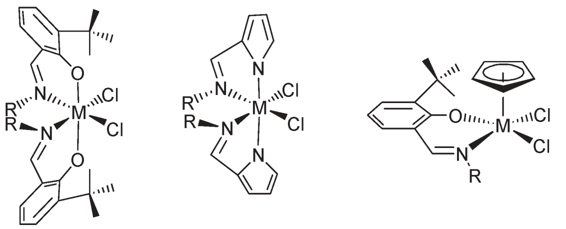
Hybrid catalysts: the synthesis, structure and ethene polymerisation activity of (salicylaldiminato)(pyrrolylaldiminato) titanium complexes†

Dale A. Pennington,[a] Simon J. Coles,[b] Michael B. Hursthouse,[b] Manfred Bochmann[a] and Simon J. Lancaster*[a]

Received (in Cambridge, UK) 23rd March 2005, Accepted 6th May 2005
First published as an Advance Article on the web 24th May 2005
DOI: 10.1039/b504113a

The mono(salicylaldiminato) complexes Ti{3-^{t}Bu-2-(O)$C_6H_3CH{=}N(R)$}Cl_3(THF) (where R = C_6H_5, C_6F_5) react with the metallated pyrrolylaldiminato ligand, K[2-(C_6H_5NCH)C_4H_3N], to afford the first examples of hybrid salicylaldiminato-ligated octahedral titanium complexes; the pre-catalysts give from very high to extremely high ethene polymerisation productivities when activated with MAO.

There continues to be intense interest in 1-alkene polymerisation catalysts based on octahedral group 4 metal coordination complexes with either two identical anionic bidentate ancillary ligands or a single dianionic, tetradentate ligand.[1] Notable successes include the bis(salicylaldiminato) (I, Chart 1) and bis(pyrrolylaldiminato) (II) complexes.[2,3] Whilst the combination of cyclopentadienyl and salicylaldiminato ligands, which afford stereochemically-labile five-coordinate complexes (III), have recently been published,[4] there are no reports of hybrid octahedral complexes containing two different classes of bidentate, mono-anionic ligand. We are interested in such complexes because they promise to preserve the stereochemical rigidity associated with octahedral geometries, whilst generating new catalysts with desirable properties derived from each of the two parent, homo-ligated catalysts. Coates' identification of novel high activity catalysts with two different salicylaldiminato ligands, using a combinatorial screening method, provided a partial demonstration of the potential of this approach.[5] However, to date, none of these hetero-ligated complexes have been isolated or crystallographically characterised. We report here the systematic synthesis, solid state structures and extremely high catalytic activities of (salicylaldiminato)(pyrrolylaldiminato) titanium pre-catalysts; the first octahedral hybrids of two successful catalyst families.



I II III

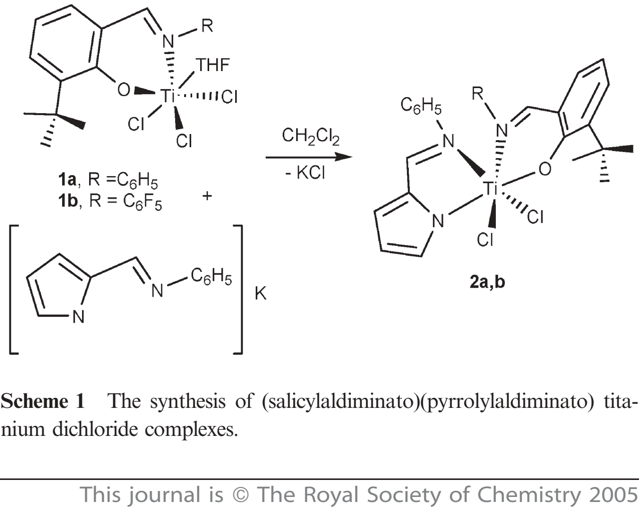
Chart 1

We recently reported the synthesis of a series of mono(salicylaldiminato) metal trichloride complexes through treatment of $MCl_4(THF)_2$ with the corresponding silyl ether (M = Ti, Zr).[6] In the case of the phenyl and perfluorophenyl titanium derivatives, identical products Ti{3-^{t}Bu-2-(O)$C_6H_3CH{=}N(R)$}Cl_3(THF) (**1a** R = C_6H_5, **1b** R = C_6F_5) were more conveniently obtained from the reaction between the free phenol and $TiCl_4(THF)_2$ in dichloromethane solution.[7]

Treatment of red-coloured dichloromethane solutions of **1a** or **1b** with one equivalent of the metallated pyrrolylaldiminato ligand K[2-(C_6H_5NCH)C_4H_3N] afforded dark red solutions of **2a** and **2b** respectively (Scheme 1). In both cases, cooling a dichloromethane/light petroleum solution to −25 °C yielded crystalline samples with the expected composition (by elemental analyses) and of sufficient quality for X-ray crystallography.

Since the bis(salicylaldiminato) titanium dichloride complexes Ti{3-^{t}Bu-2-(O)$C_6H_3CH{=}N(R)$}$_2Cl_2$ (**Ia** R = C_6H_5, **Ib** R = C_6F_5) adopt a *trans*-O,O *cis*-Cl,Cl geometry and the bis(pyrrolylaldiminato) titanium system Ti{2-(C_6H_5NCH)C_4H_3N}$_2Cl_2$ (**IIa**) gives a *trans*-pyrN,pyrN *cis*-Cl,Cl arrangement, we anticipated the distorted octahedral *trans*-O,pyrN *cis*-Cl,Cl structures found for **2a** (Fig. 1) and **2b** (Fig. 2) (pyrN = pyrrolyl nitrogen).[2f,2g,3a]‡ The key bond angles in **2a** and **2b**, and the relevant homo-ligand complexes **Ia**, **Ib** and **IIa** are collated in Table 1. In both **2a** and **2b** the O(1)–Ti–N(2) angles are intermediate between those of their parent homo-ligand complexes. The N(1)–Ti–N(3) and Cl(1)–Ti–Cl(2) angles are very similar in **2a** and **2b** and lie between those of **IIa** and **Ib**.[8]

The chloroform-d$_1$ ^{1}H NMR and ^{19}F NMR spectra of complex **2b** were consistent with a single isomer. The spectra were unchanged, even on warming to 60 °C overnight, thus indicating



Scheme 1 The synthesis of (salicylaldiminato)(pyrrolylaldiminato) titanium dichloride complexes.

---

† Electronic Supplementary Information (ESI) available: The polymerisation procedure, experimental details and characterisation data for compounds **2a** and **2b**. See http://www.rsc.org/suppdata/cc/b5/b504113a/

*S.Lancaster@uea.ac.uk

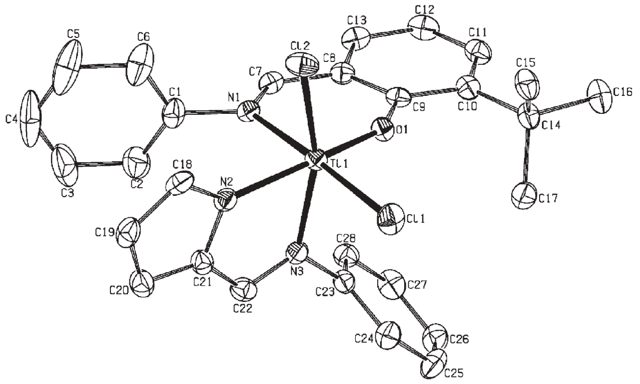


Fig. 1 X-ray crystal structure of **2a** (50% displacement ellipsoids; hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): Ti–Cl(1) 2.283(8), Ti–Cl(2) 2.296(9), Ti–O(1) 1.808(17), Ti–N(2) 2.073(2), Ti–N(1) 2.242(2), Ti–N(3) 2.140(2), O(1)–Ti–N(2) 164.42(8), N(1)–Ti–N(3) 83.18(8), Cl(1)–Ti–Cl(2) 96.63(5), O(1)–Ti–N(1) 80.52(8), N(2)–Ti–N(3) 75.57.

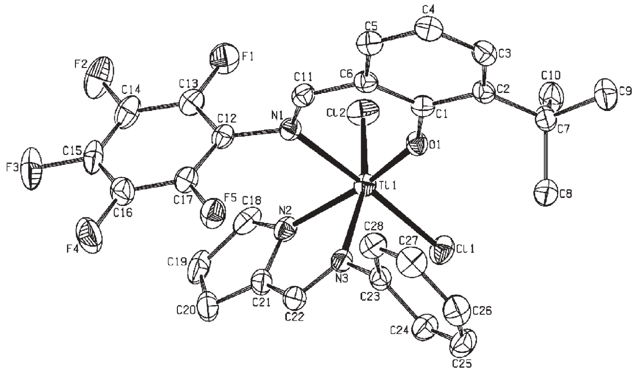


Fig. 2 X-ray crystal structure of **2b** (50% displacement ellipsoids; hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): Ti–Cl(1) 2.260(6), Ti–Cl(2) 2.297(7), Ti–O(1) 1.813(14), Ti–N(2) 2.065(17), Ti–N(1) 2.295(17), Ti–N(3) 2.146(17), O(1)–Ti–N(2) 161.56(7), N(1)–Ti–N(3) 82.63(6), Cl(1)–Ti–Cl(2) 96.68(3), O(1)–Ti–N(1) 79.26(6), N(2)–Ti–N(3) 93.52(6).

Table 1 Selected bond angles for the X-ray crystal structures of complexes **2a**, **2b**, **Ia**, **IIa** and **Ib**

	Ia	**2a**	**IIa**	**2b**	**Ib**
trans-L,L	171.62(2)[a]	164.42(8)[b]	158.04(6)[c]	161.56(7)[a]	163.61(6)[b]
cis-N,N	76.4(2)	83.18(8)	80.54(5)	82.63(6)	86.94(7)
cis-Cl,Cl	103.10(8)	96.63(5)	97.82(3)	96.68(3)	96.42(3)

[a] O–Ti–O. [b] O(1)–Ti–N(2). [c] pyrN-Ti-pyrN.

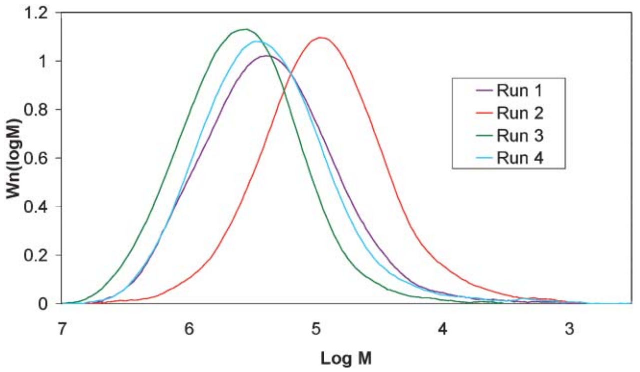


Fig. 3 Gel permeation chromatography traces for runs 1–4.

that the isolated compound is thermodynamically the most stable isomer and that ligand redistribution reactions, which would form the known homo-ligand complexes **Ib** and **IIa**, are not facile. For **2a**, the ^{1}H NMR spectrum consisted of two independent sets of signals in an approximately 2 : 1 ratio. This ratio was established immediately on dissolution of a crystalline sample and was essentially unchanged after warming to 60 °C overnight. There was no evidence that ligand redistribution yielded **Ia** and **IIa**. It therefore appears that **2a** exists as an equilibrium mixture of two isomers, and whilst it seems reasonable to assume that one of these is the isomer found in the solid-state, confirmation of the stereochemistry of the second isomer awaits further investigation.[9]

When activated with methylaluminoxane (MAO), complexes **2a** and **2b** formed very highly or extremely active catalysts for the polymerisation of ethene to moderately high molecular weight, linear polyethylene (PE) (runs 1–4, Table 2).[10] Polymerisation runs were limited to a maximum of five minutes and pre-catalyst **2b** was employed at a loading of 0.1 μmol to minimise mass transport effects.

Activating complex **2a** with 5000 equivalents of MAO at 20 °C (run 1) gave a productivity approaching that of **IIa** (run 9) and significantly higher than that of **Ia** (run 5). The molecular weight of the polymers obtained with **2a** were also between those of **Ia** and **IIa**. When the polymerisation was run at 50 °C (run 2) the productivity and molecular weight approximately halved.

Activation of complex **2b** gave rise to an extremely active catalyst (run 3), an order of magnitude more productive than **2a**

Table 2 Ethene polymerisation results for the (salicylaldiminato)(pyrrolylaldiminato) titanium mixed complexes[a]

Run	Complex(quantity/μmol)	Temp/°C	Time/min	Polymer yield/g	Productivity[b]	M_w	M_n	Polydispersity
1	**2a**(1)	20	5	0.455	5 460	157 000	63 900	2.5
2	**2a**(1)	50	5	0.197	2 370	74 900	31 400	2.4
3	**2b**(0.1)	20	2	0.298	89 500	300 000	123 000	2.4
4	**2b**(0.1)	50	2	0.127	38 200	329 000	127 000	2.6
5	**Ia**[c](1)	20	5	1.380	3 310	510 000	319 000	1.6
6	**Ia**[c](1)	50	5	1.730	4 150	315 000		
7	**Ib**[d](0.1)	20	2	0.120	35 900	400 000	97 300	4.1
8	**Ib**[d](0.1)	50	2	0.114	34 100	459 000	186 000	2.5
9	**IIa**[e](1)	20	5	0.500	6 000	75 000	30 000	2.2

[a] In 250 cm^{3}, 1 bar ethene pressure, 5 mmol MAO. [b] $\times 10^{-3}$ g PE ((mol metal) h bar)$^{-1}$. [c] From ref. 2f. [d] Results from our laboratory. [e] From ref. 3a.

and **IIa** and, under our conditions, twice as productive as **Ib**. The productivity decreased at 50 °C (run 4) in line with the reduced monomer solubility ([C_2H_4] = 0.077 M at 50 °C *vs.* 0.139 M at 20 °C). As a result of the rather similar results we obtained for **Ib**, we cannot rule out mass-transport limitations in runs 4 and 8. Interestingly, **2b** does not suffer the same temperature-dependent deterioration in molecular weight as **2a**, and at 50 °C, M_w is similar to that at 20 °C. For a given set of conditions, the molecular weights again are between those found for the parent homo-ligand complexes **Ib** and **IIa**.

The monomodal gel permeation chromatography (GPC) traces of runs 1–4 (Fig. 3), along with their relatively narrow polydispersities (2.4–2.6) (Table 2), support the assertion that the pre-catalysts give rise to single site catalysts. For **2a** in particular, where ligand redistribution would give rise to **Ia** and **IIa** (which have similar productivities but produce quite different molecular weight distributions), the GPC traces provide compelling evidence for a single hybrid active species.

In summary, we have demonstrated that the step-wise introduction of different bidentate, monoanionic ligands is possible and provides a convenient route to hybrid octahedral titanium pre-catalysts. The present case (salicylaldiminato)(pyrrolylaldiminato) titanium complexes are stable with respect to ligand redistribution and have structural and catalytic properties intermediate between their parent homo-ligand complexes. We are currently exploring the copolymerisation behaviour of this new catalyst class and the scope of our sequential approach for the preparation of other hybrid complexes.

Dale A. Pennington,[a] Simon J. Coles,[b] Michael B. Hursthouse,[b]
Manfred Bochmann[a] and Simon J. Lancaster*[a]
[a]*Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy, University of East Anglia, Norwich, UK NR4 7TJ.*
E-mail: S.Lancaster@uea.ac.uk; Fax: +44 1603 592009;
Tel: +44 1603 592009
[b]*School of Chemistry, University of Southampton, Highfield, Southampton, UK SO17 1BJ*

Notes and references

‡ Suitable crystals of **2a** and **2b** were immersed in perfluoropolyether oil, mounted on glass fibres and fixed in a low-temperature N_2 stream. Intensity data were recorded at the EPSRC National Crystallography Service at the University of Southampton on a Nonius KappaCCD diffractometer (with Mo-Kα radiation and graphite monochromator). The cells were determined using DirAx.[11] Data were collected using Collect[12] and processed using the DENZO program.[13] Absorption was corrected using SORTAV.[14] Structures were determined by direct methods routines with SHELXS-97 and refined by full-matrix least-squares methods on F^2 with SHELXL-97.[15,16] The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions and their U_{iso} values set to ride on the U_{eq} values of their parent carbon atoms. Crystal data for **2a**: $C_{28}H_{27}Cl_2N_3OTi$, M_r = 540.33, monoclinic, space group $P2_1/n$, a = 17.605(3), b = 7.9481(8), c = 20.168(4) Å, β = 112.491(19)°, V = 2607.4(7) Å^3, Z = 4, ρ_{calcd} = 1.376 Mg m^{-3}, T = 120(2) K, μ = 0.559 mm^{-1}. Of the 29623 measured reflections, 5972 were independent (R_{int} = 0.0843). The final refinement converged at R_1 = 0.0518 ($I > 2\sigma(I)$), wR_2 = 0.1112 for all data. The final difference Fourier synthesis gave a min/max residual electron density of −0.386/0.298 eÅ^{-3}. Crystal data for **2b**: $C_{28}H_{22}Cl_2F_5N_3OTi$, M_r = 630.29, monoclinic, space group $P2_1/n$, a = 18.198(2), b = 7.9915(11), c = 20.110(2) Å, β = 112.024(10)°, V = 2711.2(6) Å^3, Z = 4, ρ_{calcd} = 1.544 Mg m^{-3}, T = 120(2) K, μ = 0.575 mm^{-1}. Of the 31250 measured reflections, 6212 were independent (R_{int} = 0.0503). The final refinement converged at R_1 = 0.0415 ($I > 2\sigma(I)$), wR_2 = 0.1225 for all data. The final difference Fourier synthesis gave a min/max residual electron density of −0.451/0.394 eÅ^{-3}. CCDC 268107 and 268108. See http://www.rsc.org/suppdata/cc/b5/b504113a/ for crystallographic data in CIF or other electronic format.

1 (*a*) V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283; (*b*) G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428; (*c*) S. Park, Y. Han, S. K. Kim, J. Lee, H. K. Kim and Y. Do, *J. Organomet. Chem.*, 2004, **689**, 4263.

2 (*a*) S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847; (*b*) S. Matsui and T. Fujita, *Catal. Today*, 2001, **66**, 63; (*c*) J. Tian, P. D. Hustad and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 5134; (*d*) J. Saito, M. Mitani, J. Mohri, S. Ishii, Y. Yoshida, T. Matsugi, S. Kojoh, N. Kashiwa and T. Fujita, *Chem. Lett.*, 2001, 576; (*e*) S. Ishii, J. Saito, M. Mitani, J. Mohri, N. Matsukawa, Y. Tohi, S. Matsui, N. Kashiwa and T. Fujita, *J. Mol. Catal. A: Chem.*, 2002, **179**, 11; (*f*) J. Saito, M. Mitani, S. Matsui, Y. Tohi, H. Makio, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *Macromol. Chem. Phys.*, 2002, **203**, 59; (*g*) M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 3327; (*h*) M. Mitani, R. Furuyama, J. Mohri, S. Ishii, H. Terao, T. Nakano, H. Tanaka and T. Fujita, *J. Am. Chem. Soc.*, 2003, **125**, 4293.

3 (*a*) Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *Organometallics*, 2001, **20**, 4793; (*b*) Y. Yoshida, J. Saito, M. Mitani, Y. Takagi, S. Matsui, S. Ishii, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *Chem. Commun.*, 2002, 1298; (*c*) Y. Yoshida, J. Mohri, S. Ishii, M. Mitani, J. Saito, S. Matsui, H. Makio, T. Nakano, H. Tanaka, M. Onda, Y. Yamamoto, A. Mizuno and T. Fujita, *J. Am. Chem. Soc.*, 2004, **126**, 12023; (*d*) S. Matsui, Y. Yoshida, Y. Takagi, T. P. Spaniol and J. Okuda, *J. Organomet. Chem.*, 2004, **689**, 1155.

4 R. K. J. Bott, D. L. Hughes, M. Schormann, M. Bochmann and S. J. Lancaster, *J. Organomet. Chem.*, 2003, **665**, 135.

5 A. F. Mason and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 10798.

6 (*a*) D. A. Pennington, D. L. Hughes, M. Bochmann and S. J. Lancaster, *Dalton Trans.*, 2003, 3480; (*b*) D. A. Pennington, W. Clegg, S. J. Coles, R. W. Harrington, M. B. Hursthouse, D. L. Hughes, M. E. Light, M. Schormann, M. Bochmann and S. J. Lancaster, *Dalton Trans.*, 2005, 561.

7 This method was employed in ref. 5. Whilst it was convenient for the preparation of **1a** and **1b**, it is not applicable to more sterically-demanding aryl substituents: D. Pennington and S. J. Lancaster, unpublished results.

8 The angles between the ligands in the plane, between the *trans*-O,O ligands in **Ia**, show significantly more distortion than is the case for the other complexes.

9 DFT calculations by Fujita *et al.* (ref. 3a) on the parent homo-ligand systems suggest that the *cis*-O,pyrN *cis*-Cl,Cl *cis*-N,N isomer is the most probable candidate.

10 "Very highly active" refers to a catalyst productivity >10^6 g PE ((mol metal) h bar)$^{-1}$: see ref. 1a. We use "extremely active" to refer to catalyst productivities >10^7 g PE ((mol metal) h bar)$^{-1}$.

11 A. J. M. Duisenberg, *J. Appl. Crystallogr.*, 1992, **25**, 92.

12 R. Hooft and B. V. Nonius, *Collect, Data collection software*, 1998.

13 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.

14 R. H. Blessing, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1995, **51**, 33; R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421.

15 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 1990, **46**, 467.

16 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.