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Letter

ansa-Linked titanium macrocycle–imido complexes

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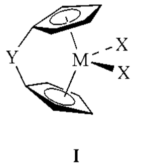
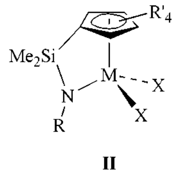
The first *ansa*-linked macrocycle–imido complexes are described; they are isolobal analogues of *ansa*-linked Group 4 bis(cyclopentadienyl) complexes and relatives of constrained geometry cyclopentadienyl–amido olefin polymerisation catalysts.

ansa-Linked metallocenes of the generic type **I**, their bridged bis(tetrahydroindenyl) analogues, and the so-called constrained geometry cyclopentadienyl–amide systems such as **II** have been immensely important in the development of well-defined homogeneous Ziegler–Natta catalysts.[1] Indeed, the reaction chemistry in general of *ansa*-linked metallocenes very often differs substantially from that of their non-bridged analogues, and this phenomenon has been referred to as the "*ansa* effect".[2] The key differences between compounds of the type **I** and **II** and their non-bridged analogues can be traced to the configurational stability and geometric restrictions imposed by the *ansa* bridge.

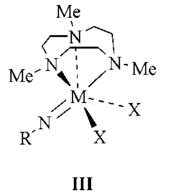
We are exploring the chemistry and catalytic applications of recently reported compounds of the type **III**.[3] These are new analogues of Group 4 metallocenes since both the *fac*-coordinating triazacyclononane and dianionic imide ligands are isolobal with the cyclopentadienide anion.[4] We were very interested to prepare *ansa*-linked analogues of **III** because such target compounds will allow important comparisons to be made both with the *ansa*-metallocence complexes (**I**) and the cyclopentadienyl–amide systems (**II**), as well as with **III**. Such studies will clearly contribute to the understanding and wider applicability of the *ansa* effect.[5]



I
M = Group 4 metal;
Y = SiMe$_2$, CR$_2$, C$_2$H$_4$



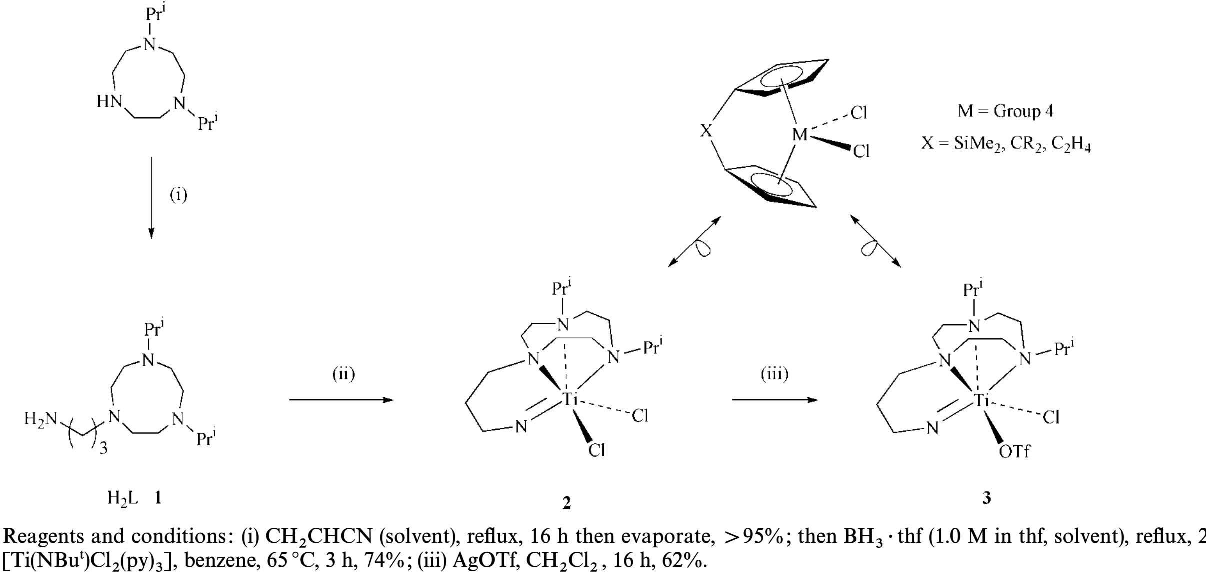
II
M = Ti, Zr;
X = halide, alkyl



III
M = Ti, Zr;
X = halide, alkyl

The new chemistry is summarised in Scheme 1.† The synthetic approach chosen for the synthesis of the *ansa*-linked macrocycle–imides is to use a propylamine-functionalised triazacyclononane pro-ligand. This allows for the simultaneous incorporation of the new macrocyclic and imido functionalities into the titanium coordination sphere. Analogous protocols are generally used for the synthesis of *ansa*-compounds **I** and **II**. The new proligand H_2L **1** is readily prepared in gram-quantities *via* a straightforward, two-stage synthesis in 64% overall yield starting from Pr^i_2[9]aneN$_3$.[6] Subsequent reaction of H_2L with [Ti(NBu^t)Cl$_2$(py)$_3$][7] in benzene gave the new *ansa*-linked titanium macrocycle–imido complex [Ti(L)Cl$_2$] **2** in 74% isolated yield.

The new *ansa*-linked compound **2** was characterised by NMR spectroscopy, EI mass spectrometry (molecular ion observed) and elemental analysis.† For example, the ^1H NMR spectrum of **2** shows four doublets for the diastereotopic isopropyl groups of the macrocycle, as well as signals for all six chemically inequivalent hydrogens of the three diastereotopic methylene groups of the propylene *ansa*-link, consistent with the expected C_1 symmetry. Although repeated attempts to



H_2L **1**

2

3

Scheme 1 Reagents and conditions: (i) CH$_2$CHCN (solvent), reflux, 16 h then evaporate, >95%; then BH$_3$ · thf (1.0 M in thf, solvent), reflux, 24 h, 64%; (ii) [Ti(NBu^t)Cl$_2$(py)$_3$], benzene, 65 °C, 3 h, 74%; (iii) AgOTf, CH$_2$Cl$_2$, 16 h, 62%.

obtain diffraction-quality crystals of **2** were unsuccessful, we have prepared and crystallographically characterised the mono-triflate derivative [Ti(L)Cl(OTf)] **3** (Scheme 1) in order to establish unambiguously the mononuclear, *ansa*-linked geometry proposed.‡ Two views of the molecular structure of **3** are shown in Fig. 1 along with selected bond lengths and angles.

Molecules of [Ti(L)Cl(OTf)] **3** are mononuclear in the solid state and contain six-coordinate titanium centres facially coordinated by a triazacyclic moiety. This is in turn linked *via* a propylene linkage to an imido group also bonded to titanium. The coordination sphere is completed by mutually *cis* chloride and triflate ligands. The propylene *ansa*-link has a substantial constraining effect on the angular metric parameters of **3**. The 150.5(2)° angle subtended at the imido nitrogen, N(63), is at the low end of the range of values for which an imide may still be considered a four-electron donor,[8] and is considerably less than that for the non-*ansa* complex [Ti(NBu^t)(Me$_3$[9]aneN$_3$)Cl$_2$][Bu^t–N=Ti = 171.02(2)°].[3] But despite the flexibility of the C–N$_{\mathrm{imide}}$=Ti unit, the *ansa*-link in **3** clearly "ties back" (in analogous way to that for **I** and **II**) the [9]aneN$_3$ ring and imido groups. This is evidenced by: (i) a substantial *decrease* in the angle between the N$_{\mathrm{imide}}$=Ti bond vector and the normal to the macrocycle nitrogens [N(3)N(6)N(9)] least squares plane (116.5° in **3** *cf.* 123.7° in non-*ansa*-bridged [Ti(NBu^t)(Me$_3$[9]aneN$_3$)Cl$_2$]) and (ii) an *increase* in the angle between the N$_{\mathrm{imide}}$=Ti bond vector and the [Ti(1)Cl(1)O(1)] plane (104.2° in **3** *cf.* 98.1° for the corresponding value in [Ti(NBu^t)(Me$_3$[9]aneN$_3$)Cl$_2$]). The more acute angle between the macrocycle N$_3$-donor set and the imido group in *ansa*-bridged **3** is structurally analogous to the more acute Cp$_{\mathrm{centroid}}$–M–Cp$_{\mathrm{centroid}}$ and Cp$_{\mathrm{centroid}}$–M–N$_{\mathrm{amide}}$ angles found in *ansa*-linked bis(cyclopentadienyl) **I** and cyclopentadienyl–amide **II** systems, respectively (when compared with the non-*ansa*-linked homologues). Interestingly, given the significant angular constraints imposed by the *ansa*-linkage, the Ti–Cl, Ti=N$_{\mathrm{imide}}$ and Ti–N$_{\mathrm{macrocycle}}$ distances are not significantly different from the related, non-*ansa*-linked complex [Ti(NBu^t)(Me$_3$[9]aneN$_3$)Cl$_2$].[3]

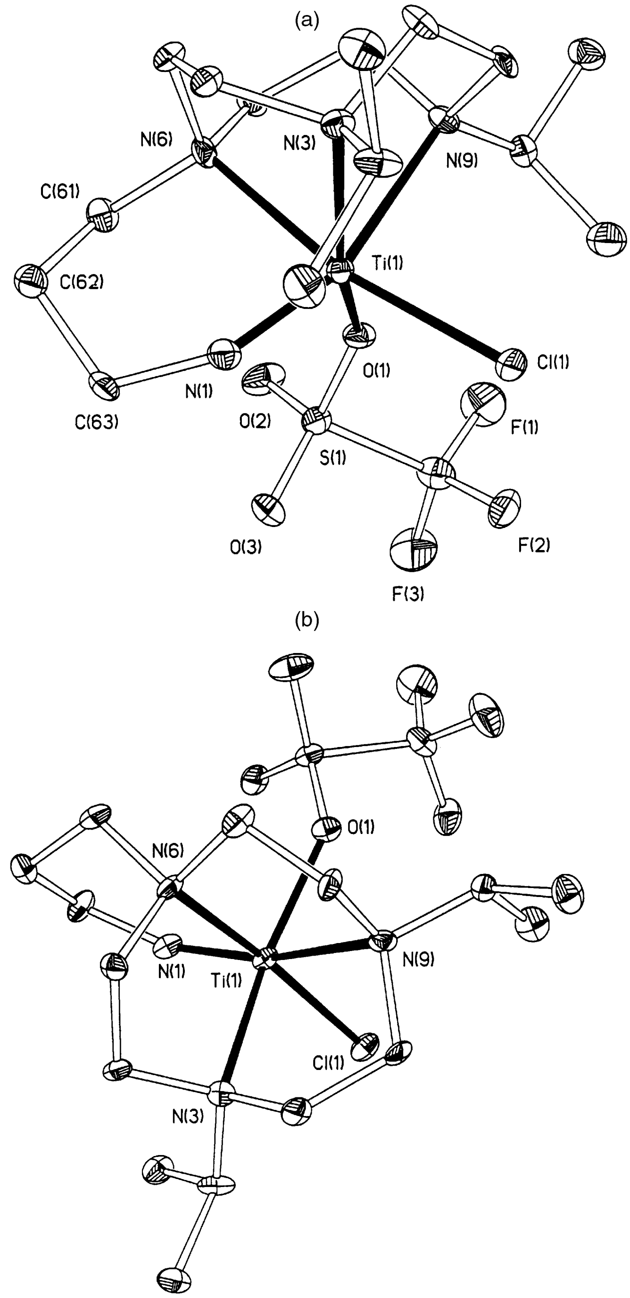


Fig. 1 Displacement ellipsoid (25% probability) plots for [Ti(L)Cl(OTf)] 3. (a) General view and (b) viewed perpendicular to the macrocycle [N(3)N(6)N(9)] plane. Hydrogen atoms are omitted. Selected bond lengths (Å) and angles (°): Ti(1)–N(1) 1.699(3), Ti(1)–N(3) 2.278(2), Ti(1)–N(6) 2.259(3), Ti(1)–N(9) 2.449(3), Ti(1)–Cl(1) 2.3817(9), Ti(1)–O(1) 2.070(2), Ti(1)–N(1)–C(63) 150.5(2), Cl(1)–Ti(1)–O(1) 96.51(6), N(1)–Ti(1)–N(3) 100.1(1), N(1)–Ti(1)–N(6) 84.1(1), N(1)–Ti(1)–N(9) 159.6(1), N(1)–Ti(1)–Cl(1) 104.26(9), N(1)–Ti(1)–O(1) 97.6(1).

The crystal structure of [Ti(L)Cl(OTf)] **3** supports that proposed in Scheme 1 for [Ti(L)Cl$_2$] **2** and establishes these compounds as the first complexes of the new *ansa*-linked macrocycle–imido ligand set. The dianionic ligand L is an isoelectronic analogue of the dianionic *ansa*-bis(cyclopentadienyl) ligand set, and the compounds **2** and **3** are isolobal analogues of *ansa*-linked Group 4 metallocene complexes. Moreover, the compounds **2** and **3** are the first examples of any pendant-arm macrocyclic ligand bearing a dianionic donor group,[9] although non-macrocyclic Group 5 and 6 compounds with chelating imide groups have previously been described.[10]

The proligand H$_2$L **1** and its homologues promise to give access to a rich and interesting derivative macrocycle–imido chemistry in which the *ansa*-link macrocycle ring substituents may be varied to influence reactivity and structure through ligand set steric and electronic effects. There is considerable scope for development of this work since protocols both for the asymmetric functionalisation of triazacycles[9] and for the synthesis of transition metal imides[8] are well-established in the literature. We are currently exploring the reaction and catalytic chemistry of early transition metal *ansa*-linked macrocycle–imido complexes such as **2** and **3**, as well as related *ansa*-linked macrocycle–amido and –alkoxy (*i.e.* monoanionic) systems.

Acknowledgements

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Notes and references

† Proligand **1** has been characterised by ^{1}H and ^{13}C NMR spectroscopy and high resolution mass spectrometry. Satisfactory elemental analysis for complex **2** has been obtained. Characterising data for **3**, which co-crystallises with *ca.* 15% [Ti(L)(OTf)$_2$], have been obtained as far as possible. Representative ^{1}H NMR data (500 MHz): for **1**: $\delta(\mathrm{C_6D_6})$ 2.80 (m, 4 H, $\mathrm{C\underline{H}_2CH_2N(CH_2)_3NH_2}$ or $\mathrm{CH_2C\underline{H}_2N(CH_2)_3NH_2}$), 2.79 (sept, $J = 6.5$, 2 H, $\mathrm{CHMe_2}$), 2.66 (t, $J = 8.0$, 2 H, $\mathrm{H_2NCH_2CH_2C\underline{H}_2}$ or $\mathrm{H_2NC\underline{H}_2CH_2CH_2}$), 2.65 (m, 4 H, $\mathrm{CH_2C\underline{H}_2N(CH_2)_3NH_2}$ or $\mathrm{C\underline{H}_2CH_2N(CH_2)_3NH_2}$), 2.52 (s, 4 H, $\mathrm{Pr^iNC\underline{H}_2C\underline{H}_2NPr^i}$), 2.51 (t, $J = 6.5$, 2 H, $\mathrm{H_2NC\underline{H}_2CH_2CH_2}$ or $\mathrm{H_2NCH_2CH_2C\underline{H}_2}$), 1.50 (apparent quint, apparent $J = 6.5$, 2 H, $\mathrm{C\underline{H}_2CH_2NH_2}$), 0.94 (d, $J = 6.5$, 12 H, $\mathrm{CH\underline{Me}_2}$), 0.80 (br s, 2 H, $\mathrm{NH_2}$); for **2**: $\delta(\mathrm{C_6D_6})$ 3.98 (ddd, $J = 17.0, 11.5, 6.0$, 1 H, 1 × $\mathrm{TiNC\underline{H}_2}$), 3.82

(apparent sept, apparent $J = 6.5$, 1 H, $\mathrm{C\underline{H}Me_2}$), 3.61 (m, 1 H, 1 × $\mathrm{TiNCH_2CH_2C\underline{H}_2}$), 3.58, 3.48 (2 × m, 2 H, 2 × $\mathrm{NCH_2CH_2N}$), 3.37 (apparent sept, apparent $J = 6.5$, $\mathrm{C\underline{H}Me_2}$), 3.06–3.19 (3 × m, 3 H, 3 × $\mathrm{NCH_2CH_2N}$), 2.91 (apparent dt, $J = 12.0$, 3.0, 1 H, 1 × $\mathrm{TiNCH_2CH_2C\underline{H}_2}$), 2.71–2.87 (4 × m, 4 H, 4 × $\mathrm{NC\underline{H}_2CH_2N}$), 2.56–2.64 (3 × m, 3 H, 2 × $\mathrm{NC\underline{H}_2CH_2N}$, 1 × $\mathrm{TiNC\underline{H}_2}$), 2.24 (ddd, $J = 13.0$, 4.0, 2.5, 1 H, $\mathrm{NC\underline{H}_2CH_2N}$), 2.06, 1.96 (2 × m, 2 H, $\mathrm{TiNCH_2C\underline{H}_2}$), 1.81, 1.30, 1.20, 1.04 (4 × d, $J = 6.5$, 4 × 3 H, 4 × $\mathrm{CH\underline{Me}_2}$).

‡ Crystal data for **3**. $\mathrm{C_{16}H_{32}ClF_3N_4O_3STi}$, $M = 500.86$, monoclinic, space group $P2_1/n$, $a = 9.2840(6)$, $b = 19.097(2)$, $c = 12.7810(7)$ Å, $\beta = 99.091(4)°$, $U = 2237.6$ Å^3, $Z = 4$, $\mu = 0.64$ mm^{-1}, $T = 170$ K, $2780 > 3\sigma(I)$ reflections ($R_{\mathrm{merge}} = 0.06$) used in refinement, no. of parameters refined 262, final R indices: $R = 0.0526$, $R_{\mathrm{w}} = 0.0359$. CCDC reference number 440/189. See http://www.rsc.org/suppdata/nj/b0/b002341h/ for crystallographic files in .cif format.

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