlaps with the corresponding MAO signals. These features are in accordance with the interaction of the methyl group of compound **1** with the aluminium atoms present in the MAO which act as Lewis acidic sites[57−61] (Structure A in Scheme 3) or, alternatively, with abstraction of this methyl group to generate an anionic aluminium centre which interacts with the cationic titanium atom through methyl group bridging (Structure B in Scheme 3). The broadness could be due to the closer position of the methyl group, initially bound to titanium, to the "diversification" centres provided by different Lewis acidic sites present in MAO.[62,63] The broadening of Ti-Me resonances of an adduct with MAO has also been reported by Talsi et al.[59,64] When the polarity of the solvent is high, as in this case, methyl group abstraction by MAO is favoured and solvent-separated ion pairs are preferentially formed.[65−67] After allowing the sample to stand for one day in solution, the ^{1}H NMR spectrum shows clear formation of the chlorinated compound $Ti(\eta^5\text{-}C_5H_5)[1,2\text{-}C_6H_4(NCH_2t\text{Bu})_2]Cl$ which indicates chloro abstraction from the solvent.

When the same reaction is carried out in a less polar solvent such as C_6D_6, the process proceeds in a different way. Initially, after mixing the reagents at room temperature for 5 min, the ^{1}H NMR spectrum features are consistent with the formation of the zwitterionic species in which the methyl ligand acts as a bridging group between the titanium and aluminium centres (Structure A in Scheme 3 favoured).



Scheme 3

It is believed that the formation of separated ions, in this case, is not favoured because there is no stabilisation conferred by solvent coordination. After 1 d in solution, no significant changes in the ^{1}H NMR spectrum were observed.

When the solution in C_6D_6 was saturated[68–70] with ethylene, polyethylene was not formed. However, the addition of a polar monomer such as methyl methacrylate (MMA) to the C_6D_6 solution caused the displacement of the MAO initially attached to the titanium centre. The ^{1}H NMR spectrum shows signals indicating the presence of the methylated compound **1** (Scheme 3) and a complicated set of resonances assignable to products exhibiting interactions between MMA and MAO.

Treatment of compound **1** with an excess of solid MAO was rather difficult to study by NMR spectroscopy because the signals of the products overlap with the MAO resonances. We suggest the excess aluminium centres provided by such a large amount of solid MAO, used generally for polymerisation runs, could cause the deactivation of the $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]R$ catalysts by transmetallation reactions of the diamido groups in a similar way to observations made in the reaction of $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Cl$ with TMA.

Conclusion

The synthesis and characterisation of new monocyclopentadienyl diamido alkyl titanium $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]R$ compounds from the reaction of the corresponding chloro derivatives with Grignard reagents has been described. After activation with methylaluminoxane, the diamido complexes exhibit low activity towards α-olefin polymerisation. While the chloro derivatives $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Cl$ can be easily methylated by reaction with MgClMe, reaction with trimethylaluminium results in the transmetallation of the diamido ligand to produce dinuclear aluminium compounds. This behaviour must be associated with the low activity of the chloro and alkyl derivatives in the ethylene and styrene polymerisations. The reactivity of the alkyl complexes $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]R$ with MAO has also been studied by NMR spectroscopy. This indicated the formation of intermediate species which can be considered to exert an important effect on the catalytic activity of these precatalysts in the α-olefin polymerisation process.

Experimental Section

General Considerations: All manipulations of air- and moisture-sensitive materials were performed under argon using Schlenk and high-vacuum line techniques or in a glove box model MO40-2. Solvents were predried with activated molecular sieves (4 Å) and were then purified by distillation under argon before use by employing the appropriate drying/deoxygenating agent. Deuterated solvents were degassed by several freeze-thaw cycles and stored in ampoules equipped with Young's Teflon valves over activated molecular sieves (4 Å). C, H and N microanalyses were performed with a Perkin–Elmer 2400 microanalyser. NMR spectra, measured at 25 °C, were recorded with a Varian Unity FT-300 (^{1}H NMR at 300 MHz, ^{13}C NMR at 75 MHz) spectrometer and chemical shifts were referenced to $SiMe_4$ via the ^{13}C resonances and the residual protons (^{1}H) of the deuterated solvent. MAO was purchased from Witco as a toluene solution (10% wt). Reagent grade styrene (Aldrich) was distilled under reduced pressure from calcium hydride and stored in a refrigerator under argon. The polymerisation solvent was dried by heating to reflux in the presence of sodium/benzophenone under argon. MgClMe (3 M solution in THF) and MgClBz (2 M solution in THF) were purchased from Aldrich and used as received. The chlorinated compounds $TiCp^{Rx}[1,2\text{-}C_6H_4(NR')_2]Cl$ [$Cp^{Rx} = \eta^5\text{-}C_5H_5, \eta^5\text{-}C_5(CH_3)_5, \eta^5\text{-}C_5H_4(SiMe_3)$; $R' = CH_2tBu$, Pr] and the *N*,*N'*-dialkyl-1,2-phenylenediamines $1,2\text{-}C_6H_4(NHR')_2$ ($R' = CH_2tBu$, Pr) were prepared as described in previous work.[28]

Preparation of MAO Samples: To obtain MAO with a reduced amount of TMA, a sample of commercial MAO was distilled under vacuum at 20 °C. The white powder obtained (polymeric MAO with residual TMA ca. 3 wt-%) was stored in dry box before use in the preparation of the samples. Calculated quantities of the desired compound and solid MAO were taken into the dry box to prepare the samples with the desired Ti/Al ratio. Solids were mixed and the selected solvent was added directly to the NMR tube equipped with a Young's Teflon valve. All operations were carried out at room temperature.

Polymerisation Procedure: For ethylene polymerisation, the typical procedure was as follows. Toluene (50 mL), solid MAO (Al/Ti = 400) and the desired precatalyst (10 mg) in a sealed glass vial were placed in a high-pressure glass reaction vessel (Büchi). Subsequently, the polymerisation temperature was adjusted and the mixture was pressurized to 5 atm for 1 h before cracking the vial. After 15 min of venting of the ethylene gas and quenching with HCl/CH_3OH (10 mL), the reaction was stopped. The solution was then poured into a large excess of this solvent mixture and the resultant polyethylene was separated by filtration, washed several times (HCl/CH_3OH) and dried under vacuum overnight. Polymerisation of styrene was performed under argon in toluene at 50 °C using solid MAO as the cocatalyst according to the following procedure. Toluene (30 mL), styrene (5 mL) and MAO were injected into the Schlenk flasks with magnetic stirring at the desired temperature. The titanium compound was dissolved in toluene (5 mL) and added to the mixture. In a manner similar to the polyethylenes, the polystyrenes were coagulated with a large excess of acidified methanol and isolated by filtration.

Characterisation of Polymers: The thermal properties of the samples were studied using a Perkin−Elmer DSC 6 instrument calibrated by measuring the melting point of indium. Thus, 5−10 mg each of the dried polymers were fused into standard aluminium pans and measured using the following temperature programme for polyethylene samples: first a heating phase (10 °C/min) from 50 to 200 °C, followed by a cooling phase (−10 °C/min) to 50 °C. The peak maximum of the second heating curve was indicated as the melting point (T_m). ΔH_m derived from the data of the second heating course of the DSC was selected. Polystyrene samples were subjected to the following steps: heating at 10 °C/min from 30 to 270 °C and then cooling at 10 °C/min from this temperature to 30 °C and finally heating at 10 °C/min from 30 to 270 °C to obtain the melting peak temperature (T_m). The NMR-PS samples were prepared by dissolving the polymer in tetrachloro-1,2-dideuterioethane. The spectra were recorded at 25 °C.

$Ti(\eta^5\text{-}C_5H_5)[1,2\text{-}C_6H_4(NCH_2\textit{t}Bu)_2](CH_3)$ (1): A 3 M solution of MeMgCl in THF (0.42 mL, 0.93 mmol) was added to a solution of $Ti(\eta^5\text{-}C_5H_5)[1,2\text{-}C_6H_4(NCH_2\textit{t}Bu)_2]Cl$ (0.50 g, 1.27 mmol) in hexane (50 mL) at −78 °C. The cooling bath was removed and the reaction mixture was warmed to room temperature after stirring for 12 h. The resultant residue was filtered and the solution cooled to −40 °C to afford **1** as a red solid (0.35 g, 74%). $C_{22}H_{34}N_2Ti$ (374.40): calcd. C 70.58, H 9.15, N 7.48; found C 70.50, H 9.29, N 7.51. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.33 (s, 4 H, Ph), 6.15 (s, 5 H, C_5H_5), 3.89 (d, J = 12.6 Hz, 2 H, CH_2), 3.83 (d, J = 12.6 Hz, 2 H, CH_2), 0.71 (s, 18 H, *t*Bu), −0.90 (s, 3 H, CH_3) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.36 (m, 4 H, Ph), 6.28 (s, 5 H, C_5H_5), 4.01(s, 4 H, CH_2), 0.73 (s, 18 H, *t*Bu), −1.46 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 126.1, 118.9 (Ph), 124.8 (*ipso*-Ph), 113.1 (C_5H_5), 65.6 (CH_2), 33.3 (Ti-CH_3), 35.7 (*ipso*-*t*Bu), 28.6 (*t*Bu) ppm.

$Ti(\eta^5\text{-}C_5Me_5)[1,2\text{-}C_6H_4(NCH_2\textit{t}Bu)_2](CH_3)$ (2): Compound **2** was prepared by treating $Ti(\eta^5\text{-}C_5Me_5)[1,2\text{-}C_6H_4(NCH_2\textit{t}Bu)_2]Cl$ (1.86 g, 4.00 mmol) in hexane with a 3 M solution of MeMgCl in THF (1.33 mL) according to the procedure described for **1** and was obtained as a dark solid (1.40 g, 3.15 mmol, 78%). $C_{27}H_{44}N_2Ti$ (444.54): calcd. C 72.95, H 9.98, N 6.30; found C 72.98, H 9.87, N 6.15. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.22 (m, 4 H, Ph), 3.86 (d, J = 13.2 Hz, 2 H, CH_2), 3.67 (d, J = 13.2 Hz, 2 H, CH_2), 1.56 (s, 15 H, C_5Me_5), 0.96 (s, 3 H, CH_3), 0.91 (s, 18 H, *t*Bu) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.24 (m, 2 H, Ph), 7.18 (m, 2 H, Ph), 3.87 (d, J = 13.2 Hz, 2 H, CH_2), 3.59 (d, J = 13.2 Hz, 2 H, CH_2), 1.58 (s, 15 H, C_5Me_5), 0.78 (s, 18 H, *t*Bu), 0.57 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 124.6 (*ipso*-Ph), 123.3, 116.6 (Ph), 117.9 (*ipso*-C_5Me$_5$), 61.2 (CH_2), 50.5 (Ti−CH_3), 36.9 (*ipso*-*t*Bu), 29.5 (*t*Bu), 10.5 (C_5Me$_5$) ppm.

$Ti[\eta^5\text{-}C_5H_4(SiMe_3)][1,2\text{-}C_6H_4(NCH_2\textit{t}Bu)_2](CH_3)$ (3): Compound **3** was prepared by treating $Ti[\eta^5\text{-}C_5H_4(SiMe_3)][1,2\text{-}C_6H_4(NCH_2\textit{t}Bu)_2]Cl$ (0.22 g, 0.47 mmol) with a 3 M solution of MeMgCl in THF (0.16 mL) according to the procedure described for **1** and was obtained as a red-brown oil (0.11 g, 2.46 mmol, 52%). The isolated oil consisted mainly of **3** and some LiCl as an impurity which could not be removed. The correct elemental analytical data could not be obtained, although satisfactory spectroscopic data were obtained. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.31 (s, 4 H, Ph), 6.53, 6.28 (AA′BB′ spin system, 2 H, 2 H, C_5H_4), 4.00 (d, J = 12.0 Hz, 2 H, CH_2), 3.95 (d, J = 12.0 Hz, 2 H, CH_2), 0.75 (s, 18 H, *t*Bu), 0.28 (s, 9 H, $SiMe_3$), −0.91 (s, 3 H, CH_3) ppm. ^1H NMR (300 MH, $CDCl_3$, 25 °C): δ = 7.33 (m, 4 H, Ph), 6.46, 6.31 (AA′BB′ spin system, 2 H, 2 H, C_5H_4), 4.00 (s, 4 H, CH_2), 0.73 (s, 18 H, *t*Bu), 0.19 (s, 9 H, $SiMe_3$), −1.49 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 125.5 (*ipso*-Ph), 126.2, 119.1 (Ph), 115.2 (*ipso*-C_5H_4), 120.1, 114.9 (C_5H_4), 66.1 (CH_2), 35.8 (*ipso*-*t*Bu), 33.2 (Ti−CH_3), 28.9 (*t*Bu), 0.29 ($SiMe_3$) ppm.

$Ti(\eta^5\text{-}C_5H_5)[1,2\text{-}C_6H_4(NCH_2CH_2CH_3)_2](CH_3)$ (4): A 3 M solution of MeMgCl in THF (0.53 mL) was added to a stirred solution of $Ti(\eta^5\text{-}C_5H_5)[1,2\text{-}C_6H_4(NCH_2CH_2CH_3)_2]Cl$ (0.54 g, 1.59 mmol) in hexane (50 mL) at −78 °C. The cooling bath was removed and the reaction mixture was slowly warmed to room temperature and stirred for 12 h. The residue was filtered and the solution concentrated and cooled. Compound **4** was obtained as a dark oil (0.37 g, 1.16 mmol, 73%). $C_{18}H_{26}N_2Ti$ (318.30): calcd. C 67.92, H 8.23, N 8.80; found C 68.30; H 8.15; N 9.01. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.33 (m, 2 H, Ph), 7.00 (m, 2 H, Ph), 6.11 (s, 5 H, C_5H_5), 3.67 (m, 4 H, CH_2), 1.35 (m, 4 H, CH_2), 0.65 (t, J = 7.5 Hz, 6 H, CH_3), −0.25 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 125.0, 115.1 (Ph), 129.7 (*ipso*-Ph), 113.1 (C_5H_5), 57.5 (N−CH_2), 35.9 (Ti−CH_3), 24.9 (CH_2), 12.1 (CH_3) ppm.

$Ti(\eta^5\text{-}C_5Me_5)[1,2\text{-}C_6H_4(NCH_2CH_2CH_3)_2](CH_3)$ (5): A 3 M solution of MeMgCl in THF (0.17 mL) was added to a solution of $Ti(\eta^5\text{-}C_5Me_5)[1,2\text{-}C_6H_4(NCH_2CH_2CH_3)_2]Cl$ (0.21 g, 0.51 mmol) in hexane (50 mL) at −78 °C. The cooling bath was removed and the reaction mixture was slowly warmed to room temperature and stirred for 12 h. After filtration, the resultant solution was concentrated and cooled to −20 °C. Complex **5** was obtained as a black oil (0.12 g, 0.31 mmol, 60%). $C_{23}H_{36}N_2Ti$ (388.43): calcd. C 71.12, H 9.34, N 7.21; found C 70.83, H 9.15, N 7.01. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.28 (m, 2 H, Ph), 6.89 (m, 2 H, Ph), 3.64 (m, 2 H, N−CH_2), 3.47 (m, 2 H, N−CH_2), 1.68 (s, 15 H, C_5Me_5), 1.60 (m, 4 H, CH_2), 0.80 (t, J = 7.5 Hz, 6 H, CH_3), 0.82 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 130.0 (*ipso*-Ph), 123.0, 113.4 (Ph), 119.5 (*ipso*-C_5Me$_5$), 53.3 (N−CH_2), 48.1 (Ti−CH_3), 23.4 (CH_2), 12.4 (CH_3), 10.7 (C_5*Me*$_5$) ppm.

$Ti[\eta^5\text{-}C_5H_4(SiMe_3)][1,2\text{-}C_6H_4(NCH_2CH_2CH_3)_2](CH_3)$ (6): Compound **6** was prepared by treating $Ti[\eta^5\text{-}C_5H_4(SiMe_3)][1,2\text{-}C_6H_4(NCH_2CH_2CH_3)_2]Cl$ (0.17 g, 0.41 mmol) with a 3 M solution of MeMgCl in THF (0.14 mL, 0.41 mmol) according to the procedure described for **4** and was obtained as a dark oil (0.11 g, 0.28 mmol, 68%). $C_{21}H_{34}N_2SiTi$ (390.48): calcd. C 64.60, H 8.78, N 7.17; found C 65.06, H 8.92, N 7.12. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.32 (m, 2 H, Ph), 6.99 (m, 2 H, Ph), 6.40, 6.29 (AA′BB′ spin system, 2 H, 2 H, C_5H_4), 3.78 (m, 4 H, CH_2), 1.36 (m, 4 H, CH_2), 0.67 (t, J = 7.5 Hz, 6 H, CH_3), 0.22 (s, 9 H, $SiMe_3$), −0.23 (s, 3 H, CH_3) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.22 (m, 2 H, Ph), 6.94 (m, 2 H, Ph), 6.47, 6.45 (AA′BB′ spin system, 2 H, 2 H, C_5H_4), 3.86 (m, 4 H, CH_2), 1.46 (m, 4 H, CH_2), 0.79 (t, J = 7.5 Hz, 6 H, CH_3), 0.19 (s, 9 H, $SiMe_3$), −0.69 (s, 3

H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 125.8 (*ipso*-C_5H_4), 125.0, 115.2 (Ph), 120.3, 115.5 (C_5H_4), 58.4 (N−CH_2), 35.0 (Ti-CH_3), 23.7 (CH_2), 12.0 (CH_3), 0.60 ($SiMe_3$) ppm, the signal for *ipso*-Ph is not observed.

Ti(η^5-C_5H_5)[1,2-C_6H_4(NCH_2tBu)$_2$](CH_2Ph) (7): A 2 м solution of BzMgCl in THF (0.63 mL, 1.27 mmol) was added dropwise to a stirred solution of Ti(η^5-C_5H_5)[1,2-C_6H_4(NCH_2tBu)$_2$]Cl (0.50 g, 1.27 mmol) in hexane (50 mL) at −78 °C. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 12 h. The white precipitate formed was filtered and the resultant solution cooled to −40 °C. A red-brown solid was collected after filtration which was characterised as **7** (0.30 g, 0.66 mmol, 53%). $C_{28}H_{38}N_2Ti$ (450.50): calcd. C 74.65, H 8.50, N 6.22; found C 74.30, H 8.40, N 6.10. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.35 (s, 4 H, Ph), 7.17, 6.86, 6.57 (t, t, d, 5 H, CH_2*Ph*), 6.01 (s, 5 H, C_5H_5), 3.89 (d, *J* = 13.8 Hz, 2 H, CH_2), 3.81 (d, *J* = 13.5 Hz, 2 H, CH_2), 0.89 (s, 2 H, C*H_2*Ph), 0.68 (s, 18 H, *t*Bu) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.50 (m, 2 H, Ph), 7.40 (m, 2 H, Ph), 6.97, 6.60, 6.32 (t, t, d, 5 H, CH_2*Ph*), 6.07 (s, 5 H, C_5H_5), 4.05 (d, *J* = 13.8 Hz, 2 H, CH_2), 3.97 (d, *J* = 13.5 Hz, 2 H, CH_2), 0.74 (s, 18 H, *t*Bu), 0.44 (s, 2 H, C*H_2*Ph) ppm. $^{13}C\{^1H\}$ NMR (75 MH, C_6D_6, 25 °C): δ = 150.0 (*ipso*-CH_2*Ph*), 126.4, 118.9 (Ph), 128.1, 127.8, 120.8 (CH_2*Ph*), 124.9 (*ipso*-Ph), 114.8 (C_5H_5), 65.8 (CH_2), 61.52 (*C*H_2Ph). 35.8 (*ipso*-*t*Bu), 29.1 (*t*Bu) ppm.

Ti(η^5-C_5Me_5)[1,2-C_6H_4(NCH_2tBu)$_2$](CH_2Ph) (8): Compound **8** was prepared by treating Ti(η^5-C_5Me_5)[1,2-C_6H_4(NCH_2tBu)$_2$]Cl (0.50 g, 1.07 mmol) in toluene (50 mL) at −78 °C with a 2 м solution of BzMgCl in THF (0.54 mL) according to the procedure described for **7**. Recrystallisation of the final product with pentane afforded **8** as a dark-red solid (0.40 g, 0.77 mmol, 72%). $C_{33}H_{48}N_2Ti$ (520.64): calcd. C 76.13, H 9.29, N 5.38; found C 76.43, H 9.37, N 5.61. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.23 (s, 4 H, Ph), 7.22, 7.12, 6.95 (t, t, d, 5 H, CH_2*Ph*), 4.05 (d, *J* = 13.5 Hz, 2 H, CH_2), 3.97 (d, *J* = 13.5 Hz, 2 H, CH_2), 2.67 (s, 2 H, C*H_2*Ph), 1.45 (s, 15 H, C_5Me_5), 0.95 (s, 18 H, *t*Bu) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.33 (m, 2 H, Ph), 7.21 (m, 2 H, Ph), 7.18, 6.95, 6.89 (t, t, d, 5 H, CH_2Ph), 3.92 (d, *J* = 13.5 Hz, 2 H, CH_2), 4.14 (d, *J* = 13.5 Hz, 2 H, CH_2), 2.39 (s, 2 H, C*H_2*Ph), 1.42 (s, 15 H, C_5Me_5), 0.86 (s, 18 H, *t*Bu) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 151.3 (*ipso*-CH_2*Ph*), 127−128 (CH_2*Ph*), 123.7, 117.6 (Ph), 124.7 (*ipso*-Ph), 119.0 (*ipso*-*C*$_5$Me$_5$), 74.5 (*C*H_2Ph), 60.9 (CH_2), 37.4 (*ipso*-*t*Bu), 30.1 (*t*Bu), 10.6 (*C*$_5$Me$_5$) ppm.

Ti[η^5-C_5H_4($SiMe_3$)][1,2-C_6H_4(NCH_2tBu)$_2$](CH_2Ph) (9): Compound **9** was prepared by treating Ti[η^5-C_5H_4($SiMe_3$)][1,2-C_6H_4(NCH_2tBu)$_2$]Cl (0.22 g, 0.47 mmol) with a 2 м solution of BzMgCl in THF (0.23 mL) according to the same procedure described for **8** and was obtained as a red-brown oil (0.15 g, 0.28 mmol, 61%). $C_{31}H_{46}N_2SiTi$ (522.68): calcd. C 71.24, H 8.87, N 5.36; found C 70.80, H 8.72, N 5.20. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.33 (s, 4 H, Ph), 7.17, 6.86, 6.64 (t, t, d, 5 H, CH_2*Ph*), 6.51, 6.18 (AA′BB′ spin system, 2 H, 2 H, C_5H_4), 3.99 (d, *J* = 13.5 Hz, 2 H, CH_2), 3.93 (d, *J* = 13.8 Hz, 2 H, CH_2), 0.85 (s, 2 H, C*H_2*Ph), 0.71 (s, 18 H, *t*Bu), 0.31 (s, 9 H, $SiMe_3$) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.45 (m, 2 H, Ph), 7.38 (m, 2 H, Ph), 6.96, 6.66, 6.32 (t, t, d, 5 H, CH_2*Ph*), 6.34, 6.15 (AA′BB′ spin system, 2 H, 2 H, C_5H_4), 3.96 (s, 4 H, CH_2), 0.73 (s, 18 H, *t*Bu), 0.45 (s, 2 H, C*H_2*Ph), 0.28 (s, 9 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 150.8 (*ipso*-CH_2*Ph*), 126.5, 119.6 (Ph), 126−128 (CH_2*Ph*), 124.9 (*ipso*-Ph), 122.5, 115.9 (C_5H_4), 66.1 (CH_2), 60.2 (*CH_2*Ph), 35.9 (*ipso*-*t*Bu), 29.2 (*t*Bu), 1.6 ($SiMe_3$) ppm, the signal for *ipso*-C_5H_4 is not observed.

Ti(η^5-C_5H_5)[1,2-C_6H_4($NCH_2CH_2CH_3$)$_2$](CH_2Ph) (10): A 2 м solution of BzMgCl in THF (1.27 mL) was added dropwise to a stirred solution of Ti(η^5-C_5H_5)[1,2-C_6H_4($NCH_2CH_2CH_3$)$_2$]Cl (0.85 g, 2.51 mmol) in hexane (50 mL) at −78 °C. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 12 h. The white precipitate formed was filtered and the resultant solution cooled to −40 °C. A dark oil was collected after filtration and was characterised as **10** (0.69 g, 1.75 mmol, 70%). Due to its high solubility in all common solvents **10** could not be recrystallised and an accurate analysis was not possible. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.36 (m, 2 H, Ph), 6.97 (m, 2 H, Ph), 7.12, 6.84, 6.63 (t, t, d, 5 H, CH_2*Ph*), 6.01 (s, 5 H, C_5H_5), 3.57 (m, 4 H, CH_2), 1.63 (s, 2 H, C*H_2*Ph), 1.27 (m, 4 H, CH_2), 0.59 (t, *J* = 7.3 Hz, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 149.2 (*ipso*-CH_2*Ph*), 126.2 (*ipso*-Ph), 125.4, 114.5 (Ph), 125−128 (CH_2*Ph*), 115.5 (C_5H_5), 62.9 (*C*H_2Ph), 57.2 (N−CH_2), 23.9 (CH_2), 11.8 (CH_3).

Ti(η^5-C_5Me_5)[1,2-C_6H_4($NCH_2CH_2CH_3$)$_2$](CH_2Ph) (11): Compound **11** was prepared by treating Ti(η^5-C_5Me_5)[1,2-C_6H_4($NCH_2CH_2CH_3$)$_2$]Cl (0.80 g, 1.96 mmol) with a 2 м solution of BzMgCl in THF (0.98 mL) according to the procedure described for **10** and was obtained as a black oil (0.70 g, 1.51 mmol, 77%). $C_{29}H_{40}N_2Ti$ (464.53): calcd. C 74.98, H 8.68, N 6.03; found C 74.02, H 8.32, N 5.98. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.18 (m, 2 H, Ph), 6.69 (m, 2 H, Ph), 6.80−7.11 (m, 5 H, CH_2*Ph*), 3.50 (t, *J* = 8.4 Hz, 4 H, CH_2), 2.25 (s, 2 H, C*H_2*Ph), 1.71 (s, 15 H, C_5Me_5), 1.49 (broad, 4 H, CH_2), 0.75 (t, *J* = 7.5 Hz, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 150.9 (*ipso*-CH_2*Ph*), 126−128 (CH_2*Ph*), 123.0, 113.3 (Ph), 121.0 (*ipso*-Ph), 120.6 (*ipso*-*C*$_5$Me$_5$), 73.1 (*C*H_2Ph), 53.8 (N-CH_2), 22.5 (CH_2), 12.0 (CH_3), 11.0 (C_5*Me*$_5$) ppm.

Ti[η^5-C_5H_4($SiMe_3$)][1,2-C_6H_4($NCH_2CH_2CH_3$)$_2$](CH_2Ph) (12): Compound **12** was prepared by treating Ti[η^5-C_5H_4($SiMe_3$)][1,2-C_6H_4($NCH_2CH_2CH_3$)$_2$]Cl (0.34 g, 0.83 mmol) with a 2 м solution of BzMgCl in THF (0.41 mL) according to the procedure described for **10** and was obtained as a black oil (0.25 g, 0.53 mmol, 64%). $C_{27}H_{38}N_2SiTi$ (466.58): calcd. C 69.51, H 8.21, N 6.00; found C 68.92, H 8.02, N 5.94. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 7.34 (m, 2 H, Ph), 6.92 (m, 2 H, Ph), 6.99, 6.84, 6.66 (t, t, d, 5 H, CH_2*Ph*), 6.40, 6.13 (AA′BB′ spin system, 2 H, 2 H, C_5H_4), 3.68 (t, *J* = 7.5 Hz, 4 H, CH_2), 1.68 (s, 2 H, C*H_2*Ph), 1.33 (m, 4 H, CH_2), 0.64 (t, *J* = 7.5 Hz, 6 H, CH_3), 0.19 (s, 9 H, $SiMe_3$) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.26 (m, 2 H, Ph), 6.99 (m, 2 H, Ph), 6.94, 6.64, 6.36 (t, t, d, 5 H, CH_2*Ph*), 6.45, 6.22 (AA′BB′ spin system, 2 H, 2 H, C_5H_4), 3.74 (t, *J* = 7.5 Hz, 4 H, CH_2), 1.46 (m, 4 H, CH_2), 1.39 (s, 2 H, C*H_2*Ph), 0.78 (t, *J* = 7.5 Hz, 6 H, CH_3), 0.22 (s, 9 H, $SiMe_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): δ = 149.8 (*ipso*-CH_2*Ph*), 125−128 (CH_2*Ph*), 125.4, 115.6 (Ph), 120.8, 118.1 (C_5H_4), 63.4 (*C*H_2Bz), 57.9 (N−CH_2), 24.0 (CH_2), 12.1 (CH_3), 0.78 ($SiMe_3$) ppm, the signal for *ipso*-C_5H_4 is not observed.

Al_2[1,2-C_6H_4(NCH_2tBu)$_2$]Me_4 (13): A 2 м solution of TMA (1.21 mL, 2.42 mmol) in toluene was added to a solution of 1,2-C_6H_4($NHCH_2tBu$)$_2$ (0.3 g, 1.21 mmol) in toluene (30 mL) at −78 °C. After stirring for 12 h, the solvent was completely removed and the resultant solid extracted successively with hexane/toluene mixtures. The resultant solution was concentrated and cooled to −20 °C to give a purple solid which was identified as **13** (0.32 g, 0.88 mmol, 73%). $C_{20}H_{38}Al_2N_2$ (360.50): calcd. C 66.64, H 10.62, N 7.77; found C 65.98, H 10.26, N 7.39. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ = 6.81 (m, 2 H, Ph), 6.97 (m, 2 H, Ph), 2.93 (s, 4 H, CH_2), 0.89 (s, 18 H, *t*Bu), −0.07 (s, 6 H, Al−CH_3), −0.90 (s, 6

H, Al−CH_3) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.88$ (s, 4 H, Ph), 3.02 (s, 4 H, CH_2), 1.03 (s, 18 H, *t*Bu), −0.45 (s, 6 H, Al-CH_3), −1.33 (s, 6 H, Al−CH_3) $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): $\delta = 142.8$ (*ipso*-Ph), 121.9, 114.0 (Ph), 56.7 (CH_2), 33.7 (*ipso*-*t*Bu), 29.4 (*t*Bu), −5.4, −11.1 (broad, Al−CH_3) ppm.

$Al_2[1,2\text{-}C_6H_4(NCH_2CH_2CH_3)_2]Me_4$ (14): The same procedure described for **13** using the TMA solution in toluene (2.44 mL, 4.89 mmol) and 1,2-$C_6H_4(NCH_2CH_2CH_3)_2$ (0.47 g, 2.44 mmol) gave **14** as a dark purple oil (0.40, 1.31 mmol, 54%). An elemental analysis could not be obtained due to the presence of small amounts of impurities which could not be removed. ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.85$ (m, 2 H, Ph), 6.51 (m, 2 H, Ph), 2.72 (m, 4 H, CH_2), 1.58 (m, 4 H, CH_2), 0.68 (t, $J = 7.2$ Hz, 6 H, CH_3), −0.13 (s, 6 H, Al−CH_3), −1.04 (s, 6 H, Al−CH_3) ppm. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 6.90$ (m, 2 H, Ph), 6.70 (m, 2 H, Ph), 2.99 (m, 4 H, CH_2), 1.71 (m, 4 H, CH_2), 1.01 (t, $J =$ 7.2 Hz, 6 H, CH_3), −0.47 (s, 6 H, Al−CH_3), −1.46 (s, 6 H, Al−CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6, 25 °C): $\delta = 141.6$ (*ipso*-Ph), 112.6, 122.4 (Ph), 46.5 (CH_2), 23.3 (CH_2), 12.0 (CH_3), −6.4, −13.0 (broad, Al−CH_3) ppm.

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