Stereochemical control of *cis*- and *trans*-TiCl₂ groups in six-coordinate complexes [(L)TiCl₂] (L²⁻ = N₂O₂-donor Schiff base) and reactions with trimethylaluminium to form cationic aluminium species

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The first example of a *cis*-configuration of the TiCl₂ group in a six-coordinate titanium complex [(L)TiCl₂], involving a tetradentate N₂O₂-donor Schiff base ligand (L²⁻), is reported, and reactions of such complexes with trimethyl aluminium have been shown to generate cationic aluminium species.

There is an increasing interest in the use of group 4 metallocenes, and related compounds, such as the chiral bis(indenyl) complexes involving zirconium and hafnium, in combination with aluminium trialkyls or methylaluminoxane (MAO), as alkene polymerisation catalysts.[1–4] The use of other group 4 coordination compounds in such processes may also be possible, and the d⁰ metal complexes [(L)MCl₂] (M = Ti, Zr), derived from the disodium salts of the tetradentate Schiff bases H₂L (Scheme 1), is one system being explored,[5] since the zirconium derivative, containing a *cis*-ZrCl₂ group, has already been shown to be catalytically active in the presence of an aluminium trialkyl.[6]

The stereochemistry of the MCl₂ group is an important feature of the overall structure with respect to catalytic activity, and therefore it is of significance that to date all reported titanium derivatives [(L)TiCl₂] exhibit a *trans*-geometry for the TiCl₂ fragment,[7,8] instead of the *cis*-arrangements (Scheme 1) that are analogous to that in the *ansa*-metallocenes. The *cis*-structure is, however, more common with the [(L)MCl₂] complexes of the heavier and larger group 4 elements (M = Zr, Hf),[9,10] and has also been observed with an oxovanadium(IV) species [(L)V(O)OMe].[11] It is significant that even in complexes with the same Schiff base ligand, for example the *N,N'*-ethylenebis(acetylacetoiminate) dianion (acen²⁻), the zirconium complex [(acen)ZrCl₂] adopts the *cis*-structure, whereas the corresponding titanium compound reverts to the *trans*-geometry.[8,9] Since titanium is the group 4 element that is often used in catalytic reactions, it is desirable to be able to control the stereochemistry at the metal centre. We now report the synthesis of the first *cis*-titanium Schiff base complexes, using easily accessible Schiff bases, together with some reactions of these species with aluminium trialkyls.
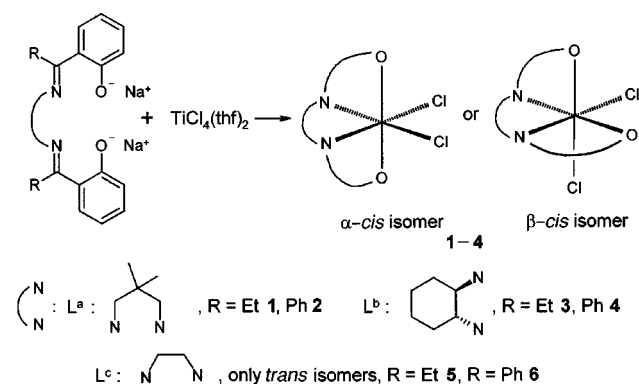
Our present studies on titanium–Schiff base complexes, where we have isolated a series of *trans*-[(L)TiCl₂] complexes,[12] have indicated that substantial steric effects within the ligand are required to achieve a folding of the ligand such that it takes up a *cis*-geometry as shown in Scheme 1. Following molecular mechanics and dynamics calculations on [(L)TiCl₂] derivatives, it appeared that complexes **1–4** should adopt a folded configuration, leading to a *cis*-geometry at the metal centre. The four neutral ligands were prepared in high yield (>90%) by condensation of the appropriate diamine (using *trans*-cyclohexane-1,2-diamine for Lᵇ) and keto derivatives, and converted to the new metal complexes [(L)TiCl₂] (50–60% yield) by the reaction shown in Scheme 1.†

The X-ray structure of [(L)TiCl₂] complex **3**‡ (Fig. 1) shows a distorted octahedral arrangement around the titanium centre, with a folded ligand and a β-*cis*-geometry for the complex. The Cl–Ti–Cl angle is 86.9(1)°. The variation in the ligand geometry has little effect on the bond distances involving the metal. The Ti–O and Ti–N distances are *ca.* 1.82 and 2.19 Å respectively, similar to those reported for the numerous *trans*-[(L)TiCl₂] complexes,[7,8] while the Ti–Cl distances are all *ca.* 2.35 Å in both the *trans*- and *cis*-derivatives [2.323(2) and 2.391(3) Å in **3**]. Similarities in the spectroscopic data (IR, NMR) between **3** and the other three [(L)TiCl₂] complexes **1, 2** and **4** indicate that these also probably form *cis*-structures, but we are still attempting to obtain suitable crystals to allow definitive X-ray studies to be undertaken.
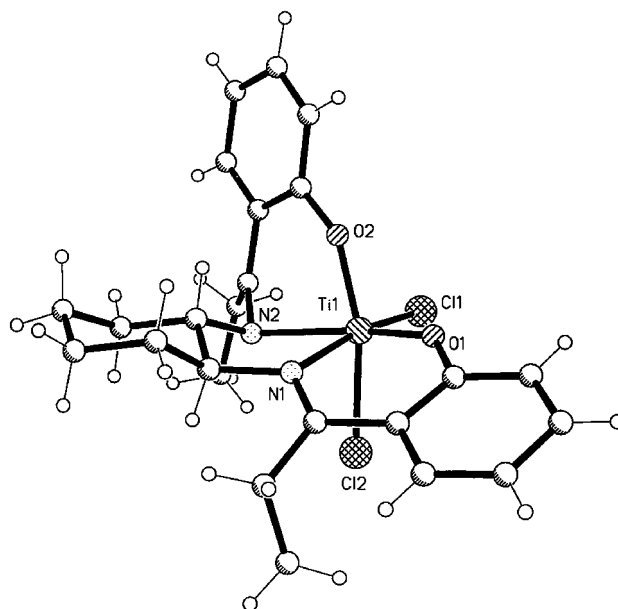

Scheme 1

Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): Ti(1)–O(1) 1.796(5), Ti(1)–O(2) 1.827(5), Ti(1)–N(1) 2.186(5), Ti(1)–N(2) 2.205(6), Ti(1)–Cl(1) 2.323(2), Ti(1)–Cl(2) 2.391(3); O(1)–Ti(1)–O(2) 99.5(2), N(1)–Ti(1)–N(2) 76.6(2), N(2)–Ti(1)–Cl(1) 99.67(16); Cl(1)–Ti(1)–Cl(2) 86.89(9).

We have confirmed that the titanium complexes **1**–**4** act as catalysts for the polymerisation of ethene in the presence of MAO, although they are not as active as the *ansa*-titanocenes.§ Since MAO often contains an appreciable quantity of trimethyl aluminium (TMA, ≈ 15% by weight in the present case) we have investigated the action of TMA on some [(L)TiCl₂] complexes. In a series of ¹H NMR experiments we have used titrations with TMA to show that complete reaction is achieved when a molar ratio [(L)TiCl₂] : TMA of 1 : 2 is attained. In more detailed experiments on the related *trans*-[(Lᶜ)TiCl₂] complexes, red–brown solids of composition [{(Lᶜ)TiCl₂}·2AlMe₃] were obtained in *ca.* 40% yield by the addition of a hexane solution of TMA to the Schiff base complex (2 : 1 mole ratio) in toluene, and subsequent removal of the solvent. The ¹H NMR spectrum of each adduct shows two singlet resonances, with appropriate relative intensities, for the two coordinated AlMe₃ molecules (the derivatives with **5** and **6** gave resonances at δ −0.21, −0.41 and −0.34, −0.53 respectively, arising from the methyl groups of the two different AlMe₃ molecules) in addition to the resonances from Lᶜ. Thus two different sites for coordination of the TMA are indicated, but we have no definitive evidence to indicate the structures of these species at present. If the initially formed red solution from **5** is allowed to stand, colourless, air-reactive crystals are quickly deposited (yield *ca.* 5%), and these were identified from X-ray data‡ as the unexpected ionic species [(Lᶜ)(AlMe)(AlMe₂)]⁺[AlCl₃Me]⁻ (**7**; Fig. 2). Part of the structure of the cation in **7** resembles the previously reported *neutral* species [(Lᶜ)AlR'] [Lᶜ, R = H; R' = Me, Et] which have the metal atom bonded centrally above the N₂O₂ plane.[13,14] In the present case, where the cation is present, the compound contains additionally an AlMe₂ fragment bonded symmetrically to two oxygen atoms of the Schiff base. The [AlCl₃Me]⁻ anion is discrete, with no significant interactions with the cation, and adopts the expected slightly distorted tetrahedral structure. Cationic aluminium alkyl complexes have recently been shown to act as transition metal-free alkene polymerisation catalysts,[15] in addition to the already established cationic group 4 species.[3] The role of the aluminium alkyl as a cocatalyst with group 4 compounds is still the subject of debate, but as a consequence of the present results it is now clear that for some titanium complexes the addition of TMA is capable of generating cationic species of aluminium in solution. It is significant that no titanium atom is present in the cation, but the titanium species is clearly involved in the overall reaction since the [AlCl₃Me]⁻ anion arises by halide abstraction from the titanium centre. Although we have not yet been able to identify the nature of the titanium species remaining in solution, it is of interest that under our conditions we have not yet observed the formation of any Ti(ɪɪɪ) or Ti–Me species, as have been found in other studies involving TMA and the different but closely related complex *trans*-[(Lᶜ)TiCl₂] [(Lᶜ; R = H)].[16]

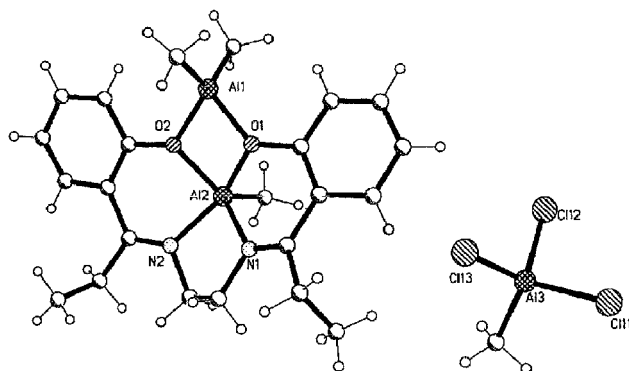**Fig. 2** Molecular structure of **7**. Selected bond lengths (Å) and angles (°): Al(1)–O(1) 1.845(6), Al(1)–O(2) 1.868(6), Al(2)–O(1) 1.873(6), Al(2)–O(2) 1.877(6), Al(2)–N(2) 1.945(7), Al(2)–N(1) 1.960(8); O(1)–Al(1)–O(2) 77.4(2), O(1)–Al(2)–O(2) 76.5(2), O(1)–Al(2)–N(2) 149.6(3), O(2)–Al(2)–N(2) 88.2(3), O(1)–Al(2)–N(1) 88.2(3), O(2)–Al(2)–N(1) 136.2(3), N(2)–Al(2)–N(1) 85.0(3).

We are continuing our studies to determine both the nature of the titanium species remaining in solution, and the effect that variations in the Schiff bases has on the overall reaction involved.

Notes and references

† *Typical procedure*: sodium hydride (2 mol) was added slowly to a solution of the ligand (1 mol) in THF, the suspension was stirred until the evolution of H₂ was complete, and the mixture then refluxed for 2 h. The solution–suspension was cooled to −78 °C and a solution of [TiCl₄(thf)₂] (1 mol) in thf was then added slowly. The resultant suspension was stirred at 50 °C for 5 h, and then filtered through a fine filter stick. The filtrate was evaporated to dryness, and the solid obtained was washed with hot toluene to remove any thf (yield *ca.* 40%). A higher yield (50–60%) can be obtained by extracting the original solid filtered off (mainly NaCl) with toluene. All the new compounds were fully characterised by IR, mass and NMR spectroscopy and elemental analysis.

‡ *Crystal data* for **3**: C₂₄H₂₈Cl₂N₂O₂Ti·CHCl₃, *M* = 614.65, *T* = 150(2) K, monoclinic, space group *P*2₁/*c*, *a* = 16.446(3), *b* = 9.796(2), *c* = 18.160(4) Å, *β* = 111.32(3)°, *U* = 2725.3(9) Å3, *Z* = 4, *μ* = 0.831 mm⁻¹. 12060 reflections (4283 independent) were collected in the range *θ* 2.29–25.12° using a Delft Instruments FAST TV area detector diffractometer. Final *R*1 = 0.053 and *wR*2 = 0.129.

For **7**: C₂₄H₃₄Al₃Cl₃N₂O₂, *M* = 569.82, *T* = 230(2) K, orthorhombic, *Pna*2₁, *a* = 15.7057(15), *b* = 9.7173(9), *c* = 19.5089(15) Å, *U* = 2977.4(5) Å³, *Z* = 4, *μ* = 0.419 mm⁻¹. 5592 reflections (3804 independent) were collected in the range *θ* 2.09–23.00° using a Siemens SMART CCD area-detector diffractometer. Final *R*1 = 0.074 and w*R*2 = 0.161. Refinement was by full-matrix least squares on *F*² for all data using SHELXL-97.[17] Hydrogen atoms were added at calculated positions and refined using a riding model. CCDC 182/1135. See http://www.rsc.org/suppdata/cc/1999/323/ for crystallographic files in .cif.format.

§ Preliminary polymerisation tests using a 1000-fold excess of MAO with the neutral compounds **1**–**4**, in toluene solution at 23 °C and ethene at 30 psi, show they possess low activities of *ca.* 20–100 (g polymer) (mmol catalyst)⁻¹ h⁻¹, while similar runs with several analogous *trans*-[TiCl₂] complexes show a much lower activity (< 1) for these systems.

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