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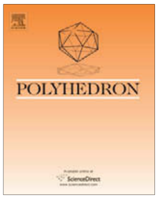

Early transition metal derivatives stabilised by the phenylenediamido $1,2\text{-}C_6H_4(NCH_2tBu)_2$ ligand: Synthesis, characterisation and reactivity studies: Crystal structures of $[Ta\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}_2Cl]$ and $[Zr\{(1,2\text{-}C_6H_4(NCH_2tBu)_2\}(NMe_2)(\mu\text{-}NMe_2)]_2$

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ABSTRACT

$Li_2[1,2\text{-}C_6H_4(NCH_2tBu)_2]$ reacts with one equiv of $[TiCl_4(THF)_2]$ in refluxing toluene to give the chelate compound $[Ti\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}Cl_2(THF)]$ (**1**), isolated as a black product, while the reaction of the dilithio diamido salt with one equiv of $[ZrCl_4(THF)_2]$ in refluxing toluene affords the dinuclear zirconium derivative $[Zr\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}Cl(THF)(\mu\text{-}Cl)]_2$ (**2**), obtained as an orange solid. Treatment of the dilithio diamido salt with $TaCl_5$ in a 2:1 molar ratio in toluene yields $[Ta\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}_2Cl]$ (**3**) as a red product. The reaction of $1,2\text{-}C_6H_4(NHCH_2tBu)_2$ with $[Zr(NMe_2)_4]$ in toluene at room temperature affords the dinuclear zirconium complex $[Zr\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}(NMe_2)(\mu\text{-}NMe_2)]_2$ (**4**). The dibenzyl derivative $[Ti\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}(CH_2Ph)_2]$ (**5**) is obtained by the reaction of **1** with 2 equiv of $Mg(CH_2Ph)Cl$ at −78 °C. Compound **1** reacts with the lithium amide reagent $LiN(SiMe_3)_2$ to afford $[Ti\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}Cl\{N(SiMe_3)\}]$ (**6**). The μ-oxo titanium derivative $[(Ti\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}\{CH_2Ph\})_2(\mu\text{-}O)]$ **7** is precipitated when compound **5** is maintained in solution. The tendency of these compounds to coordinate donor ligands and their reactivity with Lewis acid reagents are described. All compounds were analytically and spectroscopically characterised and the molecular structures of the diamine $1,2\text{-}C_6H_4(NHCH_2tBu)_2$ and the complexes **3** and **4** were established by single-crystal X-ray diffraction studies. The lack of correlation between the degree of metallacycle folding and phenylene ring distortion is observed in the solid state structures. The performance of precursors **1**, **3** and **5** were evaluated in ethylene polymerisation upon activation with $B(C_6F_5)_3$, methylaluminoxane (MAO) and sMAO as cocatalysts, with very modest activities.

1. Introduction

In recent years olefin polymerisation investigations have focused on the development of non-Cp based catalysts giving rise to previously unknown polymerisation behaviours and new polyolefin materials [1].

Bis(phenoxido-imino) group 4 metal complexes and titanium and zirconium derivatives with chelating diamido ligands [2,3] are currently receiving considerable attention, largely because of their potential use as homogeneous catalyst precursors for the α-olefin polymerisation process [4]. Chelating diamido ligands are versatile in view of the large number of possible available substituents attached to the nitrogen atoms [5]. Corresponding group 5 metal complexes are less active in polymerisation, so they have not been widely studied as potential catalysts for olefin polymerisation, although they are more tolerant of functionalised olefin monomers [6,7].

We are interested in the synthesis and chemical behaviour of MCp′(LL)X derivatives (Cp′ = substituted or unsubstituted η^5-cyclopentadienyl ring; LL = chelating diamido [8–10] and dialkoxo [11–13] ligands). The synthesis and characterisation of new chloro diamido complexes of titanium and zirconium $MCp^{R'}[1,2\text{-}C_6H_4(NR)_2]Cl$ [M = Ti, Zr; $Cp^{R'} = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5(CH_3)_5$, $\eta^5\text{-}C_5H_4(SiMe_3)$; R = *n*Pr, Np] have been described [8–10]. These complexes were tested as potential catalysts for ethylene and styrene polymerisation after activation with MAO. In this context, we report here a series of dichloro titanium, zirconium and chloro tantalum complexes bearing the bulky diamido ligand $[1,2\text{-}C_6H_4(NCH_2tBu)_2]^{2-}$ not supported by a cyclopentadienyl ring. The presence of the ligand $[1,2\text{-}C_6H_4(NCH_2tBu)_2]^{2-}$ in the metal

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environment not only provides the delicate electronic balance and electronic relief to the Lewis acidic metal centre on account of its electron rich nitrogen atoms, but the bulky neopentyl substituents also render enough steric protection to the electrophilic metal centre.

2. Results and discussion

The synthesis of *N*,*N*′-alkyl 1,2-phenylenediamines 1,2-$C_6H_4(NHR)_2$ [R = $CH_2CH_2CH_3$ (*n*Pr), CH_2*t*Bu (Np)] has been reported [8] in three steps, lithiation of the corresponding primary 1,2-phenylenediamine, reaction with the appropriate acyl chloride and reduction using $LiAlH_4$. However, no crystallographic data were published. In the course of the present study, the solid state structure of the compound 1,2-$C_6H_4(NHCH_2tBu)_2$ has been confirmed by single-crystal X-ray diffraction (Fig. 1). Crystals suitable for the X-ray diffraction were obtained from methanol at room temperature. The angles around the nitrogen atom show the expected values for a geometry consistent with secondary amine species [14].

The addition of Li*n*Bu to a stirred suspension of the diamine 1,2-$C_6H_4(NHCH_2tBu)_2$ in cold hexane resulted in the immediate deposition of the corresponding lithium salt, which further reacts in toluene with $[MCl_4(THF)_2]$ (M = Ti, Zr) or $TaCl_5$. This strategy allows the preparation of a series of titanium, zirconium and tantalum chloro derivatives synthesized by a metathesis reaction (Scheme 1). Reaction of $Li_2[1,2\text{-}C_6H_4(NCH_2tBu)_2]$ with one equiv of $[TiCl_4(THF)_2]$ in refluxing toluene produces the chelate compound $[Ti\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}Cl_2(THF)]$ (**1**) isolated as a black product. According to literature precedents [15–17], the initial formation of a bis-diamido compound $[Ti\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}_2]$ could be suggested, which quickly should undergo an exchange reaction with the remaining $[TiCl_4(THF)_2]$ to give complex **1**. The THF coordination seems to be the driving force for this process since it avoids the possibility of metal reduction that sometimes occurs during conventional $TiCl_4$ metathesis reactions. Treatment of the dilithio diamido salt with $[ZrCl_4(THF)_2]$ in refluxing toluene affords the dinuclear zirconium derivative $[Zr\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}Cl(THF)(\mu\text{-}Cl)]_2$ (**2**), obtained as an orange solid. The reaction of $Li_2[1,2\text{-}C_6H_4(NCH_2tBu)_2]$ with $ZrCl_4$ or $[ZrCl_4(THF)_2]$ in a molar ratio of 2:1 and the ligand redox reactivity of the corresponding coordinated zirconium complexes have been recently described [18]. The standard procedure described for group 4 metal complexes was also used for tantalum. Thus, when the dilithio diamido salt reacts with $TaCl_5$ in 2:1 molar ratio in toluene, formation of $[Ta\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}_2Cl]$ (**3**) as a red product is observed immediately.

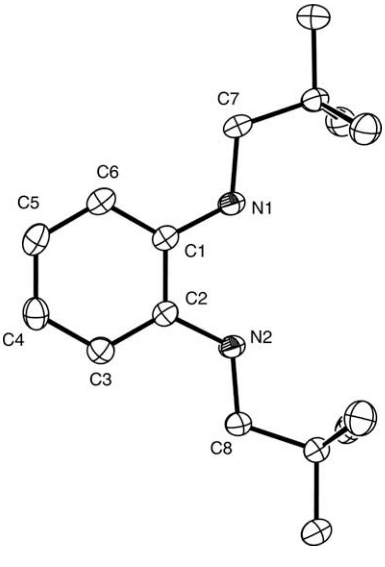


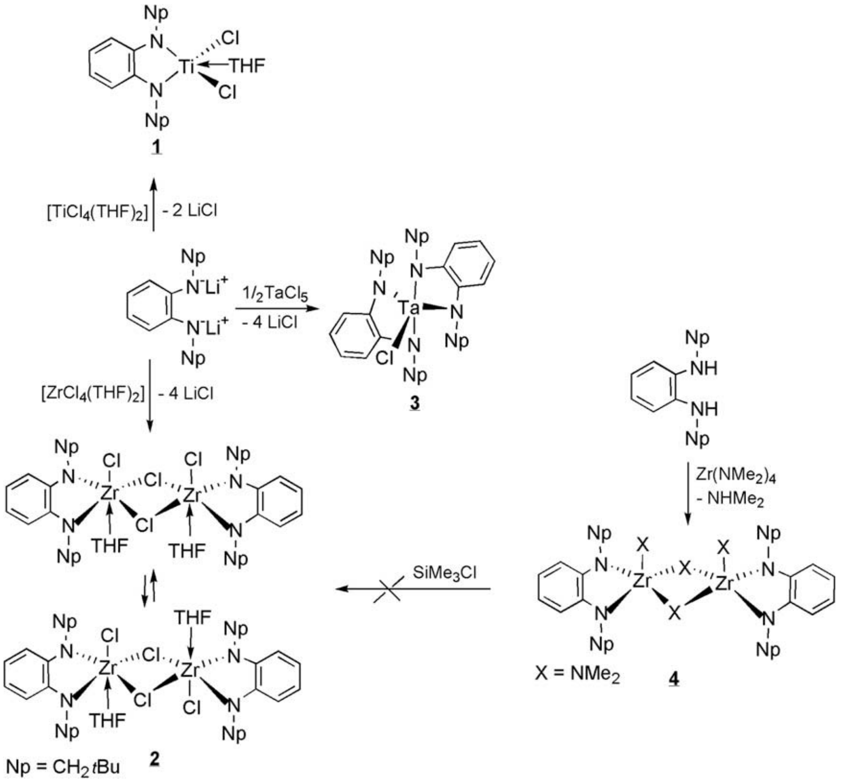
Fig. 1. ORTEP view of 1,2-$C_6H_4(NHCH_2tBu)_2$ with 30% probability ellipsoids, hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å) and angles (°): C(8)–N(2) = 1.457(2), C(2)–N(2) = 1.418(2), C(1)–C(2) = 1.418(2), C(2)–C(3) = 1.391(2), C(3)–C(4) = 1.400(2), C(4)–C(5) = 1.378(3), C(5)–C(6) = 1.400(3), C(1)–C(6) = 1.396(2), N(1)–C(7) = 1.454(2), N(1)–C(1) = 1.409(2), C(8)–N(2)–C(2) = 119.53(14), C(7)–N(1)–C(1) = 121.06(15).

Complexes **1–3** are air and moisture sensitive in solution and in the solid state, although they can be stored unaltered for weeks under an inert atmosphere. The complexes were characterised by the usual analytical and spectroscopic methods (NMR spectra for different solvents are given in the Section 5 as consequence for resolution and assignment). The elemental analysis value found for **2** was inaccurate, caused by small amounts of LiCl in the mixture, which could not be removed. The molecular structure of **3** has been confirmed by single-crystal X-ray diffraction.

The formulation of **1** was based on NMR and analytical data in accordance with analogous complexes [19]. We suggest a five coordinate titanium centre in which the metal atom is surrounded by two chlorine atoms, the diamido chelating ligand and a molecule of coordinated THF to stabilise the final product. The ^1H NMR spectra (C_6D_6 or $CDCl_3$, 25 °C) are indicative of a C_{2v} symmetry and exhibits the expected signals assigned to the resonances arising for the phenylenediamido ligand, two signals for the phenyl ring, one signal for the methylenic and one singlet for the *tert*-butyl protons. The ^1H NMR spectra also indicate one coordinated THF molecule (δ 4.01 and 1.93 versus δ 3.76 and 1.85 for the free THF molecule in $CDCl_3$). Similar results were also observed in the ^{13}C NMR spectra under the same conditions. However, attempts to grow crystals of this product were unsuccessful.

The resonances observed in the NMR spectra at room temperature for the zirconium complex **2** in C_6D_6 or $CDCl_3$ broaden to a greater degree than those observed for the titanium species **1**. On the basis of the structural properties for the titanium compound **1** and the comparable amido compound **4**, we propose for **2** a dinuclear structure connected by two chlorine atoms comparable to that found in similar diamido complexes [20–24]. As in analogous compounds, in this structural disposition each zirconium centre must adopt an octahedral coordination surrounded by terminal diamido, one chloro and one THF ligand, with two chlorine atoms located in bridge positions. Variable temperature ^1H NMR studies were investigated for this compound. Resonances for the THF ligand are observed in the spectra at 40 °C. Upon cooling the sample to −70 °C all proton resonances sharpened and the data are consistent with the presence of two products (see Section 5). These spectroscopic observations suggest that at room temperature two rapidly interconverting forms are present in solution. These two forms are separated (with a 1:1 integrating ratio) at low temperature and would have the two diamido ligands and the two bridging chlorine atoms in the equatorial plane and the terminal THF and the chloro substituents in the *cis* or *trans* axial positions, respectively (Scheme 1).

We thought that problems for the spectroscopic characterisation of **2** might be eliminated by using an alternative synthetic route through amine elimination. The reaction of 1,2-$C_6H_4(NHCH_2tBu)_2$ with $[Zr(NMe_2)_4]$ in toluene at room temperature affords the dinuclear zirconium complex $[Zr\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}(NMe_2)(\mu\text{-}NMe_2)]_2$ (**4**) as a yellow solid in high yield (Scheme 1). The ^1H NMR spectra (C_6D_6 or $CDCl_3$, 25 °C) of **4** display three resonances for the NMe_2 fragments coordinated to the zirconium centre: one signal at δ 2.93 for six protons and two singlets at δ 2.85 and 1.55 (C_6D_6) integrating for three protons each one. The CH_2 attached to nitrogen atoms appears diastereotopic as doublets of an AB spin system. This spectroscopic pattern can be explained



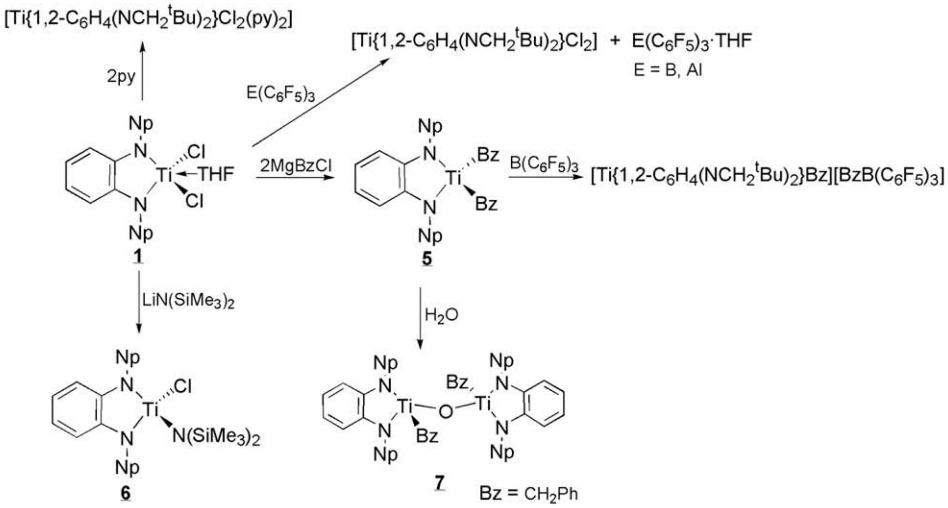
Scheme 1. Synthesis of titanium, zirconium and tantalum phenylenediamido complexes.

by considering the complex as a dinuclear species connected through two NMe_2 units. The geometry at the zirconium atoms should be described as a distorted square pyramid with the NMe_2 fragment occupying axial positions and two NMe_2 units bridging the two metal centres. An indication of this conformation is provided by the proton resonance of the methyl groups positioned on the bridging amido ligand: two of which appear at δ 2.85, with the others at δ 1.55. Such a highfield shift would be expected if these methyl groups were positioned towards the phenylene ring and experience the influence of its magnetic anisotropy. On heating the sample, coalescence of the methyl signals of the NMe_2 is observed at 70 °C, indicating rapid positional equilibration of the NMe_2 moieties on the NMR timescale. For this process we have obtained Gibbs activation energy values ($\Delta G^{\#}$) of 65 ± 0.8 kJ/mol at 343 K. Similar results were also observed in the ^{13}C NMR spectra under the same conditions. The unequivocal arrangement of metal atoms in this complex has been established by X-ray diffraction studies (see *infra*). Addition of THF to C_6D_6 solutions of **4** did not reveal any tendency of THF coordination even upon heating the sample to 100 °C (in a Young's Teflon valve NMR tube). The lack of coordination could be ascribed to the crowded environment around zirconium which decreases the Lewis acidity at the metal and hinders THF approaching. The conversion of the amido compound **4** to the chloro derivative **2** was tried by using $SiMe_3Cl$ as a chloro transfer reagent, but a mixture of unidentified products was obtained.

The ^1H NMR spectra (C_6D_6 or CD_2Cl_2, 25 °C) of complex **3** show one signal for the CH_2 protons attached to the nitrogen atoms and two multiplets for the aromatic protons, indicating the presence of a molecule in solution that exhibits equivalent phenylenediamido fragment ligands in contrast to the molecular disposition observed in the solid state by X-ray diffraction studies (see *infra*). This fact prompted us to carry out structural investigations in solution. However, on cooling the sample to −70 °C unambiguous correlations could not be established and a clear resolution of the signals was not observed.

The coordinated THF molecule in **1** is labile and tends to dissociate from the titanium centre in the presence of a donor ligand. Conversion of **1** to $[Ti\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}Cl_2(py)_2]$ was studied by NMR spectroscopy and occurs immediately at room temperature after adding free pyridine to a solution of **1** in $CDCl_3$ (Scheme 2). The NMR data show pyridine coordination [25] of two molecules with three broadened peaks at δ 9.62, 8.00 and 7.62 assigned to the coordinated pyridine and two multiplets at δ 3.76 and 1.85 due to free liberated THF, suggesting a six coordinated geometry around the titanium atom. The spectroscopic signals are broadened and the methylene resonances are not observed in the spectra, which indicate a coordination environment that is fluxional on the NMR timescale. Reactions of **1** with Lewis acids such as $E(C_6F_5)_3$ (E = B, Al) in $CDCl_3$ were monitored by NMR spectroscopy and show the abstraction of the coordinated THF to form $[Ti\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}Cl_2]$, concomitant with the formation of the adduct $E(C_6F_5)_3{\cdot}THF$ (Scheme 2). In a similar way, treatment of **2** with $B(C_6F_5)_3$ gives a CD_2Cl_2 solution in which the presence of a mixture of the species "$Zr[1,2\text{-}C_6H_4(NCH_2tBu)_2]Cl_2$" and $B(C_6F_5)_3{\cdot}THF$ is spectroscopically detected. We can conclude that the tendency of the titanium compound **1** and the zirconium complex **2** to coordinate donor ligands such as pyridine or THF reflects their acidic nature and the accessibility of the metal centre, and prompted us to investigate the polymerisation behaviour of this compound along with the reaction of the alkyl derivatives with different cocatalysts.

Methylation of **1** with MgMeCl in ether at −78 °C gave an unstable, intractable and unresolved mixture of products with a regrettably uninformative ^1H NMR spectrum. Due to the unexpected poor behaviour of the methyl ligand to create a stable coordination environment at the titanium centre, the use of voluminous ligands was explored to stabilise the alkyl compounds. The dibenzyl



Scheme 2. Reactions of the titanium phenylenediamido compound **1**.

derivative [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Bz_2] (**5**) (Bz = CH_2Ph) was obtained by the reaction in toluene of **1** with 2 equiv of MgBzCl in THF solution at −78 °C (Scheme 2). Recrystallisation from hexane at −30 °C affords, after filtration, higher purity material as a red oil. The ^1H NMR spectrum of **5** indicates that THF dissociation has occurred. The data are consistent with a compound with a degree of high symmetry. The four equivalent methylene protons in the "CH_2N" linkage appear as a singlet. The two equivalent benzyl ligands exhibit a singlet resonance integrating for four protons for the methylenic protons and three sets of *o*-, *m*-, and *p*-phenyl resonances. The expected signals for the phenylenediamido ligand are also observed. Complex **1** reacted readily with the lithium amide reagent $LiN(SiMe_3)_2$ to afford [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl{N($SiMe_3$)}] (**6**) (Scheme 2). Thermolysis of **6** was carried out in the attempt to eliminate $SiMe_3Cl$ and to generate an imido [25] derivative, but after heating an NMR sample at 80 °C for 12 h only a mixture of unidentified products was observed.

When compound **5** is maintained in solution (toluene or hexane), the oxo derivative [(Ti{1,2-$C_6H_4(NCH_2tBu)_2$}{CH_2Ph})$_2$(μ-O)] **7** (Scheme 2) precipitates as red crystals, indicating the extreme sensitivity of **5** to moisture and confirming the formation of a benzyl derivative in the alkylating reaction of **1**. All attempts to obtain this product as a single and pure substance by controlled hydrolysis of **5** were unsuccessful with only a mixture of free amine and unidentified products being obtained. The molecular structure of **7** has been determined by X-ray diffraction methods although the crystals studied gave X-ray diffraction data of poor quality (Fig. 2).[2]

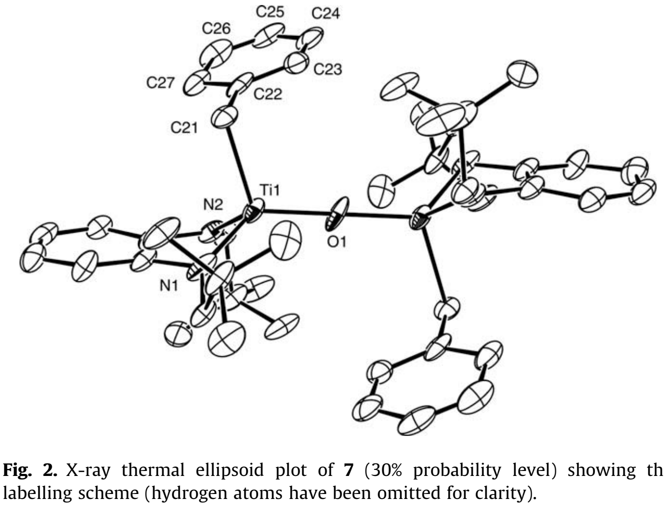


Fig. 2. X-ray thermal ellipsoid plot of **7** (30% probability level) showing the labelling scheme (hydrogen atoms have been omitted for clarity).

Compound **2** was treated with various alkylating reagents under different reaction conditions. However, all the attempts proved unfruitful and uninformative broad signals were observed in the corresponding NMR spectra.

Addition of $B(C_6F_5)_3$ to a solution of **5** in C_6D_6 at room temperature affords a cationic species, which was characterised by ^1H, ^{13}C and ^{19}F NMR spectroscopy. The NMR spectra featured downfield benzyl resonances assigned to a cationic-electron deficient benzyl titanium derivative. From these spectroscopic data, we propose the formation of the ionic [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Bz][BzB$(C_6F_5)_3$] species (Scheme 2). The large difference (4.5 ppm) between *p*-F and *m*-F chemical shifts of the $[BzB(C_6F_5)_3]^-$ anion suggests a strong interaction between the anion and the titanium centre, as observed for related cationic species [26–28]. The relative solubility of this complex in benzene is also consistent with its zwitterionic character. The same electrophilic reaction was tested and observed in CD_2Cl_2 at low temperature (−70 °C) and the spectroscopic study reveals that the abstraction reaction was facile even at this temperature. No reaction was observed when the tantalum complex **3** was reacted with $LiB(C_6F_5)_4$ in an attempt to form a cationic species from which activation of *t*Bu groups attached to nitrogen atoms due to the electronic deficiency could be enforced.

Given our interest in the polymerisation chemistry of diamido [9] or dialkoxo [11,12] early metal complexes, we undertook preliminary studies on α-olefin polymerisation and the complexes **1**, **3** and **5** were tested as catalysts for ethylene polymerisation in the presence of $B(C_6F_5)_3$, methylaluminoxane (MAO) and sMAO (MAO used as an $AlMe_3$-free solid) [29] as cocatalysts. The dichloro complex **1** and the dibenzyl compound **5** showed very low activity (≈10 Kg PE/mol$_{cat}$ atm h). These activities are much lower than those of the best know non-cyclopentadienyl group 4 metal com-

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[2] Crystal data for **7**: $C_{46}H_{66}N_4OTi_2$, M_r = 786.83, crystal size 0.39 × 0.34 × 0.22 mm^3, Triclinic, space group $P\bar{1}$, a = 9.915(5) Å, b = 11.342(6) Å, c = 11.626(11) Å, α = 70.75(4)°, β = 86.79(6)°, γ = 65.67(4)°, V = 1119.9(13) Å^3, Z = 1, ρ_{calcd} = 1.167 Mg m^{-3}, μ = 0.393 mm^{-1}, Mo Kα radiation (λ = 0.71073 Å). Data collection was performed at 200(2) K on a Nonius KappaCCD single crystal diffractometer. Reflections collected/unique 13251/3902 [R_{int} = 0.8802]. The final cycle of full matrix least-squares refinement based on 3902 reflections and 242 parameters converged to final values of $R_1(F^2 > 2\sigma(F^2))$ = 0.1853, $wR_2(F^2 > 2\sigma(F^2))$ = 0.4554, $R_1(F^2)$ = 0.2648, $wR_2(F^2)$ = 0.5446). Largest diff. peak/hole 0.879/−1.484 eÅ^{-3}.

plexes such as McConville's titanium compounds [30], but are similar to other related complexes [31,32]. GPC results are indicative of polyethylenes that have very broad polydispersities (Mw/Mn values of 4–6) [9,31]. DSC measurements of the polymers show melting temperatures (T_m) for the polymers produced that are typical of high density polyethylene. These results may be a consequence of the gradual generation of low active Ti active species upon losing the diamido ligand from these diamido titanium precursors. It is a general observation that the complexes containing the *n*Pr amido ligand show higher polymerisation activities compared with the Np derivatives [8], suggesting that the activity is highly influenced by the steric effect [33] at the titanium centre caused by the *n*-propyl or neopentyl substituents at the nitrogen atom of the diamido ligand. Similar cases of strongly bulky substituents influencing catalytic polymerisation activity have been observed for related amidinate complexes [34,35]. The non-metallocene tantalum diamido complex **3** has no site for two alkyls, one of which is required for the propagation and the other of which is the source of cationic formation, and it was inactive in ethylene polymerisation.

3. Crystal structures of [Ta{1,2-$C_6H_4(NCH_2t\mathrm{Bu})_2$}$_2$Cl] (3) and [Zr{(1,2-$C_6H_4(NCH_2t\mathrm{Bu})_2$}($NMe_2$)(μ-$NMe_2$)]$_2$ (4)

Red single crystals of **3**$\cdot C_6D_6$ were grown in a saturated C_6D_6 solution at room temperature and the molecular structure established by X-ray diffraction studies. Selected bond lengths and angles for the structure are listed in Table 1. The molecular structure shows the tantalum atom bonded to a chlorine atom and two chelating phenylenediamido ligands (Fig. 3). In the crystal, the compound presents a twofold axis along the Ta–Cl bond. The coordination geometry of the Ta(V) centre can be described as a distorted trigonal bipyramid [36]. The Ta, Cl, N(2) and N(2)^i (i: $-x+1$, y, $-z+3/2$) atoms are in exactly the same plane, defining the trigonal bipyramidal equatorial plane. The N(1) and the N(1)^i atoms occupy the trigonal bipyramidal axial positions with a N(1)–Ta–N(1)^i angle of 167.37(10)°. Both N(1) and N(2) coordinated nitrogen atoms are essentially planar with a sum of angles of 359.5° and 354.7°, respectively. Ta–Cl [2.4123(8) Å] bond lengths compare well with related Ta(V) complexes [10]. Compound **3** is almost isostructural to the previously reported bisphenylenediamido Nb(V) complex [Nb{4,5-Me_2-1,2-$C_6H_2(NSiMe_3)_2$}$_2$Cl] [37].

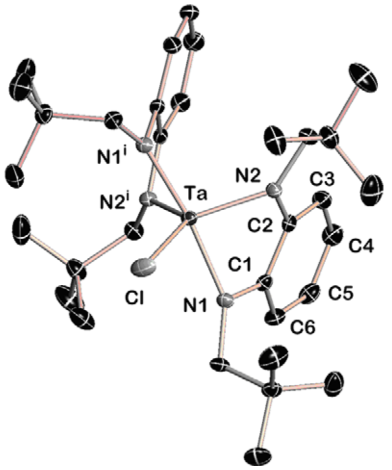

Fig. 3. X-ray thermal ellipsoid plot of **3** (50% probability level) showing the labelling scheme (i: $-x+1$, y, $-z+3/2$, hydrogen atoms have been omitted for clarity).

Table 1
Selected bond distances (Å) and angles (°) for complexes **3**$\cdot C_6D_6$ and **4**.[a]

*Compound **3**·C_6D_6*			
Ta–N(1)	2.0108(18)	N(2)–Ta–N(2)[b]	108.11(10)
Ta–N(2)	1.9733(17)	N(2)–Ta–N(1)[b]	103.44(7)
Ta–Cl	2.4123(8)	N(2)–Ta–N(1)	84.07(7)
Ta–C(1)	2.588(2)	N(1)[b]–Ta–N(1)	167.37(10)
Ta–C(2)	2.559(2)	N(2)–Ta–Cl	125.95(5)
N(1)–C(1)	1.412(3)	N(1)–Ta–Cl	83.69(5)
N(2)–C(2)	1.417(3)	C(1)–N(1)–C(11)	119.70(17)
C(1)–C(6)	1.411(3)	C(1)–N(1)–Ta	96.67(12)
C(1)–C(2)	1.424(3)	C(11)–N(1)–Ta	143.17(14)
C(2)–C(3)	1.408(3)	C(2)–N(2)–C(21)	121.18(17)
C(3)–C(4)	1.383(3)	C(2)–N(2)–Ta	96.63(13)
C(4)–C(5)	1.397(3)	C(21)–N(2)–Ta	136.93(14)
C(5)–C(6)	1.377(3)		
*Compound **4***			
N(7)–Zr(1)	2.024(5)	C(1)–N(1)–C(17)	119.6(5)
N(1)–Zr(1)	2.085(5)	C(1)–N(1)–Zr(1)	102.7(4)
N(2)–Zr(1)	2.120(5)	C(17)–N(1)–Zr(1)	136.4(5)
N(5)–Zr(1)	2.274(5)	C(2)–N(2)–C(13)	120.1(5)
N(6)–Zr(1)	2.349(5)	C(2)–N(2)–Zr(1)	103.9(4)
N(8)–Zr(2)	2.037(5)	C(13)–N(2)–Zr(1)	135.2(4)
N(3)–Zr(2)	2.087(5)	C(8)–N(3)–C(18)	118.7(5)
N(4)–Zr(2)	2.118(5)	C(8)–N(3)–Zr(2)	101.0(3)
N(5)–Zr(2)	2.366(5)	C(18)–N(3)–Zr(2)	138.5(4)
N(6)–Zr(2)	2.283(5)	C(7)–N(4)–C(23)	123.0(5)
C(1)–Zr(1)	2.761(7)	C(7)–N(4)–Zr(2)	102.8(3)
C(2)–Zr(2)	2.808(6)	C(23)–N(4)–Zr(2)	133.0(4)
C(7)–Zr(1)	2.742(6)	C(38)–N(5)–C(37)	107.9(5)
C(8)–Zr(1)	2.795(5)	C(38)–N(5)–Zr(1)	114.7(4)
N(1)–C(1)	1.410(10)	C(37)–N(5)–Zr(1)	108.9(4)
N(2)–C(2)	1.400(9)	C(38)–N(5)–Zr(2)	111.6(4)
N(3)–C(8)	1.423(8)	C(37)–N(5)–Zr(2)	114.1(4)
N(4)–C(7)	1.414(8)	Zr(2)–N(5)–Zr(1)	99.69(17)
		C(40)–N(6)–C(39)	107.3(6)
		C(40)–N(6)–Zr(2)	112.7(4)
		C(39)–N(6)–Zr(2)	108.8(4)
		C(40)–N(6)–Zr(1)	114.1(5)
		C(39)–N(6)–Zr(1)	113.8(4)
		Zr(1)–N(6)–Zr(2)	99.94(18)

[a] E.s.d's are given in parentheses.
[b] Symmetry transformation used to generate equivalent atoms $-x+1$, y, $-z+3/2$.

The related chelating diamido ligands and the Ta atom form a "TaN_2C_2" metallacycle that is bent through the N···N axis (N(1)–Ta–N(2) and N(1)–C(1)–C(2)–N(2) planes dihedral angle of 52.05(9)°). The "TaN_2C_2" metallacycle structural parameters indicate that the phenylenediamido ligand is bonded to the metal in a η^4 fashion showing σ^2,π-enediamido behaviour [38]. This type of σ^2-*N*,*N'*-π-phenylenediamido coordination allows the donation of electron density from the phenylene ring to the metal and should quench the electrophilicity of Ta(V). Similar structural features have been reported for analogous X-ray structures of chelating phenylenediamido group 5 metal complexes found in the CSD [39]. Thus, the Ta(V) complexes [Ta(η^5-C_5Me_5){1,2-$C_6H_4(NSiPr^i_3)_2$}Cl_2], [Ta{η^5-1,3-$C_5H_3(SiMe_3)_2$}{1,2-$C_6H_4(NSiMe_3)_2$}Cl_2], and the Nb(V) derivative [Nb{4,5-Me_2-1,2-$C_6H_2(NSiMe_3)_2$}$_2$Cl] present sp^2 planar coordinated N atoms and are bent through the N···N axis "MN_2C_2" (M = metal) metallacycles (dihedral angle range 53.8–58.7°) [40,41]. The Ta–C(1) and Ta–C(2) bond lengths [2.588(2) and 2.559(2) Å, respectively] for compound **3** are in good agreement with π-bonding involving the C_{ipso} atoms at the phenylene ring. Slightly shorter Ta–C bond lengths (range 2.40–2.54 Å) are present in the previously described phenylenediamido Ta(V) complexes with a σ^2,π-enediamido type of coordination [40,41]. Rather short Ta–N bond lengths [1.9733(17) and 2.0108(18) Å] are observed in the molecular structure of **3**, consistent with a significant p_π–d_π contribution, similar to that found for other amido groups bound to tantalum [40–43]. The 1,2-$C_6H_4(NCH_2t\mathrm{Bu})_2$ phenylenediamido ring is distorted with the carbon–carbon bond distances ranging from the longest bond for C(1)–C(2) (1.424(3) Å) to both C(3)–C(4) and

C(5)–C(6) as the shortest bonds (1.383(3), 1.377(3) Å), while the N–C_{ipso} distances (1.412(3) and 1.417(3) Å) are consistent with single bond formulation.

Yellow single crystals of **4** suitable for X-ray diffraction studies, grown in a saturated hexane solution at −40 °C, were used to unequivocally establish the molecular structure of this complex, shown in Fig. 4. Selected bond distances and angles for the structure are listed in Table 1. This compound crystallised as an enantiomeric pure isomer due to conformation chirality arising from the relative disposition of the phenylene rings in the solid state. By contrast, C_2-symmetry is inferred for **4** in solution as deduced from the NMR spectroscopic data.

The environment around each Zr atom is approximately square pyramidal with one of the NMe_2 ligands in the axial position. The zirconium atoms are not located in the planar base of the square pyramid, as distances of 0.728 Å from the Zr(2) to the N(4)N(3)N(6)N(5) plane and 0.726 Å from Zr(1) to the N(5)N(6)N(1)N(2) plane were measured. There is a central Zr(1)N(5)N(6)Zr(2) core that appears puckered (Zr(2)N(6)Zr(1) 99.94(18)°, Zr(2)N(5)Zr(1) 99.69(17)°). In this central unit, the Zr–N bond lengths range from 2.274(5) to 2.366(5) Å and the endocyclic angles at N(5) or N(6) are wider than those at Zr(1) or Zr(2). Within the molecule, the Zr–N bond lengths vary significantly, ranging from 2.024(5) to 2.366(5) Å, with the longest length corresponding to the bridging ligands (N(5) and N(6)) and the shortest to the distances between the metal and the terminal NMe_2 groups. This feature can be related to the degree of donation from the respective amido ligand to the metal centre, indicating a p_π–d_π bonding contribution for the amido moieties closer to it [18,30,44]. In addition, the sum of the angles around the nitrogen atoms in those groups (N(1), N(2), N(3) and N(4)) are essentially planar, with a tetrahedral disposition for the bridging N(5) and N(6) atoms.

As observed in **3**, and in similar structures reported for group 4 eneamido complexes [45,46], the "$Zr[C_6H_4(NCH_2tBu)]$" metallacycle is folded along the N···N axis (41.88° and 43.83° dihedral angles between the NZrN and NCCN planes). The "ZrN_2C_2" metallacycle's structural parameters indicate that the phenylenediamido ligands are bonded to the metal in a η^4 fashion showing a σ^2,π-enediamido manner [38]; the Zr–C_{ipso} bond distances [2.742(6)–2.808(6) Å range] are also in good agreement with π-bonding involving C_{ipso} atoms at the phenylene ring.

Analysis of the η^2-*N*,*N′*-phenylenediamido ligand's geometrical parameters reported in the CSD for group 4 and 5 metal complexes has been performed [8,10,37,40,41,47–50]. Bent and planar "MN_2C_2" metallacycles with wide folding through the N···N axis degree range have been reported (0–58° N-metal-N/N–C_{ipso}–C_{ipso}–N dihedral angle range) [51]. As should be expected, short M–C_{ipso} distances correspond to highly bent metallacycles and long M–C_{ipso} distances are found for planar or slightly bent metallacycles, with very few exceptions. The N–C_{ipso} bond lengths are in the 1.33–1.46 Å range for both group 4 and 5 η^2-phenylenediamido metal complexes. Furthermore, in the analysed complexes the phenylene ring is distorted, showing a long C_{ipso}–C_{ipso} bond length (range 1.41–1.47 Å) and two short ring bond lengths, generally corresponding to C(3)–C(4) and C(5)–C(6) (a range of 1.35–1.39 Å is observed in compound **3**, although in compound **4** the shortest bond length corresponds to C(4)–C(5) with values of 1.372(17) Å in one ring and 1.345(13) Å in the other one). Surprisingly, we have found that a distortion of the phenylene ring is present for both bent and planar "MN_2C_2" metallacycles and it seems not to depend on the degree of metallacycle folding. The absence of a direct correlation for the degree of metallacycle folding and phenylene ring distortion could imply that the phenylenediamido ligand ring distortion is not related to the π-coordination of the ligand.

4. Conclusions

In summary, we report the synthesis of early metal complexes stabilised by coordination of the $[1,2\text{-}C_6H_4(NCH_2tBu)_2]^{2-}$ ligand that are fully characterised by various methods. Direct reaction of $Li[1,2\text{-}C_6H_4(NCH_2tBu)_2]$ with $[TiCl_4(THF)_2]$ or $TaCl_5$ in toluene gives the monomeric derivatives in reasonable yield, while dimeric complexes were obtained for zirconium. The results indicate that monomeric titanium and tantalum complexes require the presence of additional Lewis base molecules to stabilise the final product. Reactions of the titanium compounds with Lewis acids show the abstraction of the coordinated Lewis base. Voluminous alkyl ligands are required to stabilise the alkyl compounds and the dibenzyl derivative $[Ti\{1,2\text{-}C_6H_4(NCH_2tBu)_2\}Bz_2]$ can be obtained.

η^2-Phenylenediamido group 4 and 5 metal complexes show distorted phenylene rings with the C_{ipso}–C_{ipso} bond length as the longest length and generally the two conjugated C–C bonds as

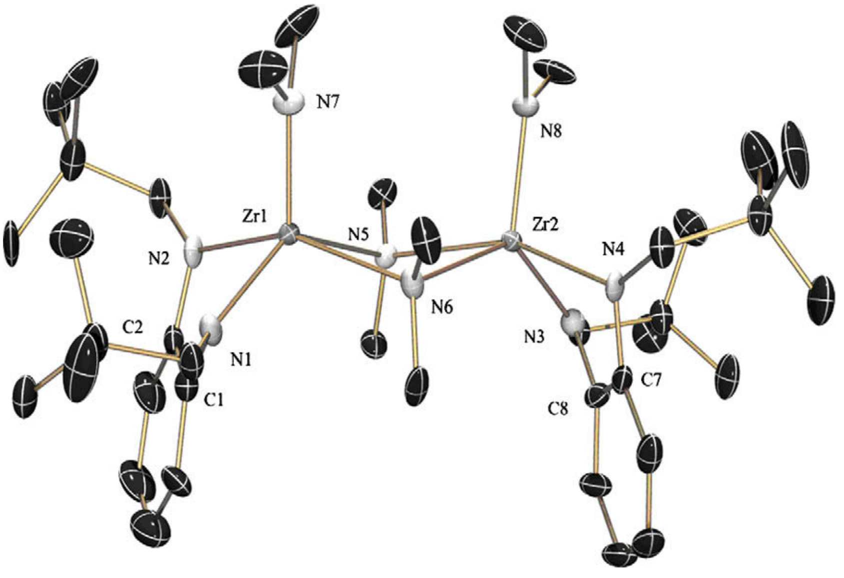

Fig. 4. X-ray thermal ellipsoid plot of **4** (30% probability level) showing the labelling scheme (hydrogen atoms have been omitted for clarity).

the shortest lengths. However, the direct correlation for the degree of metallacycle folding and phenylene ring distortion could imply that the phenylenediamido ligand ring distortion is not related to the π-coordination of the ligand.

5. Experimental

5.1. General considerations

All manipulations were performed with rigorous exclusion of oxygen and moisture under argon using Schlenk and high-vacuum line techniques or in a glove box model MO40-2. Solvents were predried by standing over activated 4 Å molecular sieves and then purified by distillation under argon before use by employing the appropriate drying/deoxygenated agent. Deuterated solvents were degassed by several freeze–thaw cycles and stored in ampoules equipped with Young's Teflon valves over activated 4 Å molecular sieves. C, H and N microanalyses were performed on a Perkin–Elmer 2400 microanalyzer. NMR spectra were recorded on a Bruker AV400 (^{1}H NMR at 400.13 MHz, ^{13}C NMR at 100.60 MHz and ^{19}F NMR at 376.40 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, while ^{19}F resonance were measured relative to external $CFCl_3$. Spectra were recorded at 25 °C unless otherwise stated. Li*n*Bu (1.6 M in hexane solution), MgMeCl (3 M in THF), MgBzCl (2 M in THF), pyridine, $LiN(SiMe_3)_2$ and $TaCl_5$ were purchased from Aldrich. $Br(C_6F_5)$ was purchased from ABCR. MAO, 30 wt% solution in toluene was received from Crompton GmbH. Compounds $[TiCl_4(THF)_2]$ [52], $[ZrCl_4(THF)_2]$ [52], $B(C_6F_5)_3$ [53–56], $Al(C_6F_5)_3 \cdot 0.5C_7H_8$ [7] and $[Zr(NMe_2)_4]$ [57], were synthesized following established procedures.

Polymerisation grade ethylene was used as received. Ethylene polymerisation was carried out in a glass reactor with magnetic stirring. The polymerisation solvent (toluene) was dried by refluxing over sodium-benzophenone and distilled before use in an inert atmosphere. MAO (Witco 10%) was used as a solution in toluene. Melting temperatures of the polymers were measured by differential scanning calorimetry (DSC) on a Perkin Elmer DSC6 instrument.

5.2. Synthesis of [Ti{1,2-C_6H_4(NCH_2*t*Bu)$_2$}Cl_2(THF)] (**1**)

Li*n*Bu (1.6 M in hexane, 4.02 mmol, 2.5 mL) was slowly added to a suspension of 0.500 g (2.01 mmol) of 1,2-C_6H_4($NHCH_2$*t*Bu)$_2$ in hexane (50 mL) at −78 °C. The reaction mixture was warmed to room temperature over 4 h and a white precipitate of Li_2[1,2-C_6H_4(NCH_2*t*Bu)$_2$] was formed with evolution of butane. The desired amount of the lithium salt (0.296 g, 1.14 mmol) and 0.380 g of $[TiCl_4(THF)_2]$ (1.14 mmol) were introduced in a Young's ampoule and toluene (50 mL) was charged at −78 °C. A red–brown suspension was immediately obtained. After 2 h, the reaction mixture was heated at reflux for 12 h. After cooling, all volatiles of the dark solution were removed under vacuum and the black product was extracted into hexane. Recrystallisation with cold hexane afforded the product identified as [Ti{1,2-C_6H_4(NCH_2*t*Bu)$_2$}Cl_2(THF)] **1**, as a black solid (0.268 g, 0.613 mmol, 54% yield). *Anal.* Calc. for $C_{20}H_{34}N_2Cl_2OTi$ (436.98 g/mol): C, 54.92; H, 7.77; N, 6.40. Found: C, 54.56; H, 8.59; N, 6.73%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.36 (m, 2H, Ph), 7.07 (m, 2H, Ph), 4.25 (s, 4H, CH_2), 3.74 (m, 2H, THF), 1.26 (m, 2H, THF), 0.85 (s, 18H, *t*Bu). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.54 (m, 2H, Ph), 7.24 (m, 2H, Ph), 4.31 (s, 4H, CH_2), 4.01 (m, 2H, THF), 1.93 (m, 2H, THF), 0.82 (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (100.60 MHz, C_6D_6, 25 °C): δ 126.0, 115.7 (Ph), 123.9 (*ipso*-Ph), 71.0 (CH_2), 66.9 (THF), 36.0 (*ipso*-*t*Bu), 28.9 (*t*Bu), 25.4 (THF).

5.3. Synthesis of [Zr{1,2-C_6H_4(NCH_2*t*Bu)$_2$}Cl(THF)(μ-Cl)]$_2$ (**2**)

The same procedure described for **1** using 0.300 g (1.15 mmol) of Li[1,2-C_6H_4(NCH_2*t*Bu)$_2$] and 0.435 g of $[ZrCl_4(THF)_2]$ (1.15 mmol) gives [Zr{1,2-C_6H_4(NCH_2*t*Bu)$_2$}Cl(THF)(μ-Cl)]$_2$ **2**, obtained as an orange product which was washed with hexane (0.673 g, 0.700 mmol, 61% yield). The elemental analysis value found for **2** was inaccurate, caused by small amounts of LiCl in the mixture, which could not be removed. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 6.94 (br, 2H, Ph), 6.68 (br, 2H, Ph), 3.87 (br, 4H, CH_2), 1.08 (s, 18H, *t*Bu). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.98 (br, 4H, Ph), 3.94 (br, 4H, CH_2), 0.89 (s, 18H, *t*Bu), THF resonances not observed. ^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): δ 6.92 (br, 2H, Ph), 6.75 (br, 2H, Ph), 3.87 (br, 4H, CH_2), 3.89 (br, 2H, THF), 1.15 (m, 2H, THF), 1.07 (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (100.60 MHz, $CDCl_3$, 25 °C): δ 128.3, 114.7 (Ph), 74.0 (THF), 60.7 (CH_2N), 36.6 (*ipso*-*t*Bu), 25.5 (THF), 28.1 (*t*Bu), *ipso*-Ph not observed. ^{1}H NMR (400 MHz, CD_2Cl_2, −70 °C): **isomer A**: δ 6.98 (m, 2H, Ph), 6.86 (m, 2H, Ph), 4.00 (d, *J* = 14.4 Hz, 2H, AB spin system, CH_2), 3.34 (d, *J* = 14.4 Hz, 2H, AB spin system, CH_2), 4.31 (br, 2H, THF), 2.02 (m, 2H, THF), 0.92 (s, 18H, *t*Bu); **isomer B**: δ 6.37 (m, 2H, Ph), 6.30 (m, 2H, Ph), 4.30 (br, 2H, CH_2), 3.70 (br, 2H, CH_2), 4.40 (br, 2H, THF), 2.02 (m, 2H, THF), 0.92 (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (100.60 MHz, CD_2Cl_2, −70 °C): **isomer A**: δ 125, 116 (Ph), 75.0 (THF), 60 (CH_2N), 27 (THF), 28 (*t*Bu), *ipso* of Ph and *ipso* of *t*Bu not observed; **isomer B:** δ 119, 112 (Ph), 75.0 (THF), 58 (CH_2N), 27(THF), 30 (*t*Bu), *ipso* of Ph and *ipso* of *t*Bu not observed.

5.4. Synthesis of [Ta{1,2-C_6H_4(NCH_2*t*Bu)$_2$}$_2$Cl] (**3**)

The same procedure described for **1** using 0.207 g (0.79 mmol) of Li[1,2-C_6H_4(NCH_2*t*Bu)$_2$] and 0.14 g of $TaCl_5$ (0.40 mmol) gives [Ta{1,2-C_6H_4(NCH_2*t*Bu)$_2$}$_2$Cl] **3** as a red solid (0.130 g, 0.183 mmol, 46% yield). *Anal.* Calc. for $C_{32}H_{52}N_4ClTa$ (709.18 g/mol): C, 54.19; H, 7.33; N, 7.89. Found: C, 54.32; H, 7.09; N, 7.73%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.01 (m, 4H, Ph), 6.79 (m, 4H, Ph), 4.68 (s, 8H, CH_2), 0.71 (s, 36H, *t*Bu). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.08 (m, 4H, Ph), 6.97 (m, 4H, Ph), 4.03 (s, 8H, CH_2), 0.75 (s, 36H, *t*Bu). ^{13}C{^{1}H} NMR (100.60 MHz, C_6D_6, 25 °C): δ 137.8 (*ipso*-Ph), 129.3, 119.2 (Ph), 66.9 (CH_2N), 30.1 (*ipso*-*t*Bu), 28.4 (*t*Bu).

5.5. Synthesis of [Zr{1,2-C_6H_4(NCH_2*t*Bu)$_2$}(NMe_2)(μ-NMe_2)]$_2$ (**4**)

A solution of 0.185 g (0.75 mmol) of 1,2-C_6H_4($NHCH_2$*t*Bu)$_2$ was added to 0.20 g of $Zr(NMe_2)_4$ (0.74 mmol) in toluene (50 mL). The solution was maintained at room temperature for 16 h and gradually became golden yellow. The volatiles were evaporated and hexane was added. The solution was set at −30 °C for 12 h and a microcrystalline yellow powder precipitated. The solid was isolated by filtration and dried in vacuum. Recrystallisation with cold hexane led to the product identified as [Zr{1,2-C_6H_4(NCH_2*t*Bu)$_2$}(NMe_2)(μ-NMe_2)]$_2$ **4** (0.495 g, 0.581 mmol, 78% yield). *Anal.* Calc. for $C_{40}H_{76}N_8Zr_2$ (850.84 g/mol): C, 56.46; H, 8.93; N, 13.16. Found: C, 56.10; H, 9.01; N, 13.20%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 6.99 (m, 2H, Ph), 6.90 (m, 2H, Ph), 3.88 (d, 2H, *J* = 13.2 Hz, AB spin system, CH_2), 3.65 (d, 2H, *J* = 13.2 Hz, AB spin system, CH_2), 2.93 (s, 6H, N*Me*$_2$), 2.85 (s, 3H, N*Me*$_2$), 1.55 (s, 3H, N*Me*$_2$), 0.87 (s, 18H, *t*Bu). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.85 (m, 2H, Ph), 6.67 (m, 2H, Ph), 3.82 (d, 2H, *J* = 13.4 Hz, AB spin system, CH_2), 3.60 (d, 2H, *J* = 13.4 Hz, AB spin system, CH_2), 3.09 (s, 6H, N*Me*$_2$), 3.03 (s, 3H, N*Me*$_2$), 1.45 (s, 3H, N*Me*$_2$), 0.71 (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (100.60 MHz, C_6D_6, 25 °C): δ 135.1 (*ipso*-Ph), 120.1, 115.8 (Ph), 60.6 (CH_2N), 44.4, 43.2, 42.05 (N*Me*$_2$), 35.2 (*ipso*-*t*Bu), 28.8 (*t*Bu). ^{13}C{^{1}H} NMR (100.60 MHz, $CDCl_3$, 25 °C): δ 136.1 (*ipso*-Ph) 118.9, 115.2 (Ph), 60.4 (CH_2N), 44.1, 43.3, 42.3 (N*Me*$_2$), 35.3 (*ipso*-*t*Bu), 28.8 (*t*Bu).

5.6. [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}$Cl_2(py)_2$]

Pyridine was added at room temperature into a Teflon-valved NMR tube containing a chloroform-d (0.5 mL) solution of [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl_2(THF)]. The reaction mixture turned brown and the ^{1}H and ^{13}C NMR spectra were obtained, showing the formation of [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}$Cl_2(py)_2$]. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 9.62 (br, 4H, py), 8.00 (br, 2H, py), 7.62 (br, 4H, py), 6.36 (m, 2H, Ph), 5.88 (m, 2H, Ph), 0.75 (s, 18H, *t*Bu), CH_2 protons not observed.

5.7. Reaction of [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl_2(THF)] with $B(C_6F_5)_3$ or $Al(C_6F_5)_3$

In a glovebox, chloroform-d or benzene-d_6 (0.5 mL) was added at room temperature to a Teflon-valved NMR tube containing the solid mixture of [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl_2(THF)] and $B(C_6F_5)_3$. The ^{1}H and ^{13}C NMR spectra obtained showed the formation of [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl_2] with $B(C_6F_5)_3$·(THF) also present. **[Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl_2]**: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.34 (m, 2H, Ph), 7.00 (m, 2H, Ph), 4.16 (s, 4H, CH_2), 0.75 (s, 18H, *t*Bu). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.64 (m, 2H, Ph), 7.31 (m, 2H, Ph), 4.29 (s, 4H, CH_2), 0.86 (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (100.60 MHz, C_6D_6, 25 °C): δ 129.0, 116.0 (Ph), 67.8 (CH_2), 35.8 (*ipso-t*Bu), 28.6 (*t*Bu), *ipso*-Ph not observed. **$B(C_6F_5)_3$·(THF)**: ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 3.23 (m, 2H, OCH_2), 0.85 (m, 2H, CH_2). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 4.25 (m, 2H, OCH_2), 2.13 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (100.60 MHz, C_6D_6, 25 °C): δ 75.7 (THF), 25.4 (THF). ^{19}F NMR (376.40 MHz, $CDCl_3$, 25 °C): δ −128.7 (broad, *o*-C_6F_5), −143.7 (broad, *p*-C_6F_5), −160.7 (broad, *m*-C_6F_5). ^{19}F NMR (376.40 MHz, C_6D_6, 25 °C): δ −131.6 (broad, *o*-C_6F_5), −152.6 (broad, *p*-C_6F_5), −161.8 (broad, *m*-C_6F_5).

A similar procedure using [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl_2(THF)] and $Al(C_6F_5)_3$ gives a mixture of the same compound [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl_2] and $Al(C_6F_5)_3$.(THF). **$Al(C_6F_5)_3$·(THF)**: ^{19}F NMR (376.40 MHz, $CDCl_3$, 25 °C): δ −123.2 (s broad, *o*-C_6F_5), −151.7 (s broad, *p*-C_6F_5), −161.0 (s broad, *m*-C_6F_5).

5.8. Reaction of [Zr{1,2-$C_6H_4(NCH_2tBu)_2$}Cl(THF)(μ-Cl)]$_2$ (**2**) with $B(C_6F_5)_3$

In a glovebox, dichloromethane-d_2 (0.5 mL) was added via a syringe at room temperature to a Teflon-valved NMR tube containing the solid [Zr{1,2-$C_6H_4(NCH_2tBu)_2$}Cl(THF)(μ-Cl)]$_2$ and $B(C_6F_5)_3$. The ^{1}H and ^{13}C NMR spectra were obtained showing formation of "Zr[1,2-$C_6H_4(NCH_2tBu)_2$]Cl_2" with $B(C_6F_5)_3$·(THF) also present. **Zr[1,2-$C_6H_4(NCH_2tBu)_2$]Cl_2**: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.21 (m, 2H, Ph), 7.17 (m, 2H, Ph), 4.05 (s, 4H, CH_2), 0.88 (s, 18H, *t*Bu). **$B(C_6F_5)_3$·(THF)**: ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 4.28 (m, 2H, OCH_2), 2.12 (m, 2H, CH_2). ^{19}F NMR (376.40 MHz, CD_2Cl_2, 25 °C): δ −132.1 (broad, *o*-C_6F_5), −154.6 (broad, *p*-C_6F_5), −162.9 (broad, *m*-C_6F_5).

5.9. Synthesis of [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Bz_2] (**5**)

A solution of **1** (0.250 g, 0.57 mmol) in toluene (50 mL) was cooled to −78 °C and a solution of Mg(CH_2Ph)Cl in THF (2 M, 1.14 mmol, 0.57 mL) was added. The reaction immediately turned red. The mixture was warmed to room temperature and stirred for 5 h. The solvent was pumped off and subsequent extraction into hexane afforded a red oil, which was recrystallised from cold hexane giving the product identified as [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Bz_2] **5** (0.198 g, 0.416 mmol, 73% yield). *Anal.* Calc. for $C_{30}H_{40}N_2Ti$ (476.17 g/mol): C, 70.66; H, 8.40; N, 5.88. Found: C, 70.45; H, 8.51; N, 5.88%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.26 (m, 2H, Ph), 7.15 (m, 2H, Ph), 6.99 (t, *J* = 7.2 Hz, CH_2*Ph*), 6.94 (t, *J* = 7.2 Hz, CH_2*Ph*), 6.86 (d, *J* = 7.2 Hz, CH_2*Ph*), 3.79 (s, 4H, CH_2), 2.40 (s, 4H, C*H*$_2$Ph), 0.71 (s, 18H, *t*Bu). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.21 (m, 2H, Ph), 7.10 (m, 2H, Ph), 7.19 (t, *J* = 7.6 Hz, CH_2*Ph*), 6.94 (t, *J* = 7.6 Hz, CH_2*Ph*), 6.73 (d, *J* = 7.6 Hz, CH_2*Ph*), 3.84 (s, 4H, CH_2), 2.18 (s, 4H, C*H*$_2$Ph), 0.75 (s, 18H, *t*Bu). ^{13}C{^{1}H} NMR (100.60 MHz, C_6D_6, 25 °C): δ 128.7 (*ipso*-Bz), 129.3, 127.2, 125.3 (Bz), 126.7, 115.5 (Ph), 123.1 (*ipso*-Ph), 81.02 (*C*H_2Ph), 64.6 (*C*H_2N), 34.6 (*ipso-t*Bu), 28.6 (*t*Bu). ^{13}C{^{1}H} NMR (100.60 MHz, CD_2Cl_2, 25 °C): δ 144.4 (*ipso*-Bz), 129.1, 126.8, 124.9 (Bz), 122.8, 115.3 (Ph), 80.4 (*C*H_2Ph), 64.7 (*C*H_2N), 34.8 (*ipso-t*Bu), 28.5 (*t*Bu), *ipso*-Ph not observed.

5.10. Synthesis of [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl{N($SiMe_3$)}] (**6**)

Toluene (50 mL) was added to a mixture of **1** (0.200 g, 0.46 mmol) and Li[N($SiMe_3$)]$_2$ (0.076 g, 0.46 mmol), at room temperature. The reaction immediately turned black. The mixture was stirred for 5 h. The solvent was pumped off and subsequent extraction into hexane afforded a black oil, which was recrystallised from cold hexane giving the product identified as [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Cl{N($SiMe_3$)}] **6** (0.159 g, 0.325 mmol, 70% yield). *Anal.* Calc. for $C_{22}H_{44}N_3Si_2ClTi$ (489.5 g/mol): C, 53.95; H, 8.98; N, 8.57. Found: C, 53.98; H, 8.72; N, 8.36%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.26 (m, 2H, Ph), 7.15 (m, 2H, Ph), 4.45 (d, *J* = 13.5 Hz, 2H, CH_2), 3.78 (d, *J* = 13.5 Hz, 2H, CH_2), 0.83 (s, 18H, *t*Bu), 0.15 (s, 18H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (100.60 MHz, C_6D_6, 25 °C): δ 126.7, 115.5 (Ph), 123.1 (*ipso*-Ph), 67.7 (*C*H_2), 35.9 (*ipso-t*Bu), 28.6 (*t*Bu), 4.6 (Si*Me*$_3$).

5.11. Reaction of [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Bz_2] with $B(C_6F_5)_3$

About 0.010 g (21.0 mmol) of [Ti{1,2-$C_6H_4(NCH_2tBu)_2$}Bz_2] and 0.011 g (21.0 mmol) of $B(C_6F_5)_3$ were placed in a Teflon-valved NMR tube and C_6D_6 was added at room temperature (when the reaction was cooled to −78 °C in CD_2Cl_2, the solvent was vacuum transferred into the NMR tube that had previously been placed in a thermostat-controlled bath). The NMR spectrum was obtained immediately at the desired temperature. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.50 (m, 2H, Ph), 7.20–6.99 (m, 12H, Ph), 5.89 (t, *J* = 7.2 Hz, CH_2*Ph*), 5.77 (t, *J* = 7.2 Hz, CH_2*Ph*), 5.26 (d, *J* = 7.2 Hz, CH_2*Ph*), 4.15 (d, *J* = 12.8 Hz, 4H, CH_2), 3.64 (d, *J* = 13.2 Hz, 4H, CH_2), 3.89 (br, 4H, C*H*$_2$Ph), 2.70 (br, 4H, C*H*$_2$Ph), 0.56 (s, 18H, *t*Bu). ^{19}F NMR (376.40 MHz, C_6D_6, 25 °C): δ −130.4 (s broad, *o*-C_6F_5), −160.5 (s broad, *p*-C_6F_5), −165.0 (s broad, *m*-C_6F_5). ^{1}H NMR (400 MHz, CD_2Cl_2, −70 °C): δ 8.10 (m, 2H, Ph), 7.65 (m, 2H, Ph), 7.30 (t, *J* = 7.6 Hz, CH_2*Ph*), 7.19 (t, *J* = 7.2 Hz, CH_2*Ph*), 7.00–6.73 (Ph), 5.91 (d, *J* = 6.8 Hz, *CH$_2$Ph*), 4.60 (d, *J* = 13.2 Hz, 2H, CH_2), 4.16 (d, *J* = 13.2 Hz, 2H, CH_2), 2.81 (br, 4H, C*H*$_2$Ph), 2.72 (br, 4H, C*H*$_2$Ph), 0.77 (s, 18H, *t*Bu). ^{19}F NMR (376.40 MHz, CD_2Cl_2, 25 °C): δ −131.3 (s broad, *o*-C_6F_5), −165.0 (s broad, *p*-C_6F_5), −167.7 (s broad, *m*-C_6F_5).

5.12. Single-crystal X-ray structure determination of compounds 1,2-$C_6H_4(NHCH_2tBu)_2$, **3**·C_6D_6, and **4**

Relevant crystallographic data and details of the refinements for the structures are given in Table 2. Crystals of **3**·C_6D_6 were grown by slow evaporation of a C_6D_6 solution. Crystals suitable for X-ray diffraction were measured at 100(2) K on a Bruker SMART APEX diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and ϕ and ω scan modes. Crystal structures were solved by direct methods and all non-hydrogen atoms refined anisotropically on F^2 (program SHELXL-97) [58]. The deuterium atoms were located in a difference Fourier synthesis and refined with restrained C–D bond lengths. The methyl group hydrogen atoms were refined as rigid. Other hydrogen atoms were included

Table 2
Crystal data and structure refinement details for 1,2-$C_6H_4(NHCH_2tBu)_2$, **3**·C_6D_6, and **4**.

	1,2-$C_6H_4(NHCH_2tBu)_2$	**3**·C_6D_6	**4**
Formula	$C_{16}H_{28}N_2$	$C_{38}H_{52}ClD_6N_4Ta$	$C_{40}H_{38}N_4Zr$
FW	248.40	793.32	425.76
Color habit	red prism	orange prism	yellow stick
Crystal dimensions (mm^3)	2.9 × 2.5 × 1.8	0.09 × 0.07 × 0.06	0.44 × 0.38 × 0.36
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$C2/c$	$P2_12_12_1$
a (Å)	11.3619(11)	13.6723(5)	13.438(5)
b (Å)	11.462(2)	15.6431(6)	16.869(8)
c (Å)	12.748(2)	18.5698(7)	20.570(2)
β (°)	97.557(15)	110.2660(10)	90
V (Å^3)	1645.8(4)	3725.8(2)	4663(3)
Z	4	4	4
T (K)	200(2)	100(2)	200(2)
D_{calcd} ($g\,cm^{-3}$)	1.003	1.414	1.213
μ (mm^{-1})	0.058	3.052	0.481
$F(0\,0\,0)$	552	1616	1808
θ Range (°)	3.55–27.50	2.05–27.88	3.55–27.50
Number of reflections collected	36 908	25 468	82 570
Number of independent reflections/R_{int}	3772 [R_{int} = 0.078]	4316 [R_{int} = 0.0346]	10 663 [R_{int} = 0.0796]
Data/restraints/parameters	3772/0/172	4316/426/252	10 663/279/485
R_1/wR_2 ($I > 2\sigma(I)$)	R_1 = 0.0561, wR_2 = 0.1327	R_1 = 0.0221, wR_2 = 0.0494	R_1 = 0.0604, wR_2 = 0.1342
R_1/wR_2 (all data)	R_1 = 0.1206, wR_2 = 0.1559	R_1 = 0.0251, wR_2 = 0.0507	R_1 = 0.0786, wR_2 = 0.1424
Extinction coefficient	0.016(3)		0.0456(14)
Goodness-of-fit (GOF) (on F^2)	1.023	1.057	1.256
Difference in peak/hole (e Å^{-3})	0.262 and −0.154	1.026 and −0.530	0.766 and −0.773

using a riding model. The deuterated benzene molecule is disordered over two sites. The programs use neutral atom scattering factors, $\Delta f'$ and $\Delta f''$ and absorption coefficients from the International Tables for Crystallography [59].

Suitable crystals of the diamine 1,2-$C_6H_4(NHCH_2tBu)_2$ and **4** were selected, manipulated under argon with perfluoropolyether and mounted on a glass fiber. The intensity data sets were collected at 200 K on a Bruker–Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. The structures were solved, using the WINGX package [60], by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97) [58]. All non-hydrogen atoms were anisotropically refined. In **4** C15, C30 and C32 were disordered in two positions, also, in **4** some SIMU and DELU restraints were applied. Hydrogen atoms were geometrically placed and left riding on their parent atoms, with the exception of the hydrogen atom on N(1) and N(2) for the diamine 1,2-$C_6H_4(NHCH_2tBu)_2$ that were found in the Fourier map and refined freely. Relevant crystallographic data and details of the refinements for the two structures are given in Table 2.

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Appendix A. Supplementary data

CCDC 710428, 711924 and 710429 contain the supplementary crystallographic data for (1,2-$C_6H_4(NHCH_2tBu)$ **2**, compound **3** and compound **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.05.055.

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