COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Titanium and zirconium complexes supported by dipyrrolide ligands†

Andrew Novak, Alexander J. Blake, Claire Wilson and Jason B. Love*
School of Chemistry, University of Nottingham, University Park, Nottingham, UK NG7 2RD.
E-mail: jason.love@nottingham.ac.uk; Fax: +44 115 9513563; Tel: +44 115 8467167

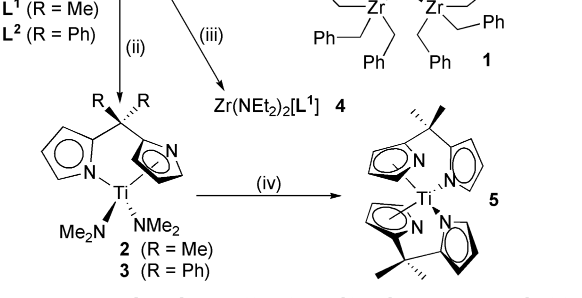
Received (in Cambridge, UK) 9th August 2002, Accepted 15th October 2002
First published as an Advance Article on the web 25th October 2002

The reactions between *meso*-disubstituted dipyrromethanes and titanium and zirconium amides and alkyls have generated the first examples of dipyrrolide complexes of Group 4 metals.

The dipyrromethane group (**L**), as well as being an important precursor to porphyrinogens,[1] and expanded and asymmetric porphyrins,[2] can act as a versatile, dianionic ligand due to bimodal κ^1/η^5 bonding capability of the pyrrolide moieties.[3] In f-element chemistry, this feature promotes intricate aggregation of reactive metal species.[4,5] For example, macrocyclic clusters of Sm^{II}[**L**] mediate the remarkable four-electron reduction of nitrogen *via* the cooperative, one-electron oxidation of four Sm^{II} centres.[6,7] Given the rich chemistry of f-element dipyrrolide compounds and the similarity of **L** to *ansa*-cyclopentadienyls,[8] it is surprising that this ligand has received scant attention in transition metal chemistry; to date, only copper-mediated asymmetric catalysis using the planar-chiral dipyrromethane ligand $[(\eta^5\text{-}C_4H_3N)(\eta^5\text{-}Cp^*Fe)]_2CH_2$ has been reported.[9] Here, we describe selected protonolysis and transamination reactions between the *meso*-disubstituted dipyrromethanes **L** and zirconium and titanium alkyls and amides (see Scheme 1). To our knowledge, the compounds described below are the first Group 4 dipyrrolide compounds and rare examples of dipyrrolide transition metal compounds.

The reaction between $\mathbf{L^1}$ and 2 molar equivalents of $Zr(CH_2Ph)_4$ at 50 °C was monitored by ^1H NMR spectroscopy, and was found to generate the orange, bimetallic zirconium complex **1** in quantitative yield after 2.5 h; prolonged reaction times or heating to higher temperatures resulted in substantial decomposition.† The ^1H NMR spectrum is structurally uninformative; at room temperature, the benzyl CH_2 protons resonate as a single AB doublet. Therefore, in order to assess the binding mode of the ligand, an X-ray diffraction study was undertaken (Fig. 1).‡ The dipyrrolide ligand assumes a σ/π coordination mode to each zirconium centre, resulting in a bimetallic structure. At first glance, each zirconium adopts a distorted trigonal bipyramidal geometry, with the pyrrolide and one benzyl ligand axial and the remaining benzyl and N interactions equatorial. This ligation mode is common in lanthanide chemistry, although the larger coordination number exhibited by the lanthanides allows for expansion to less predictable, macrocyclic structures.[4–7] Closer analysis of the bond lengths and angles between the zirconium and the dipyrrolide and benzyl ligands indicate that the bonding mode of $\mathbf{L^1}$ is not straightforward κ^1/η^5. While the benzyl ligands attached to Zr(2) are classically bound, a weak η^2-interaction between Zr(1) and benzyl C(12) exists [Zr(1)–C(12)–C(13) 101.4(2), Zr(1)···C(13) 2.952 Å]. This coincides with an η^2-pyrrolide interaction at Zr(1) [Zr(1) to N(1) and C(4) are significantly shorter than Zr(1) to C(1), C(2) and C(3)], compared to the η^3-pyrrolide ligation to Zr(2). It is therefore evident that $\mathbf{L^1}$ can adopt coordination modes that satisfy the electronic requirements of the metal.

The transamination reaction between $Ti(NMe_2)_4$ and $\mathbf{L^1}$ (or $\mathbf{L^2}$) was monitored by ^1H NMR spectroscopy and, unlike the zirconium reaction above, proceeds to generate the orange, monometallic, titanium complex **2** in quantitative yield upon mixing at room temperature.† As with **1**, limited structural information is available from the ^1H NMR spectrum, so an X-ray diffraction study was undertaken (Fig. 2).‡ In this case, the dipyrrolide ligand is seen to adopt a unique κ^1:η^5-bonding mode to the single titanium, so generating an overall psuedo-tetrahedral geometry that is reminiscent of constrained geometry catalysts (CGCs).[10] Indeed, the N(2)–Ti(1)-centroid angle of 104.4° is similar to that seen for the archetypal CGC $[\eta^5\text{-}C_5Me_4SiMe_2NBu^t]TiCl_2$ (105.50°) and that of the mixed Cp–pyrrolide titanium complex $[\eta^5\text{-}C_5H_4CH_2\text{-}\kappa^1\text{-}C_4H_3N]Ti(NMe_2)_2$ (103°).[11] In contrast to the CGC systems, the presence of the nitrogen in the pyrrolic ring reduces the



Scheme 1 *Reagents and conditions*: (i) $Zr(CH_2Ph)_4$, PhMe, 50 °C, 2.5 h; (ii) $Ti(NMe_2)_4$, PhMe; (iii) $Zr(NEt_2)_4$, PhMe; (iv) $ClSiMe_3$, PhMe.

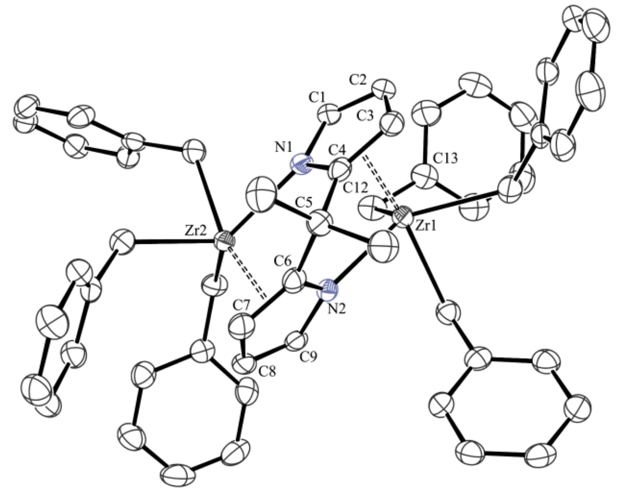


Fig. 1 The molecular structure of **1**. Selected bond lengths (Å): Zr(1)–N(2) 2.330(2), Zr(1)–N(1) 2.465(3), Zr(1)–C(4) 2.473(3), Zr(1)–C(1) 2.633(3), Zr(1)–C(2) 2.732(3), Zr(1)–C(3) 2.642(3).

---

† Electronic supplementary information (ESI) available: Full experimental, NMR and analytical data. See http://www.rsc.org/suppdata/cc/b2/b208751k/

DOI: 10.1039/b208751k

This journal is © The Royal Society of Chemistry 2002

symmetry of the π-bound ligand and so renders **2** intrinsically chiral. However, while the asymmetric unit of the solid state structure shows two molecules of the same hand, the overall structure is centrosymmetric and so confirms that **2** has crystallised as a racemic mixture. In solution, a dynamic process renders both sets of pyrrolic and Me_2N groups equivalent, a process that must involve facile, thermally induced, pyrrolic hapticity changes.[12] Unlike cyclopentadienyl-based Group 4 amido complexes where the amido group is substituted by chloride on addition of chlorosilane, **2** undergoes a conproportionation reaction when treated with $ClSiMe_3$ to form the bis(dipyrrolide) complex **5** as a dark red, crystalline material. X-Ray structural analysis confirmed this formulation,† with both dipyrrolide ligands adopting similar κ^1/η^5 bonding modes to **2** (see Scheme 1). In the ^1H NMR spectrum of **5**, a single set of resonances are seen for the dipyrrolide protons, indicating that, as with **2**, a dynamic process that equilibrates the pyrrolic rings is occurring.

In order to determine if the reaction pathway forming bimetallic **1** or monometallic **2** is dependant on the metal radius or on the type of ancillary ligand (amido or alkyl), the reactions between $\mathbf{L^1}$ and $Zr(NEt_2)_4$ and $Ti(CH_2SiMe_3)_4$ were monitored by NMR spectroscopy. The former reaction in C_6D_6 showed that a 1 : 1 reaction occurs, and that the evolved $HNEt_2$ was easily removed under vacuum; presumably **4** has a similar structure to **2**. The latter protonolysis reaction was more problematic; a slow reaction occurred at elevated temperatures (100 °C) yielding a paramagnetic substance that has yet to be characterised.

As the dipyrrolide complexes described above have structural similarity to CGCs, a preliminary alkene polymerisation study was undertaken. While the titanium compounds **2** and **5** showed negligible activity as ethene polymerisation catalysts,† pretreatment of **4** with $ClSiMe_3$ followed by MAO gave a species that promoted ethene polymerisation with an activity of 8.7 kg $mol^{-1}\ h^{-1}\ bar^{-1}$ (*cf.* 29.2 kg $mol^{-1}\ h^{-1}\ bar^{-1}$ using Cp_2ZrCl_2 under identical conditions). Analysis of this polymer by high temperature gel permeation chromatography showed that it was of very high molecular weight ($M_w = 1.2 \times 10^6$) and high polydispersity (PD = 80) (*cf.* $M_w = 1.27 \times 10^4$, PD = 3.9 for Cp_2ZrCl_2).

We have shown that *meso*-disubstituted dipyrromethane ligands are suitable for Group 4 metals, and can adopt various structural motifs upon ligation that appear dependent on the electronic/coordinative requirements of the metal. Importantly, some control over complex formation is possible, generating monometallic amido and bimetallic alkyl Group 4 compounds, and not the intricate clusters as seen for Yb and Sm. At present, we are investigating the reactivity of these compounds towards small molecules and are exploring routes to the elaboration of the dipyrrolide ligand periphery.

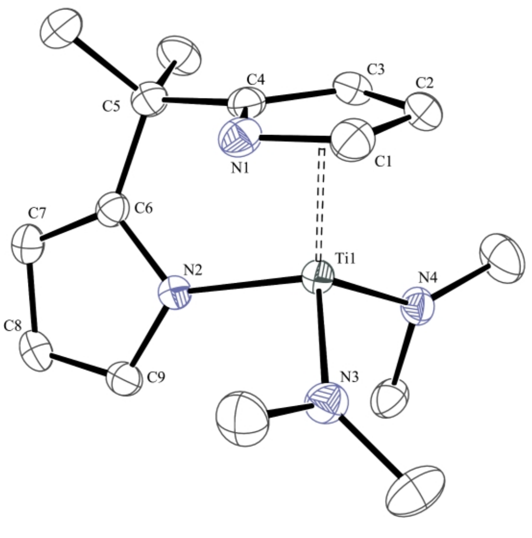


Fig. 2 The molecular structure of **2** (one molecule from the asymmetric unit is shown). Selected bond lengths (Å): Ti(1)–N(2) 2.0389(13), Ti(1)–N(3) 1.8963(13), Ti(1)–N(4) 1.8866(13), Ti(1)–cent. 1.700.

We thank the Royal Society (J. B. L., University Research Fellowship), the Nuffield Foundation (A. N., Undergraduate Research Bursary), and the University of Nottingham for support, Prof. F. G. N. Cloke and Dr G. K. B. Clentsmith for help with the ethene polymerisation studies, the EPSRC/Rapra Technology for the polymer analysis and the EPSRC for the award of the diffractometer.

Notes and references

‡ *Crystal data*: $[Zr_2(CH_2Ph)_6(\mathbf{L^1})]$ **1**, orange tablet, 0.17 × 0.12 × 0.08 mm^3, $C_{53}H_{54}N_2Zr_2$, monoclinic, space group $P2_1/c$, a = 18.8621(13), b = 11.2299(8), c = 20.6506(14) Å, β = 96.096(2)°, U = 4349.5(5) $Å^3$, Z = 4, μ = 0.517 mm^{-1}, $F(000)$ = 1864, 33815 collected reflections, 7620 unique (R_{int} = 0.055). Data were collected at 150(2) K on a Bruker SMART1000 CCD, λ = 0.71073 Å, θ = 1.98–25.00°, absorption correction applied using SADABS, solved by direct methods and refined using SHELXL-97. Final full-matrix least-squares refinement on F^2 converged at R_1 = 0.0343 for 7620 reflections with $I > 2\sigma(I)$, wR_2 = 0.0637, S = 1.043 for all data and 514 parameters. $[Ti(NMe_2)_2(\mathbf{L^1})]$ **2**, orange lozenge, 0.41 × 0.38 × 0.18 mm^3, $C_{15}H_{24}N_4Ti$, monoclinic, space group $P2_1/c$, a = 10.3274(6), b = 12.3793(7), c = 25.3112(14) Å, β = 93.705(1)°, U = 3229.2(3) $Å^3$, Z = 8, μ = 0.527 mm^{-1}, $F(000)$ = 1312, 19861 collected reflections, 7881 unique (R_{int} = 0.021), λ = 0.71073 Å, θ = 1.83–28.72°, absorption correction applied using SADABS, solved by direct methods and refined using SHELXL-97. Final full-matrix least-squares refinement on F^2 converged at R_1 = 0.0323 for 7536 reflections with $I > 2\sigma(I)$, wR_2 = 0.0799, S = 1.026 for all data and 369 parameters. CCDC 193472 and 193473. See http://www.rsc.org/suppdata/cc/b2/b208751k/ for crystallographic data in CIF or other electronic format.

1 C. Floriani, *Chem. Commun.*, 1996, 1257; B. Turner, A. Shterenberg, M. Kapon, K. Suwinska and Y. Eichen, *Chem. Commun.*, 2002, 404.
2 A. Jasat and D. Dolphin, *Chem. Rev.*, 1997, **97**, 2267; C.-H. Lee and J. S. Lindsey, *Tetrahedron*, 1994, **50**, 11427.
3 E. Campazzi, E. Solari, R. Scopelliti and C. Floriani, *Inorg. Chem.*, 1999, **38**, 6240; J. M. Tanski and G. Parkin, *Organometallics*, 2002, **21**, 587; M. Ganesan, C. D. Bérubé, S. Gambarotta and G. P. A. Yap, *Organometallics*, 2002, **21**, 1707.
4 T. Dubé, S. Conoci, S. Gambarotta and G. P. A. Yap, *Organometallics*, 2000, **19**, 1182.
5 D. M. M. Freckmann, T. Dube, C. D. Berube, S. Gambarotta and G. P. A. Yap, *Organometallics*, 2002, **21**, 1240.
6 T. Dubé, S. Conoci, S. Gambarotta, G. P. A. Yap and G. Vasapollo, *Angew. Chem., Int. Ed.*, 1999, **38**, 3657.
7 M. Ganesan, S. Gambarotta and G. P. A. Yap, *Angew. Chem., Int. Ed.*, 2001, **40**, 766.
8 H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed.*, 1995, **34**, 1143; C. E. Zachmanoglou, A. Docrat, B. M. Bridgewater, G. Parkin, C. G. Brandow, J. E. Bercaw, C. N. Jardine, M. Lyall, J. C. Green and J. B. Keister, *J. Am. Chem. Soc.*, 2002, **124**, 9525.
9 M. M.-C. Lo and G. C. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 4572; M. M.-C. Lo and G. C. Fu, *J. Am. Chem. Soc.*, 1998, **120**, 10270. *Note added at proof*: tantalum dipyrrolide compounds have been recently reported: G. Aharonian, S. Gambarotta and G. P. A. Yap, *Organometallics*, 2002, **21**, 4247.
10 A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587.
11 W. S. Seo, Y. J. Cho, S. C. Yoon, J. T. Park and Y. Park, *J. Organomet. Chem.*, 2001, **640**, 79; D. W. Carpenetti, L. Kloppenburg, J. T. Kupec and J. L. Petersen, *Organometallics*, 1996, **15**, 2668.
12 D. P. Heenan, C. Long, V. Montiel-Palma, R. N. Perutz and M. T. Pryce, *Organometallics*, 2000, **19**, 3867.