Polymerisation of ethene by the novel titanium complex [Ti($Me_3SiNCH_2CH_2NSiMe_3$)Cl_2]; a metallocene analogue

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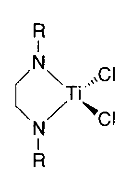
Reaction of the trimethylsilylated diamine ligand (Me_3Si)$NHCH_2CH_2NH$($SiMe_3$) with titanium(IV) precursors affords the novel distorted-tetrahedral complex [Ti($Me_3SiNCH_2CH_2NSiMe_3$)Cl_2] which, when activated by methylaluminoxane, is an active ethene polymerisation catalyst.

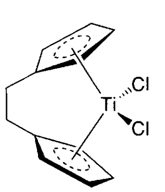
Bis(cyclopentadienyl) complexes of the group 4 metals are of great use in a wide range of applications for organic and polymer synthesis.[1] In particular, the discovery of the highly active metallocene catalysts for alkene polymerisation has received considerable attention in recent years.[2] While the use of mixed cyclopentadienyl–amide[3] and –amidine[4] complexes for catalysis has been reported, interest in the synthesis and applications of related diamide precursors (*e.g.* **A**) is only just emerging.[5] Since highly electron-deficient, usually d^0 metal centres are required for efficient catalytic systems, the somewhat poorer donation of the amide ligands in **A** might be expected to offer enhanced activity over the analogous *ansa*-metallocene complexes **B**. In this context, recent reports describing the use of zirconium–amide and –alkoxide complexes for ethene polymerisation are noteworthy.[6–8]

Here, we describe the synthesis of the novel *ansa*-metallocene analogue [Ti($Me_3SiNCH_2CH_2NSiMe_3$)Cl_2] **2**, containing a chelating diamide ligand. Preliminary results indicate that **2**, in the presence of an excess of methylaluminoxane (MAO), is an active catalyst precursor for ethene polymerisation, with activity comparable to cyclopentadienyl complexes. As such, **2** is representative of a new class of homogeneous, non-cyclopentadienyl-based alkene polymerisation catalysts.

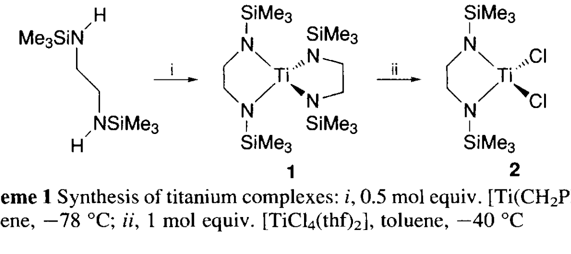
Reaction of [Ti(CH_2Ph)$_4$] with 2 mol equiv. of $Me_3SiNHCH_2CH_2NHSiMe_3$ (Scheme 1) at low temperatures results in the liberation of toluene (identified by NMR), and the formation of the disubstituted complex [Ti($Me_3SiNCH_2CH_2NSiMe_3$)$_2$] **1**, which may be isolated as thermally stable orange crystals. Complex **1** can also be prepared by lithiation of $Me_3SiNHCH_2CH_2NHSiMe_3$, followed by reaction with [$TiCl_4$(thf)$_2$].[9] Stirring solutions of **1** and 1 mol equiv. of [$TiCl_4$(thf)$_2$] for 24 h leads to the redistribution of the diamide ligands between the titanium centres and the formation of [Ti($Me_3SiNCH_2CH_2NSiMe_3$)Cl_2] **2**. Analytical, spectroscopic and mass spectrometric data are consistent with the proposed formulations.‡



A



B



Scheme 1 Synthesis of titanium complexes: *i*, 0.5 mol equiv. [Ti(CH_2Ph)$_4$], toluene, −78 °C; *ii*, 1 mol equiv. [$TiCl_4$(thf)$_2$], toluene, −40 °C

X-Ray quality crystals of **2** were grown from toluene solution.§ The molecular structure shows a distorted-tetrahedral titanium centre (Fig. 1). The Ti–Cl bond lengths [2.260(1) Å] are substantially shorter than those of [Ti(η^5-C_5H_5)$_2Cl_2$],[10] demonstrating the higher electrophilicity of the titanium centre. Similarly, the Ti–N bond lengths [1.844(2) Å] are relatively short, indicating some N → Ti π-donation character to the bonding [confirmed by an extended Hückel molecular orbital (EHMO) study, see below]. The somewhat 'open' and 'closed' Cl–Ti–Cl and N–Ti–N angles [110.73(4), 91.0(1)° respectively] presumably reflect the constraint on the geometry provided by the C_2H_4 link of the diamide ligand. It is of note that the Cl–Ti–Cl angle in [Ti(η^5-C_5H_5)$_2Cl_2$] at 94.5° is substantially more acute.

Insight into the nature of the bonding in **2** is provided by an EHMO[11] study based upon the atomic coordinates of the crystallographic study. The lowest five vacant orbitals of the Ti($Me_3SiNCH_2CH_2NSiMe_3$) fragment are mainly of d-orbital character and show a splitting characteristic of essentially square-planar coordination. Interaction between these orbitals and suitable p-orbitals of the chloride ligands leads to a splitting pattern appropriate to the approximately tetrahedral geometry. The two lowest unoccupied molecular orbitals are made up mainly of '$d_{x^2-y^2}$' and 'd_{yz}' (Fig. 2). A low-lying LUMO is of great importance to much of the chemistry of group 4 metallocene complexes (*e.g.* in the case of alkene polymer-

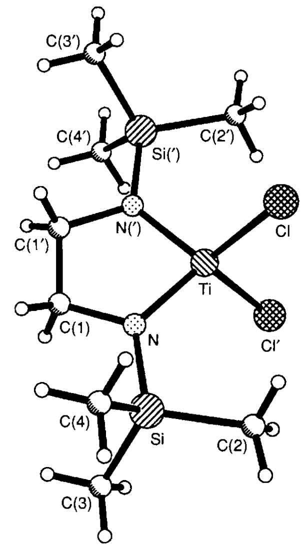


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Ti–N 1.844(2), Ti–Cl 2.2603(6), N–C(1) 1.483(3), N–Si 1.760(2), C(1)–C(1′) 1.496(4); N–Ti–N′ 91.0(1), Cl–Ti–Cl′ 110.73(4), N–Ti–Cl 113.65(5), N–Ti–Cl′ 113.29(5), N–C(1)–C(1′) 111.2(1).

isation, the Lewis-acidic metal centre is able to form α-agostic interactions with the growing polymer chain, which are thought necessary for propagation to proceed).[2] The diamide complex **2** has vacant, low-lying orbitals which can similarly fulfil this role.

Mixtures of **2** and MAO are highly active ethene polymerisation catalysts, as expected considering previous work with similar bulky diimine ligands[12] and the fact it is a metallocene analogue (Table 1). In a typical reaction, a solution of **2** (10 mg in 100 cm^3 of toluene) and MAO (100 equiv.) at 20 °C was pressurised with C_2H_4 (2.8 bar) for 1 h. The polymerisation was quenched by the addition of MeOH–HCl. Combustion analysis of the polyethylene (0.255 g) recovered satisfied the formula $(C_2H_4)_x$. While these yields are not optimised, they are comparable to those of recently reported homogeneous systems.[5]

The rate of conversion of ethene with time is shown in Fig. 3. The yield of polyethylene produced by **2** increases linearly with time, suggesting that catalytic activity remains constant. This, coupled with the fact that the activity of **2** is relatively insensitive to temperature over the range 0–50 °C, indicates the presence of a very robust system. In contrast, $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ shows a somewhat higher initial rate of conversion, but activity tails off rapidly and is close to zero after 1 h. Thus the diamine ligand gives a more stable catalyst than the metallocene type. The polyethylene produced by this system is highly insoluble and thus so far precluded investigation into polymer properties.

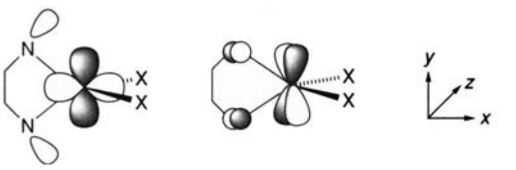


Fig 2 Simplified sketches of shapes of LUMOs of **2**

Table 1 Ethene polymerisation data for titanium complexes

T/°C	Yield of PE/g	Activity/ kg mol^{-1} bar^{-1} h^{-1}
0	0.297	3.4
21	0.255	2.9
50	0.309	3.5

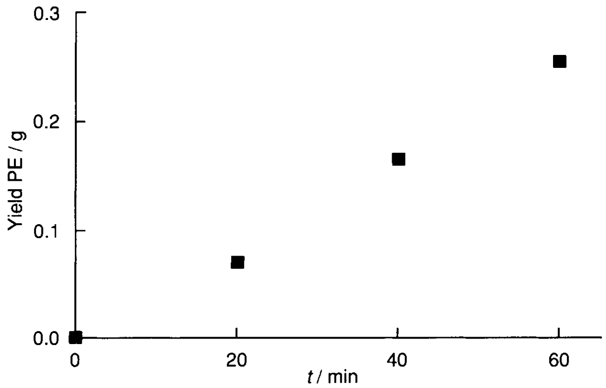


Fig. 3 Time–conversion plots for polymerisation of ethene by **2**

In conclusion, we have described here simple and versatile methods for the preparation of metallocene analogues based upon chelating diamine ligands. We are continuing investigations of their activity as catalysts for organic and polymer synthesis.

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Footnotes

† Deceased.

‡ Selected spectroscopic and analytical data for **1**: ^{1}H NMR (CDCl$_3$, 250 MHz, 295 K), δ 3.87 (s, 2 H, CH$_2$), 0.08 (s, 9 H, Me); ^{13}C, δ 49.94 (CH$_2$), −0.43 (Me). Anal. Found (required for $C_{16}H_{44}N_4Si_4Ti$): C, 42.80 (42.45); H, 9.75 (9.80); N, 12.20 (12.40%).

For **2**: ^{1}H NMR (CDCl$_3$, 250 MHz, 295 K), δ 4.54 (s, 2 H, CH$_2$), 0.26 (s, 9 H, Me); ^{13}C, δ 53.75 (CH$_2$), −1.68 (Me). Anal. Found (required for $C_8H_{22}Cl_2N_2Si_2Ti$): C, 30.10 (29.90); H, 6.90 (6.90); N, 8.60 (8.70%).

§ *Crystal data* for **2**: $C_8H_{22}Cl_2N_2Si_2Ti$, M = 321.26, orthorhombic, space group *Pbcn*, a = 6.9242(3), b = 13.6476(6), c = 17.6818(8) Å, U = 1670.9(1) Å^3, Z = 4, D_c = 1.277 g cm^{-3}, $F(000)$ = 672, T = 220 K. 6766 reflections were measured on a Siemens three-circle diffractometer equipped with a SMART CCD area detector, using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å, 2θ < 48°, μ = 0.953 mm^{-1}). Data were corrected for absorption. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$ = 0.069 (1202 independent reflections), $R = \Sigma|F_o - F_c|/\Sigma F_o$ = 0.024, S = 1.075. The heavy atoms were located using the Patterson interpretation of SHELXTL.[13] Refinements were by full-matrix least squares on F^2. Anisotropic thermal parameters were used for all non-H atoms. H atoms were given fixed isotropic temperature factors with positions constrained by the heavy-atom geometry in the refinement. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/280.

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