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Monocyclopentadienyl Phenoxido–Amino and Phenoxido–Amido Titanium Complexes: Synthesis, Characterisation, and Reactivity of Asymmetric Metal Centre Derivatives

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Reduction of phenol–imine derivatives R′N=CH(3,5-$R_2C_6H_2$-2-OH) (R = *t*Bu; R′ = C_6H_5 **1a**, *p*-MeC_6H_4 **1b**, Cy **1c**, *t*Bu **1d**, 2,6-$Me_2C_6H_3$ **1e**; R = H; R′ = *p*-MeC_6H_4 **1f**; Cy = cyclohexyl) with MBH_4 (M = Li, Na) or $AlLiH_4$ in ethyl ether or thf at room temperature affords the phenol–amine compounds R′$NHCH_2$(3,5-$R_2C_6H_2$-2-OH) **2a–c** and **2e**,**f**. The *N*-R-[2,4-di-*tert*-butyl]benzo-1-oxa-3-azine species (R = *t*Bu **2d1**, 2,6-$Me_2C_6H_3$ **2e1**) are obtained by Mannich reaction of 2,4-di-*tert*-butylphenol with RNH_2 in refluxing methanol. Intermediate **2d1** is converted in ethanol at room temperature into *N*-*tert*-butyl[2-hydroxy-3,5-di-*tert*-butyl]benzylamine (**2d**), whereas **2e** is not obtained from **2e1** by using this procedure. *N*-alkyl,*N*-*tert*-butyl[2-hydroxy-3,5-di-*tert*-butyl]benzylamine compounds *t*BuN(*R*)CH_2(3,5-*t*$Bu_2C_6H_2$-2-OH) (R = Me **2g**, Et **2h**, *n*Pr **2i**, CH_2Ph **2j**) are also prepared by the appropriate synthetic method. Treatment of **2a–c** with 1 equiv. of $TiCpCl_3$ in the presence of 2.5 equiv. of NEt_3 in hexane at room temperature gives the monocyclopentadienyl phenoxido–amido monochloride complexes TiCp[R′NCH_2(3,5-*t*$Bu_2C_6H_2$-2-O)]Cl (R′ = C_6H_5 **3a**, R′ = *p*-MeC_6H_4 **3b**, R′ = Cy **3c**). The analogous complex Ti(η^5-$C_5H_4SiMe_2Cl$)[$C_6H_5NCH_2$(3,5-*t*$Bu_2C_6H_2$-2-O)]-Cl (**4a**) results from the reaction of **2a** with Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3. Nevertheless, **2d** reacts with $TiCpCl_3$ in hexane in the presence of NEt_3 at room temperature yielding the monocyclopentadienyl phenoxido dichloride compound TiCp[*t*$BuNHCH_2$(3,5-*t*$Bu_2C_6H_2$-2-O)]Cl_2 (**5**), whereas in ethyl ether and in the absence of NEt_3 adduct **5**·HCl is obtained, which is further converted into TiCp[*t*$BuNCH_2$(3,5-*t*$Bu_2C_6H_2$-2-O)]Cl (**3d**) by addition of a NEt_3/ethyl ether solution. The reaction of $TiCpCl_3$ with **2a** in the presence of 2.5 equiv. of NEt_3 in a polar solvent (thf, CH_2Cl_2 or toluene) at room temperature affords TiCp[Ph(H)NCH_2(3,5-*t*$Bu_2C_6H_2$-2-O)]Cl (**6a**) as a mixture of two stereoisomers. All the reported compounds were characterised by the usual analytical and spectroscopic methods and the molecular structures of **2a**, **2d**, **2e** and **3d** were determined by X-ray diffraction analysis from suitable single crystals. Preliminary studies of catalytic activity for ethylene polymerisation by using solid methylaluminoxane as cocatalyst were performed.

Introduction

Over the two last decades organometallic chemists involved in polyolefin chemistry have mainly focused their attention and efforts on designing organometallic systems with a specific architecture, which depends on the nature of the ligands. Investigation and applications in olefin catalysis of new group 4 metal complexes containing heteroatom–base ligands have progressed steadily with a view to prepare new high-value-added materials compared to those obtained by using the legendary Ziegler–Natta or [MCp_2X_2] (X = halo, alkyl, aryl) metallocene precursors.[1] Preparation of nitrogen-, oxygen-, sulfur- and phosphorus-based molecules encompasses a large proportion of preligand synthesis. Particularly interesting are ligands with nitrogen and oxygen as donor atoms, due to their mode of complexation to an acidic metal centre. Examples of these ligands including phenoxido–imino[2–9] are synthesised through well-established synthetic methods from which group 4 metal complexes with tunable electronic and coordination geometry properties have been prepared. In recent years, we have reported the synthesis of a series of cyclopentadienyl titanium complexes containing chelating dialkoxido[10–12] and diamido[13,14] ligands and studied the nature of the catalytic species in the α-olefin polymerisation processes generated by the reaction of these complexes with aluminum and boron reagents as cocatalyst.[15]

In this paper we report the synthesis and characterisation of secondary phenol–amine compounds R′$NHCH_2$(3,5-$R_2C_6H_2$-2-OH) obtained from the phenol–imine derivatives R′N=CH(3,5-$R_2C_6H_2$-2-OH) and tertiary phenol–amine compounds *t*$BuN(R)CH_2$(3,5-*t*$Bu_2C_6H_2$-2-OH) derived from the corresponding benzoxazine derivatives. Phenol–amine molecules are used as ligand precursors to synthesise phenoxido–amido $TiCp^R$[R′NCH_2(3,5-*t*$Bu_2C_6H_2$-2-O)]Cl

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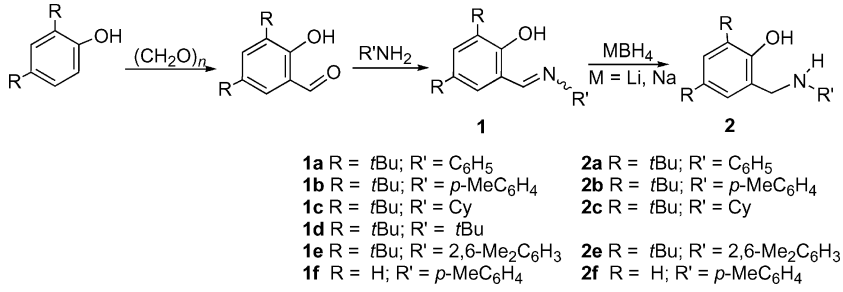
and phenoxido–amino TiCp[*t*BuNHCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl$_2$ titanium derivatives. Preliminary studies of catalytic activity for ethylene polymerisation by using solid methylaluminoxane (sMAO) as cocatalyst were performed.

Results and Discussion

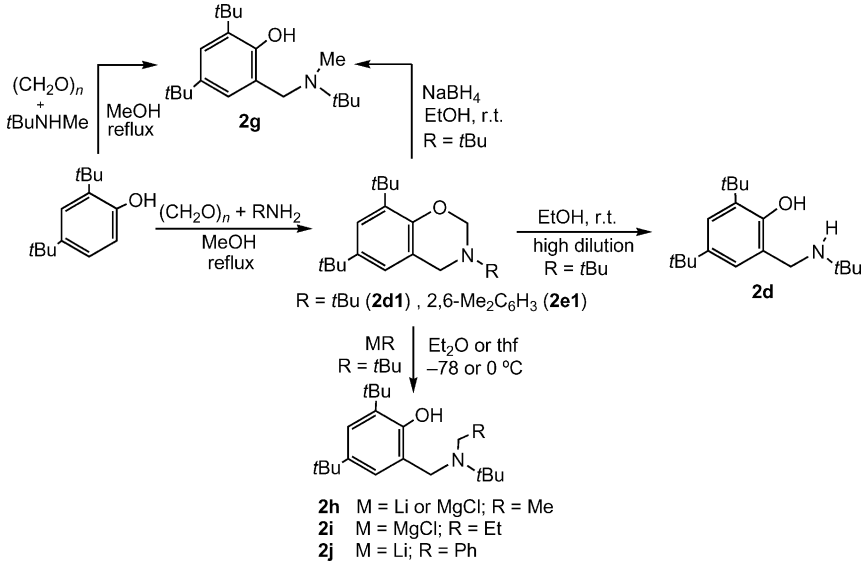
Phenol–Amine Molecules as Precursors of Phenoxido–Amido and Phenoxido–Amino Ligands

Phenol–amine compounds **2a**–**c** and **2e**,**f** (Scheme 1) were isolated in high yield by reduction of the corresponding phenol–imine derivatives **1** with MBH$_4$ (M = Li, Na) or AlLiH$_4$ in ethyl ether or thf at room temperature, in a similar way to analogous procedures previously reported in the literature.[16,17] The Mannich reaction of 2,4-di-*tert*-butylphenol with RNH$_2$ (R = *t*Bu, 2,6-Me$_2$C$_6$H$_3$) and paraformaldehyde in refluxing methanol afforded *N*-R-[2,4-di-*tert*-butyl]benzo-1-oxa-3-azine species **2d1** and **2e1**, which were isolated as pure substances after workup. Intermediate **2d1** is converted at room temperature into *N*-*tert*-butyl-[2-hydroxy-3,5-di-*tert*-butyl]benzylamine (**2d**) by using ethanol with high dilution (Scheme 2), whereas **2e1** is not converted into **2e** by this procedure. Compound **2d** is obtained as analytically pure X-ray quality needles in 20% yield after crystallisation from ethanol at –10 °C (vide infra). Molecule **2g** was synthesised from **2d1** by reduction with NaBH$_4$ in ethanol at room temperature[18] or, alternatively, by the direct Mannich reaction of 2,4-di-*tert*-butylphenol with a slight excess of *t*BuNHMe and paraformaldehyde in refluxing methanol and isolated as an analytically pure yellow oil in 80–90% yield after workup and purification. The analogous *N*-alkyl,*N*-*tert*-butyl-[2-hydroxy-3,5-di-*tert*-butyl]benzylamine substances **2h**–**j** were prepared from **2d1** by ring-opening–nucleophilic attack[19–22] on the O,N-methylene carbon atom at –78 or 0 °C with the appropriate alkyl reagent (**2h**: M = Li or MgCl, R = Me; **2i**: M = MgCl, R = Et; **2j**: M = Li, R = Ph) (Scheme 2). All compounds were isolated as analytically pure yellow oils in good yields (**2h**: 83% yield; **2i**: 78% yield; **2j**: 72% yield) after workup and purification.

Compounds **1** and **2** were obtained as solids or oils, and they are soluble in aromatic, aliphatic and chlorinated hydrocarbon solvents. The analytical composition fits well with the proposed formulations. The ^{1}H NMR spectra ($CDCl_3$, 20 °C) of compound set **1** show low-field shifted resonances assignable to the –OH (δ = 11.62–14.56 ppm) and –CH=N (δ = 8.32–9.85 ppm) protons. The presence of the amine group in compound set **2** promotes the disappearance of the conjugate system in the organic molecules and, consequently, the high-field shift in the ^{1}H NMR spec-



Scheme 1.



Scheme 2.

tra of the signals corresponding to the OH protons. The ^{1}H NMR spectra of **2a**–**c** and **2f** exhibit the characteristic signals for the OH group at $\delta \approx 8.50$ ppm. However, the respective resonances for compounds **2d** and **2e** appear at δ = 11.32 ppm and δ = 10.27 ppm, respectively, due to the large steric hindrance of the amine substituents group. The NMR spectroscopic data of **2d** in $CDCl_3$ solution exhibit an identical nature for the main signals with slight differences in chemical shifts compared to those of **2d1**. Resonances assignable to the O,N-methylene protons, two AB patterns for the methine protons of the arene ring with coupling constants ^4J = 2.1 and 2.4 Hz and the two characteristic resonances downfield shifted at δ = 78.2 and 54.3 ppm for the O,N-methylene- and the quaternary carbon atoms of the *tert*-butyl carbon atom linked to the nitrogen atom are observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2d1** in $CDCl_3$ solution. The signals for the –OH and *N*-methyl protons in the expected range δ = 4.64 and 2.23 ppm, respectively, appear in the ^{1}H NMR spectrum of **2g** ($CDCl_3$, 20 °C). Similarly, the NMR spectra of the *N*-alkyl,*N*-*tert*-butyl[2-hydroxy-3,5-di-*tert*-butyl]benzylamine series **2h**–**j** exhibit characteristic signals for the protons and the carbon atoms in the molecules.

The solid-state structures of compounds **2a**, **2d** and **2e** were confirmed by single-crystal X-ray diffraction studies (Figures 1 and 2). Selected bond lengths and angles are listed in Table 1. The synthesis of compound **2d** was previously published,[23,24] but no crystallographic data have been reported in the literature. In the three structures the chiral N1 centres show a tetrahedral environment. For compound **2d**, the two possible enantiomers crystallised together (**2d** and **2d′**) and the racemic mixture appears in the crystal. In the structure, the C10 and N1 atoms are disordered. When this disorder was treated, the disposition of the atoms C10/N1 and C10′/N1′ seems to be related to the existence of both enantiomers in the asymmetric unit as shown in Figure 1 (trying to solve the structure in a lower symmetry space group gives a resolution model with worse agreement values). For **2a** and **2e**, the presence of an aromatic substituent on the nitrogen atom provides an additional chirality feature, as the orientation of the rings gives conformational chirality, rendering these compounds diastereomeric. Interestingly only one of the possible diastereomers crystallises; although due to the absence of heavy atoms, a reliable absolute configuration cannot be determined. In the solid state, intramolecular hydrogen bonding OH···N is observed for the three compounds, in agreement with the behaviour deduced in solution from NMR spectroscopic studies. Although there are no crystallographic data for Mannich organic homologue molecules with a "CH_2NR_2" pendant arm, the molecular structures of analogous benzamide derivatives have been described,[25] which present similarities in the structural parameters of the phenolic skeleton and the *N*-alkylamino ends with that observed for **2a**, **2d** and **2e**.

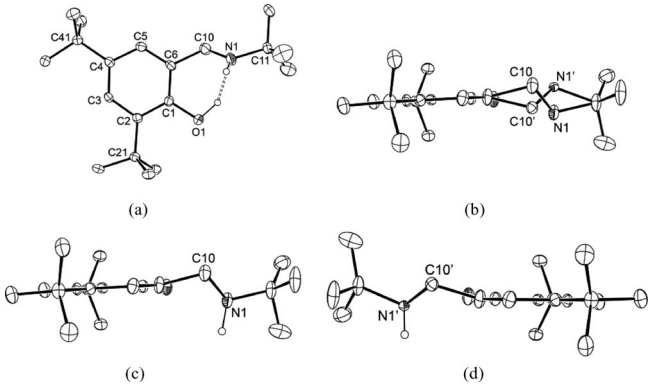


Figure 1. Molecular structures of **2d**: (a) frontal view of the structure; (b) side view showing the disorder present in the structure; (c) and (d) separated side view of both enantiomers **2d** and **2d′** (ORTEP view with 30% probability ellipsoids).

Table 1. Selected interatomic distances [Å] and angles [°] for compounds **2a**, **2d/2d′** and **2e**.

Bonds	**2a**	**2d**	**2d′**	**2e**
O1–C1	1.387(3)	1.370(2)	1.370(2)	1.385(4)
C6–C10	1.526(4)	1.553(6)	1.539(5)	1.524(4)
C10–N1	1.473(3)	1.427(6)	1.484(6)	1.494(4)
N1–C11	1.424(2)	1.513(4)	1.547(4)	1.458(4)
O1···N1	2.806	2.716	2.628	2.777
Angles				
N1–C10–C6	110.4(2)	109.1(4)	109.0(3)	110.6(3)
C11–N1–C10	118.9(2)	115.0(4)	109.1(3)	115.5(5)
C11–N1–H1	112(2)	114(3)	114(2)	109(3)
C10–N1–H1	113(2)	108(2)	111(2)	106(3)
O1–H2···N1	143	146	151	149

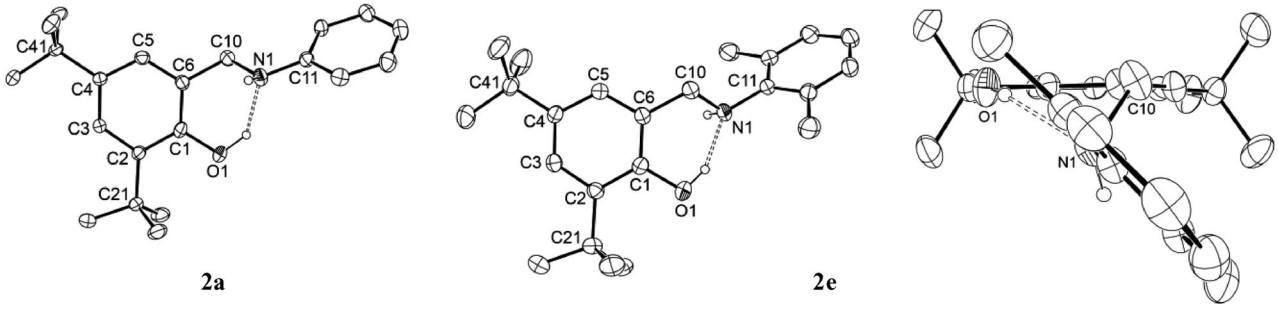
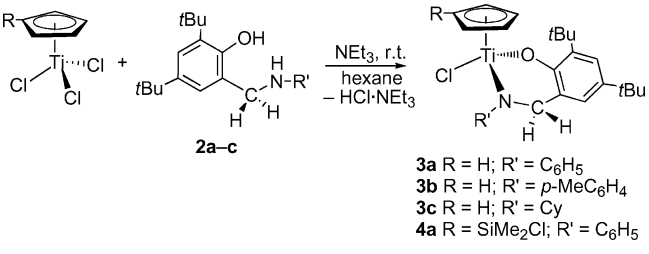


Figure 2. Molecular structures of **2a** and **2e** (a side view of **2e** showing the disposition of the aromatic rings is included) (ORTEP view with 30% probability ellipsoids).

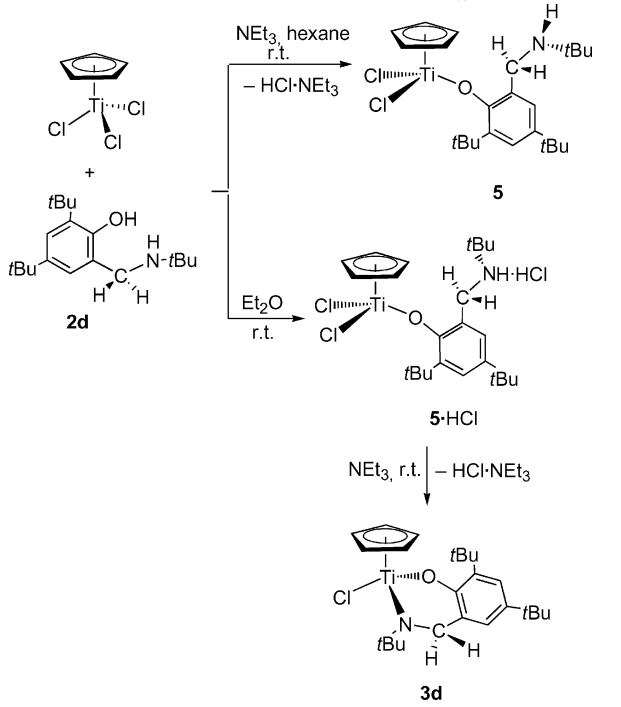
Titanium Derivatives Containing Phenoxido–Amido and Phenoxido–Amino Ligands

Compounds **2a**–**c** react with 1 equiv. of $TiCp^RCl_3$ in the presence of 2.5 equiv. of NEt_3 in hexane at room temperature to give the monocyclopentadienyl phenoxido–amido monochloride complexes $TiCp^R[R'NCH_2(3,5\text{-}tBu_2C_6H_2\text{-}2\text{-}O)]Cl$ (Cp^R = Cp, R′ = C_6H_5 **3a**, *p*-MeC_6H_4 **3b**, Cy **3c**; Cp^R = η^5-$C_5H_4SiMe_2Cl$, R′ = C_6H_5 **4a**) (Cy = cyclohexyl) (Scheme 3), which exhibit an asymmetric titanium centre. The formation of compounds **3a**–**c** and **4a** is interpreted as a result of the combination of Ti–Cl bond aminolysis and hydrolysis reactions. Nevertheless, depending on the reaction conditions (solvent nature, temperature or phenol–amine reagent) the hydrolysis reaction is favoured, leaving the N–H phenol–amine group unreacted to yield phenoxido–amine derivatives. Thus, treatment of $TiCpCl_3$ with **2d** in hexane or pentane in the presence of NEt_3 at room temperature proceeds with the formation of the monocyclopentadienyl phenoxido dichloride compound $TiCp[tBu(H)NCH_2(3,5\text{-}tBu_2C_6H_2\text{-}2\text{-}O)]Cl_2$ (**5**; Scheme 4). In this case, coordination of the amine group is hindered as a consequence of the higher steric hindrance of the *tert*-butylamine substituent relative to that of the amine substituents in **2a**–**c**. However, the same reaction carried out in refluxing hexane or toluene gives a mixture of final products in which the presence of **5** and the phenoxido–amido complex $TiCp[tBuNCH_2(3,5\text{-}tBu_2C_6H_2\text{-}2\text{-}O)]Cl$ (**3d**) is observed. Adduct **5**·HCl was obtained as a pure solid when $TiCpCl_3$ was treated with **2d** for 3 h in ethyl ether at room temperature in the absence of NEt_3. The amine functionality of the phenol–amine starting reagent is itself used as a base under these conditions, scavenging the HCl generated in the reaction to form the corresponding insoluble ammonium salt **5**·HCl, thus preventing the formation of subsequent secondary reaction products. A sample of **5**·HCl evolves through the addition of a NEt_3/ethyl ether solution into **3d**, which is obtained as the only analytically pure reaction product after ca. 7 d (Scheme 4). Formation of mononuclear phenoxido–amido derivatives **3**, instead of alternative dinuclear complexes containing bridging ligand, is favoured in these reactions due to the thermodynamic stability imposed by the six-membered ring exhibited by these species and the inherent entropy favourability.



Scheme 3.

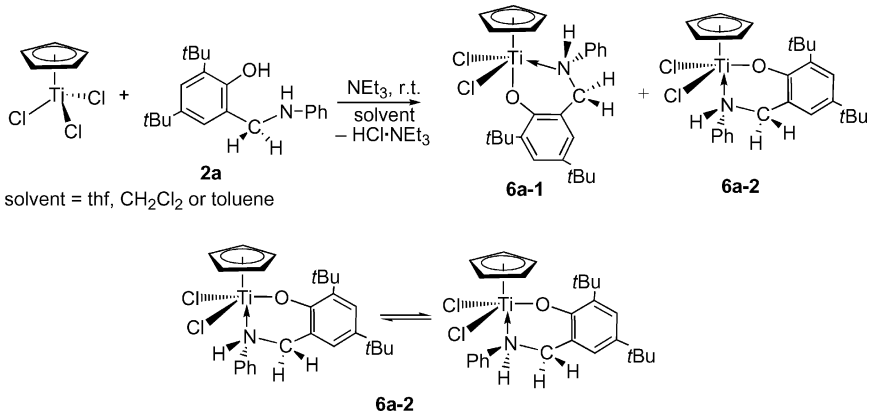
In contrast, the reaction of $TiCpCl_3$ with **2a** in the presence of 2.5 equiv. of NEt_3 in a more polar solvent (thf, CH_2Cl_2 or toluene) at room temperature proceeds with the formation of $TiCp[Ph(H)NCH_2(3,5\text{-}tBu_2C_6H_2\text{-}2\text{-}O)]Cl_2$ (**6a**) stabilised by coordination of the phenoxido ligand and the amine functionality. The NMR spectroscopic analysis reveals that **6a**, obtained according to this procedure, is indeed a mixture of two stereoisomers **6a-1** and **6a-2** (Scheme 5). Axial or equatorial coordination of the amine nitrogen atom in a bipyramidal trigonal geometry around the titanium centre is proposed.



Scheme 4.

The alkylation reactions of **3a**–**c** with 1 equiv. of LiMe, MgClMe or $MgCl(CH_2Ph)$ in hexane or ethyl ether at –78 °C gave an unstable, intractable and unresolved mixture of products whose ^1H NMR spectra were regrettably uninformative, indicating the action of reduction processes. Attempts to synthesise alkyl derivatives by treatment of $TiCpR_3$ (R = Me, CH_2Ph) with **2** were also unsuccessful. When **3d** reacts with 1 equiv. of MgClMe at –78 °C in *n*-hexane, the formation of the methyl complex $TiCp[tBuNCH_2(3,5\text{-}tBu_2C_6H_2\text{-}2\text{-}O)]Me$ was spectroscopically observed [^1H NMR (300 MHz, C_6D_6) for $TiCp[tBuNCH_2(3,5\text{-}tBu_2C_6H_2\text{-}2\text{-}O)]Me$: δ = 0.97 (s, 3 H, Ti-CH_3), 1.03, 1.47, and 1.74 (3×9 H, s, $C(CH_3)_3$), 2.66 and 3.81 (2 H, AB system, $J_{A,B}$ = 16.5 Hz, CH_2), 6.20 (s, 5 H, Cp), 7.29 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO), 7.72 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO) ppm]. Repeated efforts to obtain this compound as a pure sample on a preparative scale remain unfruitful.

Compounds **3**–**6** are air sensitive but thermally stable in solution and in the solid state, and they can be stored unaltered for weeks if strictly inert atmospheric conditions are maintained. They are soluble in aromatic and chlorinated solvents but poorly soluble in aliphatic hydrocarbons. All of these compounds were fully characterised by NMR spec-



Scheme 5.

troscopy and elemental analysis. The analytical composition fits well the proposed formulations. In addition, the X-ray molecular structure of **3d** is reported.

Compounds **3a**–**d** and **4a** are asymmetric metal-centred derivatives. Their ^{1}H NMR spectra (C_6D_6 or $CDCl_3$, 20 °C; see Exp. Sect.) show AB spin systems ($^2J \approx 16.5$ Hz) for the CH_2 protons, two signals for the *tert*-butyl groups, two doublets ($^4J \approx 2.4$ Hz) for the phenoxido and the expected resonances for the N-R substituents protons. A singlet for the cyclopentadienyl ring protons in the ^{1}H NMR spectra of **3a**–**d** is also observed, whereas the ^{1}H NMR spectrum of compound **4a** exhibits an ABCD spin system for the cyclopentadienyl ring and two singlets for the nonequivalent $SiMe_2Cl$ group protons. These spectroscopic data are consistent with a dissymmetric geometry in solution. The ^{1}H NMR spectrum of **5** (C_6D_6, 20 °C) shows a broad signal at $\delta = 7.65$ ppm assignable to the NH proton ($\delta = 9.40$ ppm for the NH·HCl protons in **5**·HCl) and the methylene protons appear as a broad signal at $\delta = 3.87$ pm ($\delta = 4.30$ ppm for **5**·HCl), high-field shifted relative to those of compounds **3** and **4** indicating that the nitrogen atom is not coordinated to the metal centre. The spectra of **5** and **5**·HCl also display the expected resonances of the cyclopentadienyl ring, phenoxido and *tert*-butyl protons. Similar characteristic results were observed in the $^{13}C\{^1H\}$ NMR spectra under the same conditions.

The ^{1}H NMR spectrum of **6a** (C_6D_6, 20 °C) exhibits two different sets of sharp signals indicating the presence of two stereoisomers. Isomer **6a-1** shows an ABX spin system for the CH_2NH fragment (pseudotriplet for the NH proton at $\delta = 3.24$ ppm and pseudodoublets for the methylene protons at $\delta = 4.26$ and 4.46 ppm, with coupling constant values of $^3J_{A,X/B,X}$ and $^2J_{A,B}$ of about 6.5 and 4.5 Hz, respectively). Isomer **6a-2** exhibits an AA′X spin system for the CH_2NH fragment (pseudotriplet for the NH proton at $\delta = 3.71$ ppm and pseudodoublet for the methylene protons at $\delta = 4.51$ ppm with coupling constant values of $^3J_{A,X} \approx 6.7$ Hz). The NH resonances for both isomers appear considerably shifted downfield with respect to that found for free amine **2a** and high-field shifted relative to that of **3a**. These spectroscopic data are in agreement with C_1 and C_s symmetry for **6a-1** and **6a-2**, respectively, and indicate that the nitrogen atom is coordinated to the metal centre. The NMR spectroscopic features for **6a-1** are consistent with a chiral species, which stems from the rigid coordination of the amine functionality, thus preventing epimerisation at the amine nitrogen atom, as well as the diverse nature of the amine substituents, which makes the nitrogen atom become a stereogenic centre. In contrast, the C_s symmetry suggested for **6a-2** in solution can be explained by a non-rigid disposition involving a rapid decoordination/coordination process of the pendant amine group leading to an equilibrium position of the methylene hydrogen atoms (Scheme 5). Similar behaviour has been observed for analogous cyclopentadienyl titanium derivatives.[26–28] Such altered behaviour is due to the different *trans* influence derived from the presence of a chloride or a cyclopentadienyl ligand located in the *trans* position with respect to the amino functionality in **6a-1** and **6a-2**, respectively.

The molecular structure of TiCp[*t*BuNCH$_2$(3,5-*t*Bu$_2$-C$_6$H$_2$-2-O)]Cl (**3d**) was confirmed by a single-crystal X-ray diffraction study. The metal is an asymmetric centre. A racemic mixture of the two possible enantiomers appears in the unit cell, and Figure 3 illustrates the view of one of the two possible isomers. The compound is mononuclear and the coordination geometry around the titanium centre is similar to that observed in analogous $TiCpL_3$ complexes.[29] The angles around the nitrogen atom show the expected values for geometry consistent with sp^2 hybridisation. The Ti–N [1.9052(18) Å] and Ti–O [1.8528(15) Å] bond lengths are comparable to those present in derivatives with an appreciable multiple bond character, suggesting pπ–dπ interactions.[30–35] Compared with similar dialkoxido or diamido derivatives TiCp′(ER)$_2$Cl (E = N, O), previously prepared in our group, the Ti–O bond length is clearly longer [1.8528(15) Å vs. 1.801 Å average].[10,11] However, the Ti–N distance remains nearly identical.[13] Finally, the Ti–O–C_{Ph}–C_{Ph}–$C_{methylene}$–N core appears as a six-membered ring, where the sp^3 methylene carbon atom is placed out of the plane defined by the rest of the atoms. The C–C distances within the cyclopentadienyl ring, Ti–Cg(centroid) distance and Ti–Cl bond length are within the range for monocyclopentadienyl and dicyclopentadienyl titanium complexes.[31,33]

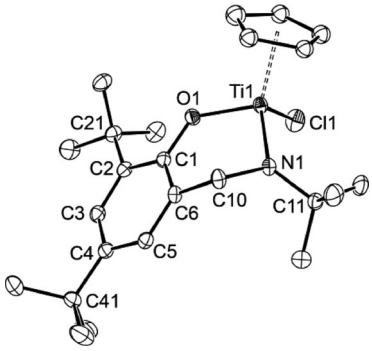


Figure 3. ORTEP view of **3d** with 30% probability ellipsoids. Selected interatomic distances [Å] and angles [°]: Ti1–Cl1 2.3120(8), Ti1–N1 1.9052(18), Ti1–O1 1.8528(15), Ti1–Cg 2.109, Cl1–Ti1–N1 106.99(6), Cl1–Ti1–O1 102.40(6), N1–Ti1–O1 94.14(7), Ti1–N1–C10 109.40(13), Ti1–N1–C11 135.04(14), C11–N1–C10 114.48(16), Ti1–O1–C1 130.37(13). Cg denotes the centroid of the Cp ligand.

Olefin Polymerisation Studies

Given our interest in the polymerisation chemistry of group 4 monocyclopentadienyl diamido[15] or dialkoxido[10,11] metal complexes, we undertook preliminary studies on α-olefin polymerisation process for these monocyclopentadienyl phenoxido–amido compounds in the presence of sMAO as cocatalyst.[36] Ethylene polymerisation was investigated by using 50 mL total volume of toluene with 10^{-4} mol of catalyst and a 400 sMAO/Ti molar ratio at 1 atm pressure for 15 min. The observed results show averages of two or, in some cases, more polymerisation runs, which showed good reproducibility. Polymerisation reactions by using a lower solvent volume (10, 20, 30 or 40 mL) were performed. The best reproducibility of the final results, maintaining the rest of the variables constant, was obtained by using 50 mL of toluene.

The catalytic activity for complexes is sensitive to temperature, increasing the polymerisation activity at low temperatures. No polymerisation was found when the reaction was carried out at 50 °C, whereas activities at 20 °C (1.0 kg Pol mol^{-1} P^{-1} h^{-1} for **3a** and 0.9 kg Pol mol^{-1} P^{-1} h^{-1} for **4a**) and 10 °C (18.4 kg Pol mol^{-1} P^{-1} h^{-1} for **3a** and 10.2 kg Pol mol^{-1} P^{-1} h^{-1} for **4a**) were observed. Compounds **3c** and **3d** are slightly more active than **3a** and **4a** under similar reaction conditions, exhibiting higher activity at 20 °C (408.0 kg Pol mol^{-1} P^{-1} h^{-1} for **3c** and 187.3 kg Pol mol^{-1} P^{-1} h^{-1} for **3d**) than that at 10 °C (166.8 kg Pol mol^{-1} P^{-1} h^{-1} for **3c** and 98.0 kg Pol mol^{-1} P^{-1} h^{-1} for **3d**).

In an effort to model the nature of the catalytic species generated in these catalyst systems, the reaction of phenoxido–amido monochloride derivative **3a** with sMAO was examined. Treatment, at –78 °C, of a solution of TiCp[PhNCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl in C$_6$D$_6$ with an excess amount of sMAO resulted in the immediate formation of a dark solution generating the expected monomethyl titanium complex TiCp[PhNCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Me (monitoring by NMR spectroscopy). The methylated compound decomposes at room temperature, and evolution by ligand transfer from titanium to aluminum probably occurred.[15]

The decreased trend in activity observed as the temperature is raised for these precatalysts in the α-olefin polymerisation might be due to a catalytically active decomposition process through ligand abstraction by MAO, which may cause a partial or complete loss of the ligand resulting in one or more inactive species for α-olefin polymerisation.[15,37] Compounds **3c** and **3d** are stabilised by coordination of phenoxido–amido ligands with higher N-donor ability compared with **3a** and **4a**, suggesting a more stable methyltitanium species obtained under these polymerisation reaction conditions. These results correlate well with those observed in the alkylation reactions of **3** with LiMe, MgClMe or MgCl(CH$_2$Ph).

The polyethylene samples obtained had melting points of 130–135 °C, characteristic of high-density polyethylene, and remarkable differences in the ΔH enthalpy values and the degree of crystallinity (α).

Conclusions

In this report we provided a contribution to the synthesis and characterisation of new and somewhat unusual phenoxido–amido and phenoxido–amino titanium complexes containing asymmetric metal centres. The new complexes are interesting from basic coordination chemistry perspectives because only a few derivatives of this type are known. Initial studies of their ethylene polymerisation performance under MAO activation conditions have been developed.

Experimental Section

General Considerations: All manipulations and reactions of air- and/or moisture-sensitive compounds were carried out under argon (Air Liquid N45, O_2: 1 ppm; H_2O: 3 ppm) by using Schlenk and high-vacuum line techniques or in a dry argon atmosphere MBraun glove box model MB150B-G. All glassware was dried under vacuum with a heat gun and purged three times by using vacuum–argon filling cycles. The solvents (Baker and SDS) used for flash column chromatography and air- and/or moisture-sensitive compounds were of reagent grade and, when necessary, were purified by distillation under argon before use by employing the appropriate drying agent, and collected under argon in a Schlenk-type vessel followed by several freeze–thaw cycles when necessary. Methanol and ethanol (SDS and Carlo Erba) were dried and purified according to literature procedures.[38] Deuterated solvents were firstly degassed by several freeze–thaw cycles, held at room temperature over fresh activated 4 Å molecular sieves (10% w/v) for several days, and then stored at room temperature over freshly activated 4 Å molecular sieves (10% w/v). Compounds TiCpCl$_3$[39,40] and Ti(η^5-C$_5$H$_4$SiMe$_2$Cl)Cl$_3$[41] were prepared by a known procedure. Aniline, *p*-toluidine, cyclohexylamine, 2,6-dimethylaniline, 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, salicylaldehyde, paraformaldehyde, 2,4-di-*tert*-butylphenol, LiBH$_4$, NaBH$_4$ and AlLiH$_4$, LiMe (1.6 M solution in Et$_2$O) or MgClMe (3 M solution in thf), MgClEt (2 M solution in Et$_2$O) and LiPh [2 M solution in cyclohexane/ethyl ether mixture (Aldrich)] were used as received. *tert*-Butylamine and *N*-*tert*-butyl-

methylamine (Aldrich) were purified under argon according to literature procedures.[38] Solid $AlMe_3$-free methylaluminoxane (sMAO) was obtained from methylaluminoxane (MAO) (CROMPTON, 10 wt.-% solution in toluene) by drying under reduced pressure at 50 °C to remove the uncoordinated $AlMe_3$ and used after washing with *n*-hexane and complete drying. Flash column chromatography purification was carried out using the Still's method[42] employing silica gel 60 (60 Å, 40–63 μm, 230–400 Mesh ASTM, E. Merck), which was oven-dried before use. TLC analysis was carried out by using precoated silica gel 60 F254 on aluminum foil (60 Å, layer thickness 0.2 mm, E. Merck), oven-dried before use with reproducible results. Usual detection means used for TLC were successively UV_{254}, I_2 on silica gel, a 5% solution of phosphomolybdic acid (Fluka) in ethanol with heating. The IR spectra were recorded at room temperature with a Perkin–Elmer Spectrum-2000 FTIR spectrophotometer. C, H and N microanalyses were performed with a Perkin–Elmer 240B and/or Heraeus CHN-O-Rapid microanalyser. The NMR samples of air- and/or moisture-sensitive compounds were prepared under argon at room temperature in a 5 mm Wilmad 507-PP tubes fitted with a J. Young Teflon valve. The NMR spectra were recorded with a Varian Mercury VX-300 PFG at 20 °C. The chemical shifts and coupling constant *J* are quoted in ppm and in Hertz, respectively, and are referenced with respect to residual proton and carbon resonances of the solvent ($CDCl_3$: ^1H: 7.25 ppm, ^{13}C: 77.1 ppm; C_6D_6: ^1H: 7.15 ppm, ^{13}C: 128.0 ppm), which is also referenced with respect to $SiMe_4$. The assignment of the signals in NMR spectra was made by using standard Varian pulse sequences for all compounds and selective ^1H–^1H homodecoupling for some. Melting points of solid samples placed in a dried capillary tube sealed under high vacuum were determined with a Bibby Stuart Scientific device with a heating rate of 0.5 °C min^{-1} with reproducible and uncorrected results. The poor solubility of the polymers in several solvents precluded analysis by GPC.

(C_6H_5)N=CH(3,5-*t*$Bu_2C_6H_2$-2-OH) (1a): Aniline (9.2 mL, 100 mmol) was added under vigorous stirring to a solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (100 mmol, 23.43 g) in methanol (250 mL), which was allowed to react for 12 h. The crystalline orange solid was filtered, dried under reduced pressure and characterised as **1a** (29.41 g, 95.0 mmol, 95% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.26 [s, 9 H, C(CH_3)$_3$], 1.31 [s, 9 H, C(CH_3)$_3$], 7.14–7.21 (5 H, m. C_6H_5N), 7.32 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 7.57 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 9.85 (s, 1 H, C*H*), 11.62 (s, 1 H, O*H*) ppm. $C_{21}H_{29}NO$ (309.4): calcd. C 81.51, H 8.79, N 4.53; found C 81.53, H 8.65, N 4.67.

(*p*-MeC_6H_4)N=CH(3,5-*t*$Bu_2C_6H_2$-2-OH) (1b): A procedure similar to that described for **1a** but with the use of *p*-toluidine (10.72 g, 100 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (23.43 g, 100 mmol) gave **1b** (30.96 g, 95.7 mmol, 96% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.31 [s, 9 H, C(CH_3)$_3$], 1.46 [s, 9 H, C(CH_3)$_3$], 2.36 (s, 3 H, CH_3), 7.19 (m, 5 H, PhN, *m-H*, PhOH), 7.42 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 8.62 (s, 1 H, C*H*) ppm, resonances for the O*H* protons not observed. ^1H NMR (300 MHz, C_6D_6): δ = 1.34 [s, 9 H, C(CH_3)$_3$], 1.69 [s, 9 H, C(CH_3)$_3$], 2.09 (s, 3 H, CH_3), 6.90 (s, 4 H, PhN), 7.03 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 7.63 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 8.16 (s, 1 H, C*H*), 14.31 (s, 1 H, O*H*) ppm. $C_{22}H_{39}NO$ (323.5): calcd. C 81.69, H 9.04, N 4.33; found C 81.33, H 9.55, N 4.41.

CyN=CH(3,5-*t*$Bu_2C_6H_2$-2-OH) (1c): A procedure similar to that described for **1a** but with the use of cyclohexylamine (11.4 mL, 100 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (23.43 g, 100 mmol) gave **1c** (28.15 g, 89.2 mmol, 89% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.18–1.83 (m, 10 H, cyclohexyl-H), 1.28 [s, 9 H, C(CH_3)$_3$], 1.43 [s, 9 H, C(CH_3)$_3$], 3.18 (m, 1 H, cyclohexyl-H), 7.05 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 7.34 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 8.35 (s, 1 H, C*H*), 14.04 (s, 1 H, O*H*) ppm. $C_{21}H_{33}NO$ (315.5): calcd. C 79.95, H 10.54, N 4.44; found C 80.11, H 10.85, N 4.41.

***t*BuN=CH(3,5-*t*$Bu_2C_6H_2$-2-OH) (1d):** A procedure similar to that described for **1a** but with the use of *tert*-butylamine (10.5 mL, 100 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (23.43 g, 100 mmol) gave **1d** (28.01 g, 96.7 mmol, 97% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 [s, 9 H, C(CH_3)$_3$], 1.32 [s, 9 H, C(CH_3)$_3$], 1.43 [s, 9 H, C(CH_3)$_3$], 7.07 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 7.34 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 8.33 (s, 1 H, C*H*), 14.56 (s, 1 H, O*H*) ppm. $C_{19}H_{31}NO$ (289.5): calcd. C 78.84, H 10.79, N 4.84; found C 79.01, H 10.63, N 4.67.

(2,6-$Me_2C_6H_3$)N=CH(3,5-*t*$Bu_2C_6H_2$-2-OH) (1e): A procedure similar to that described for **1a** but with the use of 2,6-dimethylaniline (12.3 mL, 100 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (23.43 g, 100 mmol) gave **1e** (31.15 g, 92.3 mmol, 92% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.32 [s, 9 H, C(CH_3)$_3$], 1.48 [s, 9 H, C(CH_3)$_3$], 2.20 [s, 6 H, 2 CH_3-(2,6-Me_2phenyl)], 6.98–7.09 (m, 3 H, PhN), 7.13 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 7.46 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 8.32 (s, 1 H, C*H*), 13.44 (s, 1 H, O*H*) ppm. ^1H NMR (300 MHz, C_6D_6): δ = 1.32 [s, 9 H, C(CH_3)$_3$], 1.65 [s, 9 H, C(CH_3)$_3$], 1.96 (s, 6 H, CH_3), 6.92 (s, 3 H, PhN), 6.97 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 7.63 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 7.64 (s, 1 H, C*H*), 13.88 (s, 1 H, O*H*) ppm. $C_{23}H_{31}NO$ (337.5): calcd. C 81.85, H 9.26, N 4.15; found C 81.39, H 9.23, N 4.17.

(*p*-MeC_6H_4)N=CH(C_6H_4-2-OH) (1f): A procedure similar to that described for **1a** but with the use of *p*-toluidine (10.72 g, 100 mmol) and salicylaldehyde (10.6 mL, 100 mmol) gave **1f** (17.21 g, 81.5 mmol, 82% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3 H, CH_3), 6.92–7.43 (m, 8 H, PhO, PhN), 8.65 (s, 1 H, C*H*), 13.42 (s, 1 H, O*H*) ppm. $C_{14}H_{13}NO$ (211.1): calcd. C 79.59, H 6.20, N 6.63; found C 79.49, H 6.31, N 6.58.

(C_6H_5)N(H)CH_2(3,5-*t*$Bu_2C_6H_2$-2-OH) (2a): Compound **1a** (15.47 g, 50 mmol) was added under vigorous stirring to a suspension of $NaBH_4$ (2.36 g, 55.0 mmol) in thf (150 mL). The reaction mixture was stirred for 12 h resulting in a white suspension, which was treated with a 37% solution of HCl (dissolved in 30 mL of water) until no effervescence was observed. After adding NH_3 to obtain a solution with pH 11, the solvent was completely removed under reduced pressure. The solid residue was extracted into CH_2Cl_2. The organic layer was isolated by filtration, dried with Na_2SO_4 and filtered, and the solvent was evaporated until volatiles were completely removed. The white solid obtained was poured into methanol (30 mL) and stirred for 2 h and cooled to –40 °C for 1 h. After removal of the solvent by filtration and drying under reduced pressure, a solid was isolated and characterised as **2a** (11.53 g, 37.0 mmol, 74% yield). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.33 [s, 9 H, C(CH_3)$_3$], 1.49 [s, 9 H, C(CH_3)$_3$], 2.88 (br., 1 H, N*H*), 3.39 (s, 2 H, CH_2), 6.86–7.31 (m, 5 H, PhN), 7.04 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 7.25 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 8.36 (s, 1 H, O*H*) ppm. ^1H NMR (300 MHz, C_6D_6): δ = 1.38 [s, 9 H, C(CH_3)$_3$], 1.67 [s, 9 H, C(CH_3)$_3$], 2.82 (br., 1 H, N*H*), 3.80 (s, 2 H, CH_2), 6.40 (d, $J_{H,H}$ = 8.1 Hz, 2 H, *o*-H PhN), 6.74 (t, $J_{H,H}$ = 7.4 Hz, 1 H, *p-H* PhN), 6.91 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 7.03 (d, $J_{H,H}$ = 7.7 Hz, 2 H, *m-H* PhN), 7.53 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m-H*, PhOH), 8.65 (s, 1 H, O*H*) ppm. $C_{21}H_{29}NO$ (311.5): calcd. C 80.98, H 9.38, N 4.50; found C 80.92, H 9.29, N 4.27.

(*p*-MeC$_6$H$_4$)N(H)CH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-OH) (2b): A procedure similar to that described for **2a** but with the use of **1b** (16.17 g, 50 mmol) and $NaBH_4$ (2.36 g, 55 mmol) in thf (150 mL) gave **2b** (11.31 g, 34.5 mmol, 69% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 [s, 9 H, C(CH_3)$_3$], 1.40 [s, 9 H, C(CH_3)$_3$], 2.39 (s, 3 H, CH_3), 3.75 (br., 1 H, N*H*), 4.33 (s, 2 H, CH_2), 6.77 (d, $J_{H,H}$ = 8.4 Hz, 2 H, *o*-*H* PhN), 6.99 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-*H*, PhOH), 7.05 (d, $J_{H,H}$ = 8.4 Hz, 2 H, *m*-*H* PhN), 7.27 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-*H*, PhOH), 8.71 (s, 1 H, O*H*) ppm. $C_{22}H_{31}NO$ (325.5): calcd. C 81.18, H 9.60, N 4.30; found C 80.97, H 9.82, N 4.45.

CyN(H)CH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-OH) (2c): A procedure similar to that described for **2a** but with the use of **1c** (15.76 g, 50 mmol) and $NaBH_4$ (2.36 g, 55 mmol) in thf (150 mL) gave **2c** (13.54 g, 42.6 mmol, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07–1.91 (m, 11 H, cyclohexyl-H), 1.22 [s, 9 H, C(CH_3)$_3$], 1.40 [s, 9 H, C(CH_3)$_3$], 2.52 (br., 1 H, N*H*), 3.95 (s, 2 H, CH_2), 6.85 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-*H*, PhOH), 7.20 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-*H*, PhOH) ppm; resonances for the O*H* protons not observed. $C_{21}H_{35}NO$ (317.3): calcd. C 79.44, H 11.11, N 4.41; found C 79.32, H 11.35, N 4.32.

***N*-*tert*-Butyl-[2,4-di-*tert*-butyl]benzo-1-oxa-3-azine (2d1):** A suspension of paraformaldehyde (4.15 g, 138.7 mmol), 2,4-di-*tert*-butylphenol (28.21 g, 136.26 mmol) and freshly purified *tert*-butylamine (10.00 g, 136.7 mmol) in MeOH (250 mL) was heated at refluxed with vigorous stirring and at atmospheric pressure for 4 d. The solution was cooled to room temperature and the solvent was distilled off under reduced pressure. The title compound, which solidifies on standing, was manually isolated from the resulting crude oil (17.1 g as a 1:1 molar ratio mixture by ^{1}H NMR). *N*-*t*Bu-[2,4-di-*tert*-butyl]benzo-1-oxa-3-azine **2d1** was obtained as an analytically pure pale yellow solid (8.1 g, 26.7 mmol, 21% yield based on starting 2,4-di-*tert*-butylphenol). M.p. 155 °C (decomp.). R_f = 0.5562 (silica gel; hexane/acetone, 95:5). FTIR (KBr pellets): $\tilde{\nu}$ = 2983, 2923, 1238 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 [s, 9 H, N-C(CH_3)$_3$], 1.29 [s, 9 H, C(CH_3)-phenol], 1.37 [s, 9 H, C(CH_3)-phenol], 4.13 (s, 2 H, N-CH_2-benzene), 4.96 (s, 2 H, O-CH_2-N), 6.85 (AB spin system, ^4J = 2.1 Hz, 1 H, C*H*-arom), 7.11 (AB spin system, ^4J = 2.4 Hz, 1 H, C*H*-arom) ppm. ^{13}C{^{1}H}NMR (75 MHz, $CDCl_3$): δ = 28.2 [C(*C*H$_3$)], 29.7 [C(*C*H$_3$)], 31.7 [C(*C*H$_3$)], 34.3 [*C*(CH$_3$)], 34.8 [*C*(CH$_3$)], 46.0 (N-*C*H$_2$-benzene), 54.3 [N-*C*(CH$_3$)], 78.2 (O-CH_2-N), 121.0 (*C*H-arom), 121.3 (*C*H-arom), 122.1 (*C*$_{ipso}$), 136.7 (*C*$_{ipso}$), 141.9 (*C*$_{ipso}$), 151.7 (*C*-O) ppm. $C_{20}H_{33}NO$ (303.4): calcd. C 79.15, H 10.96, N 4.62; found C 79.04, H 10.99, N 4.59.

***t*BuN(H)CH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-OH) (2d):** Benz-1-oxa-3-azine (**2d1**; 40.85 g, 134.61 mmol) was dissolved in EtOH (950 mL) with stirring. The solution was stirred vigorously at room temperature for 2 d. A fine precipitate appeared over this time, and the solution was decanted for 5 d. The pale-yellow solid was isolated by filtration through a fritted funnel and washed with EtOH (2×). The compound obtained (8.40 g) was recrystallised from EtOH at –10 °C and isolated as off-white needles after filtration, washing with cold EtOH and then suction by means of a water vacuum aspirator. It was further dried at room temperature under reduced pressure for 24 h to constant weight yielding **2d** as off-white needles (8.24 g, 28.2 mmol, 20% yield). M.p. 89 °C (decomp.). R_f = 0.4312 (silica gel; hexane/acetone, 95:5). FTIR (KBr pellets): $\tilde{\nu}$ = 2963, 2866, 1251 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 [s, 9 H, N-C(CH_3)$_3$], 1.27 [s, 9 H, C(CH_3)$_3$-phenol], 1.41 [s, 9 H, C(CH_3)$_3$-phenol], 3.89 (s, 2 H, CH_2), 6.88 (d, ^4J = 2.4 Hz, 1 H, C*H*), 7.20 (d, ^4J = 2.7 Hz, 1 H, C*H*) ppm. Signals of O*H* and N*H* are obscured by the baseline. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.76 [s, 9 H, N-C(CH_3)], 1.42 [s, 9 H, C(CH_3)-phenol], 1.76 [s, 9 H, C(CH_3)-phenol], 3.52 (s, 2 H, N-CH_2-benzene), 6.94 (d, ^4J = 2.4 Hz, 1 H, C*H*-arom), 7.52 (d, ^4J = 2.4 Hz, 1 H, C*H*-arom), 11.32 (br., 1 H, O*H*) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 28.7 [N-C(*C*H$_3$)$_3$], 29.7, 31.7 [C(*C*H$_3$)$_3$], 34.2, 34.9 [*C*(CH$_3$)$_3$], 46.8 (*C*H$_2$), 50.9 [N-*C*(CH$_3$)$_3$], 122.9 (*C*H), 123.0 (*C*$_{ipso}$), 123.1 (*C*H), 136.0, 140.4 (*C*$_{ipso}$), 154.9 (*C*-O) ppm. $C_{19}H_{33}NO$ (291.4): calcd. C 78.29, H 11.41, N 4.81; found C 78.09, H 11.79, N 4.62.

***N*-(2,6-Me$_2$C$_6$H$_4$)-[2,4-di-*tert*-butyl]benzo-1-oxa-3-azine (2e1):** A procedure similar to that described for **2d1** but with the use of a suspension of paraformaldehyde (4.15 g, 138.7 mmol), 2,4-di-*tert*-butylphenol (28.21 g, 136.26 mmol) and 2,6-dimethylaniline (16.8 mL, 136.7 mmol) in MeOH (250 mL) gave **2e1** obtained as an analytically pure pale-yellow solid (10.06 g, 21% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.32 [s, 9 H, C(CH_3)$_3$-phenol], 1.59 [s, 9 H, C(CH_3)$_3$-phenol], 2.14 [s, 6 H, 2 CH_3-(2,6-Me$_2$phenyl)], 4.10 (s, 2 H, N-CH_2-benzene), 4.68 (s, 2 H, O-CH_2-N), 6.85 (d, ^4J = 2.1 Hz, 1 H, C*H*-benzoxazine), 7.11 (d, ^4J = 2.4 Hz, 1 H, C*H*-benzoxazine), 6.93 and 7.01 [m, 3 H, 3 C*H*-(2,6-Me$_2$phenyl)] ppm. $C_{24}H_{33}NO$ (351.5): calcd. C 82.00, H 9.46, N 3.98; found C 82.04, H 9.99, N 3.59.

(2,6-Me$_2$C$_6$H$_3$)N(H)CH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-OH) (2e): A solution of $AlLiH_4$ (1 M in ethyl ether, 50 mL, 50 mmol) was added under vigorous stirring to a 0 °C solution containing **1e** (2.36 g, 55 mmol) in thf (150 mL). The reaction mixture was stirred for 12 h resulting in a white suspension to which a saturated solution of NH_4Cl in water (30 mL) was added. The resulting mixture was completely evaporated under reduced pressure, and the solid residue obtained was extracted with ethyl ether (3 × 100 mL). The organic layer was isolated by filtration, dried with Na_2SO_4 and filtered again, and the volatiles were completely removed under reduced pressure. The white solid obtained was poured into methanol (30 mL) and stirred for 2 h and then cooled to –40 °C for 1 h. After removal of the solvent by filtration and complete drying under reduced pressure, a solid was isolated and characterised as **2e** (15.76 g, 47.0 mmol, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 [s, 9 H, C(CH_3)$_3$], 1.31 [s, 9 H, C(CH_3)$_3$], 2.42 [s, 6 H, 2 CH_3-(2,6-Me$_2$-phenyl)], 3.50 (br., 1 H, N*H*), 4.14 (s, 2 H, CH_2), 6.95 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-*H*, PhOH), 6.97–7.07 (m, 3 H, PhN), 7.32 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-*H*, PhOH), 10.27 (br., 1 H, O*H*) ppm. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.37 [s, 9 H, C(CH_3)$_3$], 1.77 [s, 9 H, C(CH_3)$_3$], 1.98 [s, 6 H, 2 CH_3-(2,6-Me$_2$phenyl)], 2.97 (t, $J_{H,H}$ = 8.1 Hz, 1 H, N*H*), 3.73 (d, $J_{H,H}$ = 8.1 Hz, 2 H, CH_2), 6.83 (s, 3 H, PhN), 6.89 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-*H*, PhOH), 7.55 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-*H*, PhOH), 10.53 (s, 1 H, O*H*) ppm. $C_{23}H_{33}NO$ (337.5): calcd. C 81.37, H 9.80, N 4.71; found C 81.54, H 9.61, N 4.59.

(*p*-MeC$_6$H$_4$)N(H)CH$_2$(C$_6$H$_4$-2-OH) (2f): A procedure similar to that described for **2a** but with the use of a **1f** (15.76 g, 50 mmol) and $NaBH_4$ (2.36 g, 55 mmol) in thf (150 mL) gave **2f** (9.92 g, 46.5 mmol, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.06 (s, 3 H, CH_3), 3.80 (s, 2 H, CH_2), 6.75 (d, $J_{H,H}$ = 8.1 Hz, 2 H, *o*-*H*, PhN), 6.83–6.88 (m, 2 H, PhO), 7.04 (d, $J_{H,H}$ = 8.1 Hz, 2 H, *m*-*H*, PhN), 7.11–7.23 (m, 2 H, PhO), 8.62 (br., 1 H, O*H*) ppm. ^{1}H NMR (300 MHz, C_6D_6): δ = 2.08 (s, 3 H, CH_3), 2.86 (br., 1 H, N*H*), 3.80 (s, 2 H, CH_2), 6.36 (d, $J_{H,H}$ = 8.1 Hz, 2 H, *o*-*H*, PhN), 6.73–7.10 (m, 6 H, PhO, PhN), 8.67 (br., 1 H, O*H*) ppm. $C_{14}H_{15}NO$ (213.3): calcd. C 78.84, H 7.09, N 6.57; found C 78.69, H 6.92, N 6.43.

***t*BuN(Me)CH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-OH) (2g)**

Method 1: Benzoxazine **2d1** (1.38 g, 4.54 mmol) was dissolved under argon in ethanol (20 mL) and $NaBH_4$ (858 mg, 22.70 mmol) was added in one portion under vigorous stirring. The solution was stirred for 2 d under argon with vigorous stirring. The solvent was

then completely removed, and the residue was dissolved in CH_2Cl_2, and then, poured into a saturated solution of NH_4Cl in water. The organic layer was separated, repetitively washed with water and a saturated solution of NaCl in water and further separated. The organic phase was dried with $MgSO_4$ and filtered. After complete removal of volatiles, the crude yellow oil (1.39 g), which solidifies on standing, was purified by flash column chromatography (silica gel; *n*-hexane/acetone, 95:5). The solvent was distilled off under reduced pressure to give **2g** as a pale yellow oil (1.28 g, 4.19 mmol, 92% yield) that solidifies also on standing.

Method 2: A suspension of 2,4-di-*tert*-butylphenol (2.37 g, 11.49 mmol), *N*-*tert*-butyl-methylamine (1.00 g, 11.57 mmol) and paraformaldehyde (376 mg, 12.53 mmol) in methanol (50 mL) was heated at reflux for 2 d. A crude brownish oil (3.13 g) was isolated by complete removal of the volatiles under reduced pressure, and it was purified by flash column chromatography (silica gel; *n*-hexane/acetone, 70:30). Product **2g** was obtained as an analytically pure yellow oil (2.92 g, 9.5 mmol, 83% yield) after completely removing the volatiles. R_f = 0.7812 (silica gel; hexane/acetone, 70:30). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.22 [s, 9 H, N-C(CH_3)$_3$], 1.30 [s, 9 H, C(CH_3)$_3$-benzene], 1.43 [s, 9 H, C(CH_3)$_3$-benzene], 2.23 (s, 3 H, N-CH_3), 3.91 (s, 2 H, CH_2), 4.64 (s, 1 H, O*H*), 6.81 (d, ^4J = 2.4 Hz, 1 H, C*H*), 7.19 (d, ^4J = 2.4 Hz, 1 H, C*H*) ppm. $C_{20}H_{35}NO$ (305.5): calcd. C 78.29, H 11.41, N 4.81; found C 78.63, H 11.55, N 4.58.

***t*BuN(Et)CH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-OH) (2h):** A solution of LiMe (1.6 M in ethyl ether, 1.6 mL, 2.24 mmol) or a solution of MgClMe (3 M in thf, 0.74 mL, 2.24 mmol) was added dropwise under vigorous stirring to a solution of **2d1** (170 mg, 0.56 mmol) in ethyl ether (or thf) (30 mL) cooled under argon at –78 or 0 °C. The solution was gradually warmed to room temperature, and vigorously stirred for 2 h. The solution was poured into a saturated solution of NH_4Cl in water. The organic layer was separated, repetitively washed with water and a saturated solution of NaCl in water and further separated. The organic phase was dried with $MgSO_4$ and filtered. The solvent was completely removed under reduced pressure to give the corresponding crude substance (169 mg), which was purified by flash column chromatography (silica gel; *n*-hexane/acetone, 95:5). Product **2h** was obtained as an analytically pure yellow oil (148 mg, 0.46 mmol, 83% yield) after complete removal of volatiles. R_f = 0.5225 (silica gel; hexane/acetone, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, ^3J = 7.2 Hz, 3 H, CH$_2$-CH_3), 1.21 [s, 9 H, N-C(CH_3)$_3$], 1.27 [s, 9 H, C(CH_3)$_3$-phenol], 1.42 [s, 9 H, C(CH_3)$_3$-phenol], 2.64 (m, 2 H, N-CH_2CH$_3$), 3.84 (s, 2 H, N-CH_2-phenol), 5.11 (s, 1 H, O*H*), 6.79 (d, ^4J = 2.4 Hz, 1 H, C*H*-phenol), 7.15 (d, ^4J = 2.2 Hz, 1 H, C*H*-phenol) ppm. $C_{21}H_{37}NO$ (319.5): calcd. C 78.94, H 11.67, N 4.38; found C 78.87, H 11.55, N 4.58.

***t*BuN(*n*Pr)CH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-OH) (2i):** A solution of MgClEt (2 M in ethyl ether, 0.98 mL, 1.96 mmol) was added dropwise under vigorous stirring to a solution of **2d1** (150 mg, 0.49 mmol) in ethyl ether (or thf) (30 mL) cooled under argon at –78 or 0 °C. The solution was gradually warmed to room temperature, and vigorously stirred for 2 h. The solution was poured into a saturated solution of NH_4Cl in water. The organic layer was separated, repetitively washed with water and a saturated solution of NaCl in water and further separated. The organic phase was dried with $MgSO_4$ and filtered. The solvent was completely removed under reduced pressure to give the corresponding crude substance (134 mg), which was purified by flash column chromatography (silica gel; *n*-hexane/acetone, 95:5). Product **2i** was obtained as an analytically pure yellow oil (128 mg, 0.38 mmol, 78% yield) after complete removal of volatiles. R_f = 0.5402 (silica gel; hexane/acetone, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, ^3J = 7.1 Hz, 3 H, CH$_2$-CH_3), 1.21 [s, 9 H, N-C(CH_3)$_3$], 1.23 (m, 2 H, N-CH$_2$-CH_2-CH$_3$), 1.27 [s, 9 H, C(CH_3)$_3$-phenol], 1.41 [s, 9 H, C(CH_3)$_3$-phenol], 2.61 (m, 2 H, N-CH_2CH$_2$CH$_3$), 3.78 (s, 2 H, N-CH_2-phenol), 5.24 (s, 1 H, O*H*), 6.75 (d, ^4J = 2.4 Hz, 1 H, C*H*-phenol), 7.13 (d, ^4J = 2.4 Hz, 1 H, C*H*-phenol) ppm. $C_{22}H_{39}NO$ (333.5): calcd. C 79.22, H 11.78, N 4.20; found C 79.38, H 11.59, N 4.13.

***t*BuN(CH$_2$Ph)CH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-OH) (2j):** A solution of LiPh (1.8 M in cyclohexane/ethyl ether, 0.95 mL, 1.71 mmol) dissolved in thf was added dropwise under vigorous stirring to a solution of **2d1** (130 mg, 0.42 mmol) in ethyl ether (or thf) (30 mL) cooled under argon at –78 or 0 °C. The solution was gradually warmed to room temperature, and vigorously stirred for 2 h under. The solution was poured into a saturated solution of NH_4Cl in water. The organic layer was separated, repetitively washed with water and a saturated solution of NaCl in water and further separated. The organic phase was dried with $MgSO_4$ and filtered. The solvent was completely removed under reduced pressure to give the corresponding crude substance (157 mg), which was purified by flash column chromatography (silica gel; *n*-hexane/acetone, 95:5). Product **2j** was obtained as an analytically pure yellow oil (116 mg, 0.30 mmol, 72% yield) after complete removal of volatiles. R_f = 0.5012 (silica gel; hexane/acetone, 95:5). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 [s, 9 H, N-C(CH_3)$_3$], 1.27 [s, 9 H, C(CH_3)$_3$-phenol], 1.41 [s, 9 H, C(CH_3)$_3$-phenol], 4.38 (dt, J = 3.9, 13.6 Hz, 4 H, Phenol-CH_2, N-CH_2-C$_6$H$_5$), 7.60–7.17 (m, 7 H, 2 C*H*-phenol, C$_6H_5$-CH$_2$-N) ppm. $C_{26}H_{39}NO$ (381.6): calcd. C 81.84, H 10.30, N 3.67; found C 81.86, H 10.21, N 3.78.

Ti(η^5-C$_5$H$_5$)[PhNCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl (3a): A solution of **2a** (311.5 mg, 1 mmol) and NEt_3 (0.35 mL, 2.5 mmol) in pentane (50 mL) was added under vigorous stirring to Ti(η^5-C$_5$H$_5$)Cl$_3$ (219.3 mg, 1 mmol). After 12 h the solution appeared brown with the formation of HCl·NEt_3 as a white precipitate. The solution was filtered off and the solvent evaporated to give a solid, which was recrystallised from toluene at –30 °C and characterised as **3a** (413.1 mg, 0.90 mmol, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 [s, 9 H, C(CH_3)$_3$], 1.38 [s, 9 H, C(CH_3)$_3$], 4.45 and 6.06 (AB system, $J_{A,B}$ = 16.5 Hz, 2 H, CH_2), 6.42 (s, 5 H, Cp), 6.83 (dd, ^1J = 8.4 Hz, ^2J = 0.9 Hz, 2 H, *o*-H PhN), 7.08 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO), 7.12–7.32 (m, 3 H, PhN) ppm. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.28 [s, 9 H, C(CH_3)$_3$], 1.46 [s, 9 H, C(CH_3)$_3$], 4.18 and 6.07 (AB system, $J_{A,B}$ = 16.5 Hz, 2 H, CH_2), 6.15 (s, 5 H, Cp), 6.69 (dd, ^1J = 8.4 Hz, ^2J = 1.2 Hz, 2 H, *o*-H PhN), 6.88 (t, *p*-H PhN, $J_{H,H}$ = 7.5 Hz, 1 H, 7.08), 6.93 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO), 7.00 (t, $J_{H,H}$ = 7.2 Hz, 2 H, *m*-H PhN), 7.39 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO) ppm. $C_{26}H_{32}ClNOTi$ (457.9): calcd. C 68.20, H 7.04, N 3.06; found C 68.84, H 7.56, N 2.89.

Ti(η^5-C$_5$H$_5$)[(4-MeC$_6$H$_4$)NCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl (3b): A solution of **2b** (325.5 mg, 1 mmol) and NEt_3 (0.35 mL, 2.5 mmol) in pentane (50 mL) was added under vigorous stirring to Ti(η^5-C$_5$H$_5$)Cl$_3$ (219.3 mg, 1 mmol). After 12 h the solution appeared brown with the formation of HCl·NEt_3 as a white precipitate. The solution was filtered off and the solvent evaporated to give a solid, which was recrystallised from toluene at –30 °C and characterised as **3b** (413.6 mg, 0.87 mmol, 87% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.30 [s, 9 H, C(CH_3)$_3$], 1.50 [s, 9 H, C(CH_3)$_3$], 2.06 (s, 3 H, CH_3), 4.20 and 6.21 (AB system, $J_{A,B}$ = 16.5 Hz, 2 H, CH_2), 6.19 (s, 5 H, Cp), 6.64 (d, $^1J_1$ = 8.4 Hz, 2 H, *o*-H PhN), 6.81 (t, $J_{H,H}$ = 8.4 Hz, 2 H, *m*-H PhN), 6.96 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO), 7.45 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO) ppm. $C_{27}H_{34}ClNOTi$ (471.9): calcd. C 68.72, H 7.26, N 2.97; found C 69.57, H 8.03, N 2.51.

Ti(η^5-C$_5$H$_5$)[CyNCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl (3c): A solution of **2c** (317.3 mg, 1 mmol) and NEt_3 (0.35 mL, 2.5 mmol) in pentane

(50 mL) was added under vigorous stirring to Ti(η^5-C_5H_5)Cl_3 (219.3 mg, 1 mmol). After 12 h the solution appeared brown with the formation of HCl·NEt_3 as a white precipitate. The solution was filtered off and concentrated until a yellow precipitate appeared and then maintained at –40 °C for 12 h to give a solid, which was recrystallised from toluene at –30 °C and characterised as **3c** (356.2 mg, 0.77 mmol, 77% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.85–1.59 (m, 10 H; cyclohexyl), 1.32 [s, 9 H, C(CH_3)$_3$], 1.46 [s, 9 H, C(CH_3)$_3$], 4.25 (pt, 1 H, cyclohexyl), 6.28 (s, 5 H, Cp), 7.00 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO), 7.34 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO) ppm. $C_{26}H_{38}ClNOTi$ (463.9): calcd. C 67.31, H 8.26, N 3.02; found C 67.45, H 8.27, N 2.71.

Ti(η^5-C_5H_5)[*t*BuNCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl (3d): A solution of NEt_3 (0.35 mL, 2.5 mmol) in ethyl ether (50 mL) was added under vigorous stirring to **5**·HCl (510.8 mg, 1 mmol). After 7 d the solution appeared brown with the formation of HCl·NEt_3 as a white precipitate. The solution was filtered off and concentrated to a volume of ca. 10 mL and then maintained at –40 °C for 12 h to give a solid, which was recrystallised from toluene at –30 °C and characterised as **3d** (326.4 mg, 0.74 mmol, 74% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.97 [s, 9 H, C(CH_3)$_3$], 1.36 [s, 9 H, C(CH_3)$_3$], 1.54 [s, 9 H, C(CH_3)$_3$], 3.56 and 4.62 (AB system, $J_{A,B}$ = 16.5 Hz, 2 H, CH_2), 6.24 (s, 5 H, Cp), 7.12 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO), 7.43 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO) ppm. $C_{24}H_{36}ClNOTi$ (437.9): calcd. C 65.83, H 8.29, N 3.20; found C 66.03, H 8.12, N 3.38.

Ti(η^5-$C_5H_4SiMe_2Cl$)[PhNCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl (4a): A solution of **2a** (311.5 mg, 1 mmol) and NEt_3 (0.35 mL, 2.5 mmol) in pentane (50 mL) was added under vigorous stirring to Ti(η^5-$C_5H_4SiMe_2Cl$)Cl_3 (311.9 mg, 1 mmol). After 12 h the solution appeared brown with the formation of HCl·NEt_3 as a white precipitate. The solution was filtered off and the solvent evaporated to give a solid, which was recrystallised from toluene at –30 °C and characterised as **4a** (413.1 mg, 0.93 mmol, 93% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.73 (s, 3 H, Si-CH_3), 0.79 (s, 3 H, Si-CH_3), 1.27 [s, 9 H, C(CH_3)$_3$], 1.50 [s, 9 H, C(CH_3)$_3$], 4.23 and 5.99 (AB system, $J_{A,B}$ = 16.2 Hz, 2 H, CH_2), 6.17 and 6.53 (m, 4 H, ABCD system, C_5H_4), 6.22 (dd, $^1J_{H,H}$ = 7.2 Hz, $^2J_{H,H}$ = 1.2 Hz, 2 H, *o*-H PhN), 6.86 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-H, PhO), 6.88 (dd, $^1J_{H,H}$ = 7.8 Hz, $^2J_{H,H}$ = 1.2 Hz, 1 H, *p*-H PhN), 6.97 (t, $J_{H,H}$ = 8.7 Hz, 2 H, *m*-H PhN), 7.43 (d, $J_{H,H}$ = 2.4 Hz, 1 H, *m*-H, PhO) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 3.1 and 3.2 [Si(CH_3)$_2$], 30.1 [C(CH_3)$_3$], 32.1 [*C*(CH$_3$)$_3$], 35.1 [*C*(CH$_3$)$_3$], 35.7 [*C*(CH$_3$)$_3$], 64.5 (CH_2), 119.4–144.8 (C_5H_4 and arom.), 159.8 (C_{ipso}-PhO), 161.4 (C_{ipso}-PhN) ppm. $C_{28}H_{37}Cl_2NOSiTi$ (540.5): calcd. C 61.09, H 6.78, N 2.54; found C 61.53, H 7.14, N 2.29.

Ti(η^5-C_5H_5)[*t*Bu(H)NCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl$_2$ (5): A solution of **2d** (291.5 mg, 1 mmol) and NEt_3 (0.35 mL, 2.5 mmol) in pentane (50 mL) was added under vigorous stirring to Ti(η^5-C_5H_5)Cl_3 (219.3 mg, 1 mmol). After 12 h the solution appeared brown with the formation of HCl·NEt_3 as a white precipitate. The solution was filtered off and concentrated to a volume of ca. 10 mL and then maintained at –40 °C for 12 h to give a solid, which was recrystallised from toluene at –40 °C and characterised as **5** (251.6 mg, 0.53 mmol, 53% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.15 [s, 9 H, C(CH_3)$_3$], 1.36 [s, 9 H, C(CH_3)$_3$], 1.52 [s, 9 H, C(CH_3)$_3$], 3.87 (br., 2 H, CH_2), 6.30 (s, 5 H, Cp), 7.23 (d, $J_{H,H}$ = 2.0 Hz, 1 H, PhO), 7.42 (d, $J_{H,H}$ = 2.0 Hz, 1 H, PhO), 7.65 (br., 1 H, N*H*) ppm. $C_{24}H_{37}Cl_2NOTi$ (474.3): calcd. C 60.77, H 7.86, N 2.95; found C 60.32, H 8.34, N 2.93.

Ti(η^5-C_5H_5)[*t*Bu(H)NCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl$_2$·HCl (5·HCl): A solution of **2d** (291.5 mg, 1 mmol) in ethyl ether (50 mL) was added under vigorous stirring to Ti(η^5-C_5H_5)Cl_3 (219.3 mg, 1 mmol). After 3 h the solution appeared brown with the formation of HCl·NEt_3 as a white precipitate. The solution was filtered off and the solvent evaporated to give a solid, which was recrystallised from toluene at –30 °C and characterised as **5**·HCl (501.6 mg, 0.98 mmol, 98% yield). ^{1}H NMR (300 MHz, C_6D_6): δ = 1.33 [s, 9 H, C(CH_3)$_3$], 1.36 [s, 9 H, C(CH_3)$_3$], 1.39 [s, 9 H, C(CH_3)$_3$], 4.30 (br., 2 H, CH_2), 6.81 (s, 5 H, Cp), 7.37 (d, $J_{H,H}$ = 2.0 Hz, 1 H, PhO), 8.06 (d, $J_{H,H}$ = 2.0 Hz, 1 H, PhO), 9.40 (br., 2 H, NH_2Cl) ppm. $C_{24}H_{38}Cl_2NOTi$ (510.8): calcd. C 56.43, H 7.50, N 2.74; found C 56.37, H 7.83, N 2.41.

Ti(η^5-C_5H_5)[Ph(H)NCH$_2$(3,5-*t*Bu$_2$C$_6$H$_2$-2-O)]Cl$_2$ (6a): A solution of **2a** (311.5 mg, 1 mmol) and NEt_3 (0.35 mL, 2.5 mmol) in toluene (50 mL) was added under vigorous stirring to Ti(η^5-C_5H_5)Cl_3 (219.3 mg, 1 mmol). After 12 h the solution appeared red with the formation of HCl·NEt_3 as a white precipitated. The solution was filtered off and concentrated to a volume of 10 mL and maintained at –40 °C for 12 h to give a solid, which was recrystallised from toluene at –30 °C and characterised as a 4:1 molar ratio mixture of **6a-1**/**6a-2** (336.1 mg, 0.68 mmol, 68% yield). ^{1}H NMR (300 MHz, C_6D_6, stereoisomer **6a-1**): δ = 1.23 [s, 9 H, C(CH_3)$_3$], 1.56 [s, 9 H, C(CH_3)$_3$], 3.24 (pt, J = 6.5 Hz, 1 H, N*H*, X of an ABX spin system), 4.26 and 4.46 (pd, $^3J_{A,X/B,X} \approx$ 6.5 Hz, $^2J_{A,B}$ = 4.5 Hz, 2 H, CH_2, AB of an ABX spin system), 6.39 (s, 5 H, Cp), 6.62 (dd, ^1J = 8.4 Hz, ^2J = 1.2 Hz, 2 H, *o*-H PhN), 6.73 (t, $J_{H,H}$ = 7.2 Hz, 1 H, *p*-H PhN), 7.19–7.22 (m, 3 H, arom.), 7.46 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO) ppm. ^{1}H NMR (300 MHz, C_6D_6, stereoisomer **6a-2**): δ = 1.27 [s, 9 H, C(CH_3)$_3$], 1.60 [s, 9 H, C(CH_3)$_3$], 3.71 (pt, $J_{A,X}$ = 6.7 Hz, 1 H, N*H*, X of an AA′X spin system), 4.51 (pd, $J_{A,X}$ = 6.7 Hz, 2 H, CH_2, AA′ of an AA′X spin system), 6.32 (s, 5 H, Cp), 6.44–7.48 (m, 7 H, Ph), 7.46 (d, $J_{H,H}$ = 2.4 Hz, 1 H, PhO) ppm. $C_{26}H_{33}Cl_2NOTi$ (494.3): calcd. C 63.17, H 6.73, N 2.83; found C 63.54, H 7.91, N 2.65.

Polymerisation Procedure: Toluene (50 mL) was introduced under argon into the Schlenk reactor equipped with a magnetic stirrer and maintained at the desired temperature using external thermal control with vigorous stirring for 30 min. sMAO was then injected and the mixture stirred for 15 min. The argon was replaced by ethylene by degassing the solution under vacuum and refilling with the olefin. This procedure was repeated and the solution was finally saturated with the olefin for 15 min. As soon as the titanium complex was injected to the mixture, polymerisation time was counted. The polymerisation was terminated by methanol injection. The polymer was precipitated with a solution of HCl (5% in MeOH, 100 mL), stirred, filtered and washed successively with of a solution of HCl (5% in MeOH, 50 mL), water (100 mL) and MeOH (100 mL). The polymer was finally dried under vacuum at 50 °C for 24 h to constant weight.

Single-Crystal X-ray Structure Determination of Compounds 2a, 2d, 2e and 3d: Suitable single crystals of **2a**, **2d**, **2e** and **3d** for the X-ray diffraction study were selected. For compound **2e** data collection was carried out at 298 K, whereas data collection for **2a**, **2d** and **3d** was performed at 200(2) K, with the crystals covered with perfluorinated ether for **2a**, **2d** and **3d**. The crystals were mounted on a Bruker-Nonius Kappa CCD single crystal diffractometer equipped with a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Multiscan[43] absorption correction procedures were applied to the data. The structures were solved by using the WINGX package,[44] by direct methods (SHELXS-97) and refined by using full-matrix least-squares against F^2 (SHELXL-97).[45] All non-hydrogen atoms were anisotropically refined except for the carbon atoms in the Cp ring for **3d** that were disorder in two positions.

Table 2. Crystal data and structure refinement details for **2a**, **2d**, **2e** and **3d**.

	2a	**2d**	**2e**	**3d**
Formula	$C_{21}H_{29}NO$	$C_{19}H_{33}NO$	$C_{23}H_{33}NO$	$C_{24}H_{36}NOClTi$
Fw	311.45	291.46	339.50	437.89
Colour/habit	white/prism	white/prism	white/prism	dark red/prism
Crystal dimensions [mm]	$0.44\times0.37\times0.23$	$0.44\times0.17\times0.12$	$0.41\times0.27\times0.24$	$0.59\times0.34\times0.29$
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	Cc	$P2_1/a$
a [Å]	8.5031(7)	5.940(3)	8.556(3)	13.742(2)
b [Å]	12.582(3)	18.755(3)	32.851(13)	10.2730(12)
c [Å]	17.859(4)	16.371(4)	7.687(6)	17.477(2)
β [°]	90	94.96(2)	95.75(5)	96.354(11)
V [Å^3]	1910.7(6)	1816.9(11)	2150(2)	2452.1(5)
Z	4	4	4	4
T [K]	200	200	298	200
$\rho_{calcd.}$ [g cm^{-3}]	1.083	1.066	1.049	1.186
μ [mm^{-1}]	0.065	0.064	0.063	0.471
$F(000)$	680	648	744	936
θ range [°]	3.68–25.02	3.31–27.50	3.03–27.59	3.03–27.51
No. of rflns. collected	19096	35106	8101	19557
No. of indep. rflns./R_{int}	1927/0.0984	4165/0.1098	2473/0.0610	5637/0.0645
No. of obsd. rflns. [$I>2\sigma(I)$]	1486	2415	1737	4027
No. of data/restraints/params.	1927/0/216	4165/168/221	2473/2/247	5637/0/248
R_1/wR_2 [$I>2\sigma(I)$]	0.0429/0.0965	0.0630/0.1417	0.0496/0.1133	0.0479/0.1041
R_1/wR_2 (all data)	0.0667/0.1075	0.1251/0.1659	0.0832/0.1322	0.0795/0.1182
Extinction coefficient		0.010(2)		
GOF (on F^2)	1.045	1.063	1.022	1.029
Largest diff peak/hole [e Å^{-3}]	+0.153/–0.152	0.273 and –0.239	+0.145/–0.161	+0.432/–0.383

As well N1 and C10 in compound **2d** show some disorder that was treated. For **2d** DELU and SIMU restrains were applied. Hydrogen atoms were geometrically placed and left riding on their parent atoms except for the hydrogen atoms on: O1, N1 in compounds **2a**, **2d**, **2e**; N1′ in compound **2d**′ and C13, C14, C15 in **2a**. Compound **2d** crystallises as the racemic mixture of the two enantiomers. Compounds **2a** and **2e** are chiral and crystallised in noncentrosymmetric space groups ($P2_12_12_1$ and Cc respectively). However, the Flack parameter could not be reliably determined because of insufficient anomalous scattering effects. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. Relevant crystallographic data and details of the refinements for the four structures are given in Table 2.

CCDC-686502 (for **2a**), -686503 (for **2d**), -686504 (for **2e**) and -686505 (for **3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] L. Resconi, J. C. Chadwick, L. Cavallo, *Comprehensive Organometallic Chemistry III* (Eds.: M. P. Mingos, R. H. Crabtree), Elsevier, London, **2006**, vol. 4, ch. 9.

[2] J. Saito, M. Mitani, J. Mohri, Y. Yoshida, S. Matsui, S. Ishii, S. Kojoh, N. Kashiwa, T. Fujita, *Angew. Chem. Int. Ed.* **2001**, *40*, 2918–2920.

[3] Y. Suzuki, H. Terao, T. Fujita, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1493–1517.

[4] Y. Tohi, H. Makio, S. Matsui, M. Onda, T. Fujita, *Macromolecules* **2003**, *36*, 523–525.

[5] Y. Yoshida, J. Mohri, S. Ishii, M. Mitani, J. Saito, S. Matsui, H. Makio, T. Nakano, H. Tanaka, M. Onda, Y. Yamamoto, A. Mizuno, T. Fujita, *J. Am. Chem. Soc.* **2004**, *126*, 12023–12032.

[6] J. Saito, Y. Tohi, N. Matsukawa, M. Mitani, T. Fujita, *Macromolecules* **2005**, *38*, 4955–4957.

[7] J. Saito, Y. Suzuki, H. Makio, H. Tanaka, M. Onda, T. Fujita, *Macromolecules* **2006**, *39*, 4023–4031.

[8] H. Terao, S. I. Ishii, J. Saito, S. Matsuura, M. Mitani, N. Nagai, H. Tanaka, T. Fujita, *Macromolecules* **2006**, *39*, 8584–8593.

[9] A. Sakuma, M. S. Weiser, T. Fujita, *Polym. J.* **2007**, *39*, 193–207.

[10] M. González-Maupoey, T. Cuenca, L. M. Frutos, O. Castano, E. Herdtweck, *Organometallics* **2003**, *22*, 2694–2704.

[11] M. González-Maupoey, T. Cuenca, *Organometallics* **2006**, *25*, 4358–4365.

[12] M. González-Maupoey, T. Cuenca, L. M. Frutos, O. Castaño, E. Herdtweck, B. Rieger, *Eur. J. Inorg. Chem.* **2007**, 147–161.

[13] V. Tabernero, T. Cuenca, E. Herdtweck, *Eur. J. Inorg. Chem.* **2004**, 3154–3162.

[14] V. Tabernero, C. Maestre, G. Jiménez, T. Cuenca, C. R. de Arellano, *Organometallics* **2006**, *25*, 1723–1727.

[15] V. Tabernero, T. Cuenca, *Eur. J. Inorg. Chem.* **2005**, 338–346.

[16] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa, T. Fujita, *J. Am. Chem. Soc.* **2001**, *123*, 6847–6856.

[17] D. C. H. Oakes, B. S. Kimberley, V. C. Gibson, D. J. Jones, A. J. P. White, D. J. Williams, *Chem. Commun.* **2004**, 2174–2175.
[18] G. Palmieri, *Tetrahedron: Asymmetry* **2000**, *11*, 3361–3373.
[19] K. G. Mizuch, *Zh. Obshch. Khim.* **1953**, *23*, 861–864.
[20] H. Kapnang, G. Charles, *Tetrahedron Lett.* **1983**, *24*, 1597–1600.
[21] P. Q. Huang, S. Arseniyadis, H. P. Husson, *Tetrahedron Lett.* **1987**, *28*, 547–550.
[22] L. F. Roa, D. Gnecco, A. Galindo, J. L. Teran, S. Bernes, *Tetrahedron: Asymmetry* **2004**, *15*, 847–850.
[23] M. S. Hill, D. A. Atwood, *Main Group Chem.* **1998**, *2*, 285–292.
[24] V. C. Gibson, B. S. Kimberley, Eur. Pat. Appl., EP 953571 A1, **1999**.
[25] D. Kanamori, A. Furukawa, T. Okamura, H. Yamamoto, N. Ueyama, *Org. Biomol. Chem.* **2005**, *3*, 1453–1459.
[26] M. C. Maestre, V. Tabernero, M. E. G. Mosquera, G. Jiménez, T. Cuenca, *Organometallics* **2005**, *24*, 5853–5857.
[27] M. C. Maestre, C. Paniagua, E. Herdtweck, M. E. G. Mosquera, G. Jiménez, T. Cuenca, *Organometallics* **2007**, *26*, 4243–4251.
[28] M. C. Maestre, M. E.G. Mosquera, H. Jacobsen, G. Jiménez, T. Cuenca, *Organometallics* **2008**, *27*, in press.
[29] A. Van der Linden, C. J. Schaverien, N. Meijboom, C. Ganter, A. G. Orpen, *J. Am. Chem. Soc.* **1995**, *117*, 3008–3021.
[30] A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc., Dalton Trans.* **1989**, S1–S83.
[31] R. M. Pupi, J. N. Coalter, J. L. Petersen, *J. Organomet. Chem.* **1995**, *497*, 17–25.
[32] M. F. Lappert, P. P. Power, A. R. Sanger, R. C. Srivastava, *Metal and Metalloid Amides* (Ellis Horwood Series in Chemical Science), John Wiley and Sons, New York, **1980**.
[33] D. M. Giolando, K. Kirschbaum, L. J. Graves, U. Bolle, *Inorg. Chem.* **1992**, *31*, 3887–3890.
[34] M. H. Chisholm, J. H. Huang, J. C. Huffman, W. E. Streib, D. Tiedtke, *Polyhedron* **1997**, *16*, 2941–2949.
[35] S. Fokken, T. P. Spaniol, J. Okuda, F. G. Sernetz, R. Mulhaupt, *Organometallics* **1997**, *16*, 4240–4242.
[36] I. Tritto, S. X. Li, M. C. Sacchi, G. Zannoni, *Macromolecules* **1993**, *26*, 7111–7115.
[37] I. Kim, R. F. Jordan, *Macromolecules* **1996**, *29*, 489–491.
[38] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, Oxford, **1988**.
[39] R. D. Gorsich, *J. Am. Chem. Soc.* **1958**, *80*, 4744–4744.
[40] R. D. Gorsich, *J. Am. Chem. Soc.* **1960**, *82*, 4211–4214.
[41] S. Ciruelos, T. Cuenca, P. Gómez Sal, A. Manzanero, *Organometallics* **1995**, *14*, 177–185.
[42] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923–2925.
[43] *SORTAV*: R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.
[44] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–938.
[45] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Göttingen, Germany, **1998**.

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