

# The synthesis, structure and catalytic activity of mono(salicylaldiminato) titanium complexes

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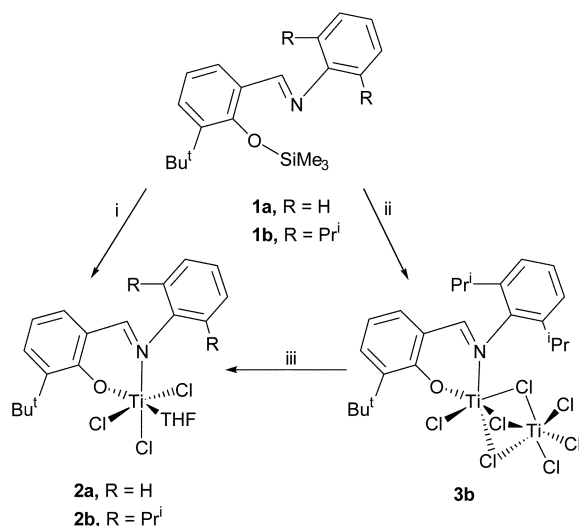
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Reaction between 3-Bu<sup>t</sup>-2-(OSiMe<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CH=N(2,6-R<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (where R = H (**1a**) or Pr<sup>i</sup> (**1b**)) and TiCl<sub>4</sub>(THF)<sub>2</sub> affords the octahedral complexes Ti{3-Bu<sup>t</sup>-2-(O)C<sub>6</sub>H<sub>3</sub>CH=N(2,6-R<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}Cl<sub>3</sub>(THF) while in the absence of THF **1b** reacts with TiCl<sub>4</sub> to give the binuclear complex [Ti{3-Bu<sup>t</sup>-2-(O)C<sub>6</sub>H<sub>3</sub>CH=N(2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)}Cl(μ-Cl)<sub>3</sub>TiCl<sub>3</sub>]; the complexes give good productivities for ethene polymerisation when activated with MAO.

Transition metal complexes of the monoanionic bidentate N, O chelate salicylaldiminato (iminophenolato) ligands have attracted considerable attention since the discovery of highly active,<sup>1</sup> and living<sup>2</sup> bis(salicylaldiminato) group 4 and neutral mono(salicylaldiminato) nickel<sup>3</sup> catalysts for the polymerisation of ethene. Following our recent report on the synthesis of salicylaldiminato cyclopentadienyl complexes of titanium and zirconium,<sup>4</sup> we report here the synthesis of mono(salicylaldiminato) complexes of titanium and preliminary results for their application in the polymerisation of ethene.

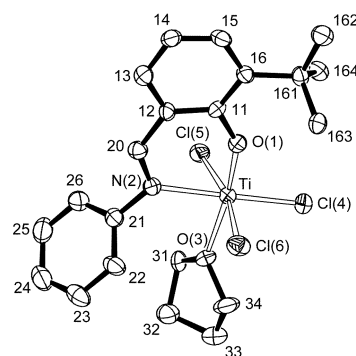
Bis(salicylaldiminato) complexes of titanium are normally prepared through reaction of two equivalents of the deprotonated iminophenol with TiCl<sub>4</sub> in tetrahydrofuran.<sup>1,2</sup> This approach is not suitable for the preparation of mono(salicylaldiminato) complexes; for example the reaction between equimolar quantities of even the bulky Li{3-Bu<sup>t</sup>-2-(O)C<sub>6</sub>H<sub>3</sub>CH=N(2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)} and TiCl<sub>4</sub> led only to an intractable mixture of products.

The deprotonation and subsequent reaction with Me<sub>3</sub>SiCl of the imino-phenols gave the silylated ligands 3-Bu<sup>t</sup>-2-(OSiMe<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CH=NR (where R = C<sub>6</sub>H<sub>5</sub> (**1a**) or 2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub> (**1b**)). These react selectively with TiCl<sub>4</sub>(THF)<sub>2</sub> in dichloromethane to give the six-coordinate mono(salicylaldiminato) titanium complexes Ti{3-Bu<sup>t</sup>-2-(O)C<sub>6</sub>H<sub>3</sub>CH=NR}Cl<sub>3</sub>(THF) (**2a** and **2b**) (Scheme 1).†



**Scheme 1** Reagents and conditions: i, dichloromethane, TiCl<sub>4</sub>(THF)<sub>2</sub>, room temperature; ii, toluene, TiCl<sub>4</sub>, overnight reflux; iii, THF

The X-ray crystal structure of **2a** (Fig. 1) confirmed the expected essentially octahedral coordination geometry.‡ The three chloride ligands are meridionally arranged. The two O ligating atoms are mutually *trans*; in this respect the geometry is similar to the bis(salicylaldiminato) titanium complex {3-Bu<sup>t</sup>-2-(O)C<sub>6</sub>H<sub>3</sub>CH=NPh}<sub>2</sub>TiCl<sub>2</sub> (O–Ti–O = 171.6°).<sup>5</sup> The bond lengths in the salicylaldiminato ligand and to the chloride ligands are similar to those observed in {3-Bu<sup>t</sup>-2-(O)C<sub>6</sub>H<sub>3</sub>CH=NPh}<sub>2</sub>TiCl<sub>2</sub><sup>5</sup> and Cp{3-Bu<sup>t</sup>-2-(O)C<sub>6</sub>H<sub>3</sub>CH=N(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)}-TiCl<sub>2</sub>.<sup>4</sup>



**Fig. 1** Structure of **2a** with thermal ellipsoids at 50% probability. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti–Cl(4) 2.281(2), Ti–Cl(5) 2.342(2), Ti–Cl(6) 2.327(2), Ti–N(2) 2.240(6), Ti–O(1) 1.791(5), Ti–O(3) 2.146(5), C(20)–N(2) 1.296(8), C(11)–O(1) 1.371(7); C(11)–O(1)–Ti 146.1(5), C(20)–N(2)–Ti 123.0(5), N(2)–Ti–Cl(4) 176.72(18), O(1)–Ti–O(3) 171.76(19), Cl(5)–Ti–Cl(6) 167.17(9).

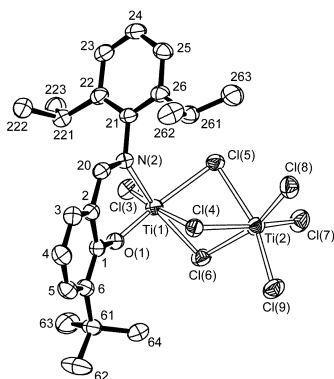
The tetrahydrofuran-free reaction between **1b** and TiCl<sub>4</sub> in hexanes led to the slow precipitation of a dark red solid (**3b**). The same product was obtained in good yield after an overnight reflux in toluene (Scheme 1). **3b** was identified as a salicylaldiminato complex by <sup>1</sup>H NMR. However, the elemental analysis afforded a N:Cl ratio of 1:7 and was consistent with the composition LTi<sub>2</sub>Cl<sub>7</sub>. **3b** does not react with a second equivalent of **1b** even after refluxing for two days in toluene solution. **3b** reacts readily with THF to give **2b** and TiCl<sub>4</sub>(THF)<sub>2</sub>. The elemental analysis of the reaction product between **1a** and TiCl<sub>4</sub> suggests a dinuclear complex analogous to **3b**.

The crystal structure of **3b** (Fig. 2) establishes that the complex is binuclear, with three bridging Cl ligands.‡ The two titanium atoms are six-coordinate with octahedral geometries. One metal centre is bonded to six chloride ligands, the other to four chlorides and the bidentate salicylaldiminato ligand. The bonding of the salicylaldiminato ligand is unremarkable, and the bond lengths are very similar to those observed for **2a**. There are few structurally characterised precedents for compounds of type **3b** with a titanium centre surrounded only by an octahedron of chloride ligands. The neutral tetranuclear complex {Cl<sub>3</sub>Ti(μ-Cl)<sub>3</sub>Ti(NPPPh<sub>3</sub>)<sub>2</sub>(μ-Cl)<sub>2</sub>} contains titanium with a similar octahedral chloride ligand coordination environment to **3b**, the terminal Ti–Cl bond lengths are similar (2.189–2.213) but the bridging Ti–Cl bond lengths cover a greater range

**Table 1** Ethene polymerisation results<sup>a</sup>

Run	Complex/ $\mu\text{mol}$	MAO/ $\text{mmol}$	$T/^\circ\text{C}$	$t/\text{min}$	Polymer yield/g	Productivity <sup>b</sup>
1	<b>2a</b> (6.3)	6.3	0	5	0.121	2.3
2	<b>2a</b> (6.3)	6.3	20	5	0.158	3.0
3	<b>2a</b> (6.3)	6.3	60	5	0.233	4.4
4	<b>2b</b> (6.0)	6.0	0	35	0.107	0.3
5	<b>2b</b> (6.0)	6.0	20	35	0.168	0.5
6	<b>2b</b> (6.0)	6.0	60	35	0.074	0.2
7	<b>3b</b> (6.0)	6.0	0	10	0.163	1.6
8	<b>3b</b> (6.0)	6.0	20	10	0.366	3.7
9	<b>3b</b> (6.0)	6.0	60	10	0.179	1.8
10	$\text{TiCl}_4$ (6.0)	6.0	20	35	0.119	0.3
11	<b>3b</b> (6.0) <sup>c</sup>	6.0	0	10	0.265	2.6
12	<b>3b</b> (6.0) <sup>c</sup>	6.0	20	10	0.412	4.1
13	<b>3b</b> (6.0) <sup>c</sup>	6.0	60	10	0.184	1.8

<sup>a</sup> In  $50\text{ cm}^3$  toluene, 1 bar ethene pressure. <sup>b</sup> In  $10^5\text{ g PE}$   $\{(\text{mol complex})\text{ h bar}\}^{-1}$ . <sup>c</sup>  $12.0\ \mu\text{mol THF}$ .



**Fig. 2** Structure of **3b** with thermal ellipsoids at 50% probability. H atoms are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Ti(1)–O(1) 1.784(2), Ti(1)–N(2) 2.138(2), Ti(1)–Cl(3) 2.1987(10), Ti(1)–Cl(4) 2.4907(10), Ti(1)–Cl(5) 2.4336(7), Ti(1)–Cl(6) 2.4091(7), C(20)–N(2) 1.285(3), C(1)–O(1) 1.352(3), Ti(2)–Cl(4) 2.4618(9), Ti(2)–Cl(5) 2.5417(7), Ti(2)–Cl(6) 2.5381(9), Ti(2)–Cl(7) 2.2106(10), Ti(2)–Cl(8) 2.1845(9), Ti(2)–Cl(9) 2.1971(7); C(1)–O(1)–Ti(1) 135.86(14), Ti(1)–Cl(4)–Ti(2) 85.38(3), Ti(1)–Cl(5)–Ti(2) 84.86(2), Ti(1)–Cl(6)–Ti(2) 85.45(3).

(2.399–2.614).<sup>6</sup> The crystal structure of the  $[\text{Ti}_2\text{Cl}_9]^-$  anion, in which both titanium centres have an octahedral face-sharing geometry, has been reported and both the terminal (2.197–2.225  $\text{\AA}$ ) and bridging Ti–Cl (2.480–2.556  $\text{\AA}$ ) bond lengths are very similar to those observed for **3b**.<sup>7</sup>

Complexes **2a**, **2b** and **3b** catalyse the polymerisation of ethene when activated with methylaluminoxane (Table 1). The productivities for **2a** compare favourably to the best results obtained for cyclopentadienyl salicylaldiminato titanium complexes.<sup>4</sup> The greater productivity of the dinuclear **3b** versus mononuclear **2b** is intriguing, since we expected the same active species to be formed in the presence of MAO.  $\text{TiCl}_4$  does form an active polymerisation catalyst when combined with MAO but its productivity is insufficient to explain the difference between the mono- and dinuclear pre-catalysts (run 10). The difference is probably not due to the THF in **2b** competing for the coordination site during polymerisation since addition of two equivalents of THF to catalysts prepared from **3b** did not significantly affect the productivity (runs 11–13). The nature of the active species derived from the reactions of **2b** and **3b** with MAO will be the subject of further investigations. Attempts to determine the polyethylene molecular weights by GPC were frustrated by low solubility.

Studies to determine whether the more open geometry of these mono(salicylaldiminato)metal catalysts favour comonomer incorporation when compared to bis(ligand) systems are underway.

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## Notes and references

† Synthesis and spectroscopic data: **2a**: A solution of 3-Bu<sup>1</sup>-2-(OSiMe<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CH=NC<sub>6</sub>H<sub>5</sub> (1.12 g, 3.45 mmol) in dichloromethane ( $20\text{ cm}^3$ ) was added to  $\text{TiCl}_4(\text{THF})_2$  (1.095 g, 3.44 mmol) in dichloromethane ( $20\text{ cm}^3$ ) at  $-78^\circ\text{C}$ . The reaction was stirred for 4 h while being allowed to warm slowly to room temperature, giving a dark red solution. Purification by recrystallisation from dichloromethane/light petroleum at room temperature gave the title compound as fine red needles.  $\delta^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) 8.17 (s, 1H, CH=N), 7.15–7.69 (m, 8H, Ar), 4.24 (m, 4H, THF), 1.72 (m, 4H, THF), 1.62 (s, 9H, *t*-Bu).  $\delta^{13}\text{C}$  (75 MHz,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) 134.5, 133.9, 129.2, 128.3, 128.0, 125.1, 124.4, 30.1, 25.7. Anal. found: C, 51.49; H, 5.38; N, 2.77; Cl, 22.60. Requires: C, 52.69; H, 5.47; N, 2.93; Cl, 22.22.

**2b**: Following a similar procedure to **2a** 3-Bu<sup>1</sup>-2-(OSiMe<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>CH=N(2,6-Pr<sup>2</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (**1b**) (1.36 g, 3.44 mmol) reacted with  $\text{TiCl}_4$  (0.38  $\text{cm}^3$ , 3.44 mmol) in dichloromethane ( $40\text{ cm}^3$ ) to give a dark red solution. The solvent was concentrated and cooled to  $-25^\circ\text{C}$  to precipitate a red/brown powder.  $\delta^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) 8.25 (s, 1H, CH=N), 6.75–7.47 (m, 6H, Ar), 4.20 (m, 4H, THF), 3.70–3.75 (m, 2H, CH(Me)<sub>2</sub>), 1.69 (s, 9H, *t*-Bu), 1.45 (d, 6H, *J* 6.68, CH(Me)<sub>2</sub>), 1.35 (m, 4H, THF), 0.99 (d, 6H, *J* 6.82, CH(Me)<sub>2</sub>).  $\delta^{13}\text{C}$  (75 MHz,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) 169.9, 142.0, 138.4, 135.1, 133.9, 128.2, 124.4, 124.3, 35.7, 30.3, 28.5, 26.4, 25.8, 23.4. Anal. found: C, 57.03; H, 6.79; N, 2.26; Cl, 19.17. Requires: C, 57.62; H, 6.81; N, 2.49; Cl, 18.90.

**3b**: A solution of **1b** (2.79 g, 7 mmol) in toluene ( $30\text{ cm}^3$ ) was added to  $\text{TiCl}_4$  (1.54  $\text{cm}^3$ , 14 mmol) in toluene ( $50\text{ cm}^3$ ) at  $-78^\circ\text{C}$ . The reaction was warmed slowly and refluxed overnight. The solvent was removed under reduced pressure yielding a crude red solid. Purification by recrystallisation in dichloromethane/light petroleum at  $0^\circ\text{C}$  gave **3b** as small dark red crystals.  $\delta^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) 8.54 (s, 1H, CH=N), 7.24–7.89 (m, 6H, Ar), 2.75–2.89 (m, 2H, CH(Me)<sub>2</sub>), 1.65 (s, 9H, *t*-Bu), 1.35 (d, 6H, *J* 6.73, CH(Me)<sub>2</sub>), 1.10 (d, 6H, *J* 6.80, CH(Me)<sub>2</sub>).  $\delta^{13}\text{C}$  (75 MHz,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ) 136.8, 133.8, 128.8, 125.0, 124.5, 124.4, 30.4, 29.5, 25.6, 23.1. Anal. found: C, 40.36; H, 4.33; N, 1.82; Cl, 37.33. Requires: C, 40.60; H, 4.44; N, 2.06; Cl, 36.47.

‡ X-ray analyses: intensity data from Rigaku R-Axis IIC image-plate diffractometer, processed in DENZO/SCALEPACK.<sup>8</sup> Structure determination and refinement with SHELX-97 programs.<sup>9</sup> Crystal data for **2a**:  $\text{C}_{21}\text{H}_{26}\text{Cl}_3\text{NO}_2\text{Ti}$ ,  $M = 478.7$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 7.385(2)$ ,  $b = 31.797(6)$ ,  $c = 9.815(2)$   $\text{\AA}$ ,  $\beta = 102.50(3)^\circ$ ,  $V = 2250.1(8)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.413\text{ Mg m}^{-3}$ ,  $F(000) = 992$ ,  $T = 140(1)$ ,  $\mu(\text{Mo K}\alpha) = 0.75\text{ mm}^{-1}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$   $\text{\AA}$ , reflections measured 7928, unique 3383 ( $R_{\text{int}} = 0.268$ ),  $F^2$  refinement,  $R_1 = 0.088$  (1907 reflections with  $I > 2\sigma_I$ ),  $wR_2 = 0.237$  (all data).

Crystal data for **3b**:  $\text{C}_{23}\text{H}_{30}\text{Cl}_7\text{NOTi}_2$ ,  $M = 680.4$ , monoclinic, space group  $P2_1/n$  (equiv. to no. 14),  $a = 9.880(1)$ ,  $b = 19.315(1)$ ,  $c = 15.511(6)$   $\text{\AA}$ ,  $\beta = 102.80(1)^\circ$ ,  $V = 2886.4(12)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.566\text{ Mg m}^{-3}$ ,  $F(000) = 1384$ ,  $T = 140(1)$  K,  $\mu(\text{Mo K}\alpha) = 1.22\text{ mm}^{-1}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$   $\text{\AA}$ , reflections measured 15791, unique 5091 ( $R_{\text{int}} = 0.043$ ),  $F^2$  refinement,  $R_1 = 0.034$  (4308 reflections with  $I > 2\sigma_I$ ),  $wR_2 = 0.094$  (all data).

CCDC reference numbers 214921 and 214922. See <http://www.rsc.org/suppdata/dt/b3/b307793b/> for crystallographic data in CIF or other electronic format.

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