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Mixed-ligand iminopyrrolato-salicylaldiminato group 4 metal complexes: Optimising catalyst structure for ethylene/propylene copolymerisations

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Abstract

Treatment of $MCl_3(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)(THF)$ (M = Ti, Zr) with a variety of different potassium iminopyrrolate salts ($K^+[RN{=}CHC_4H_3N]^-$), (R = phenyl, *cyclo*-hexyl, ethyl) afforded the corresponding titanium and zirconium mixed-ligand complexes $MCl_2(N\text{–}O)(N\text{–}N)$. The molecular structures of $TiCl_2(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)(C_2H_5N{=}CHC_4H_3N)$ (**1c**), $TiCl_2(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)(C_6H_{11}N{=}CHC_4H_3N)$ (**1b**) and $ZrCl_2(OC_6H_3\text{-}2\text{-}^tBu\text{-}6\text{-}CH{=}NC_6F_5)(C_6H_{11}N{=}CHC_4H_3N)$ (**2b**) show distorted octahedral geometries with *trans*-O^-,N^-/*cis*-Cl_2 arrangements. On activation with MAO the titanium (iminopyrrolato)(salicylaldiminato) complexes show excellent activities in ethylene polymerisation and are significantly more effective ethylene/propylene copolymerisation catalysts, both in terms of activity and propene incorporation, than either of the parent complexes. The ethylene–propylene copolymers show ca. 80% 1,2 regioselectivity and at high propylene incorporation tend towards an alternating structure.

Keywords: Titanium; Zirconium; Ethene; Copolymerization; Salicylaldiminate; Iminopyrrolate

1. Introduction

The development of new, more selective and active homogeneous polymerisation catalysts remains a driving force within organometallic chemistry. Of the non-metallocene group 4 metal complexes tested in olefin polymerisations, octahedral metal dichloride systems containing bidentate mono-anionic N,N^- or N,O^- ligands have proved to give particularly effective catalysts [1,2]. Bis(salicylaldiminato) complexes of titanium and zirconium of type **A** (Chart 1) are potent catalysts for ethylene homopolymerisations, but are inefficient copolymerisation catalyst [3–6]. They are sensitive to steric factors; for example, reducing the size of the *ortho*-substituent increases the fraction of bulky comonomer incorporated, while the activity is significantly decreased [7]. On the other hand, bis(iminopyrrolato) titanium complexes (structure **B**) give lower ethylene polymerisation productivities but achieve higher incorporation of both cyclic and terminal alkenes in the polyethylene backbone [8,9].

These limitations can be overcome with hetero-ligated group 4 metal complexes [10–14] which have been shown to combine these characteristics and are able to produce highly active catalysts capable of high levels of comonomer incorporation. The most successful systems for α-olefin co-polymerisations are the (iminopyrrolato)(salicylaldiminato)titanium complexes, which have previously been shown to combine high activity with high comonomer incorporation in copolymerisations of ethylene with 1-hexene, cyclopentene and norbornene [10]. We report here the syntheses and structures of two new titanium (N–N)(N–O)

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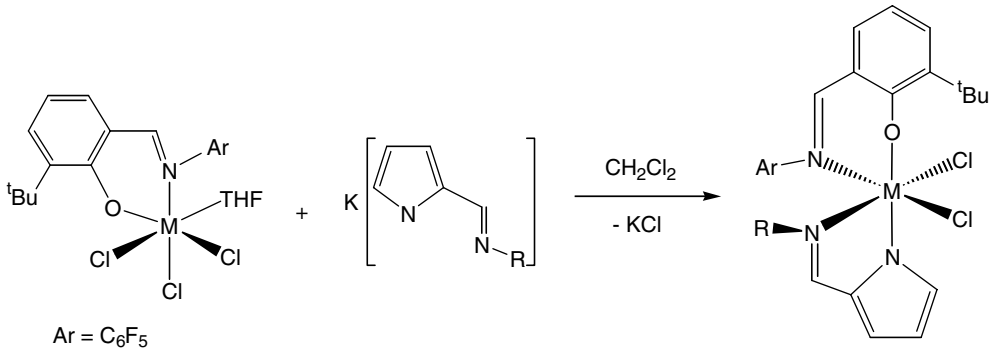


1a R = C_6H_5 (M = Ti)
1b R = cyclohexyl (M = Ti)
1c R = Et (M = Ti)
2b R = cyclohexyl (M = Zr)

Chart 1.

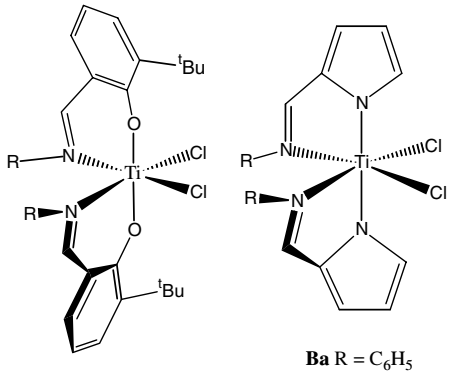
mixed-ligand complexes and that of a zirconium analogue. When activated with methylaluminoxane (MAO) the titanium complexes are shown to be highly effective ethylene–propylene copolymerisation catalysts.

2. Syntheses

The complexes $TiCl_2(OC_6H_3$-2-^{t}Bu-6-CH=NC_6F_5)-(R–N=CHC_4H_3N) (**1a**, R = Ph; **1b**, R = cyclohexyl; **1c**, R = Et) as well as $ZrCl_2(OC_6H_3$-2-^{t}Bu-6-CH=NC_6F_5)(Cy–N=CHC_4H_3N) (**2b**) were synthesised following previously published procedures [8,9] by reacting the mono(salicylaldiminato) complexes $MCl_3(OC_6H_3$-2-^{t}Bu-6-CH=NC_6F_5)(THF) (M = Ti, Zr) in dichloromethane with potassium salts of the corresponding iminopyrroles (Scheme 1). The products were obtained as dark red to orange crystals.

The ^{1}H NMR and ^{19}F NMR spectra in $CDCl_3$ of the complexes were consistent with the presence of a single stereoisomer at room temperature, with the ^{1}H NMR spectrum showing only two sharp imine peaks, one each for the iminopyrrolato and the salicylaldiminato ligands. The ^{19}F spectra of all the complexes indicate hindered rotation of C_6F_5 groups, rendering the *ortho*- and *meta*-fluorines inequivalent.

The structures of **1b, 1c** and **2b** were determined by X-ray crystallography and are shown in Figs. 1–3, respectively. Complexes **1c** and **2b** have essentially octahedral geometry, with the two anionic functions *trans* to one another while the two chloride ligands are *cis*. These structures are consistent with the most stable calculated geometry for such octahedral complexes bearing two mono-anionic ligands, and is also the geometry observed for most bis(salicylaldiminato), bis(iminopyrrolato) as well as for related mixed-ligand group 4 metal complexes [4,9–11].



Aa R = C_6F_5 (M = Ti),
Ab R = C_6H_5 (M = Ti)

Ba R = C_6H_5
Bb R = Cyclohexyl
Bc R = Et

Scheme 1.

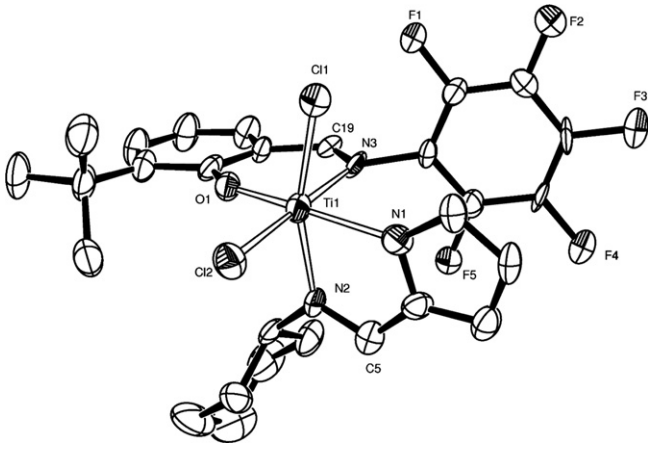


Fig. 1. ORTEP representation of the structure of **1b** showing 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) with estimated standard deviations: Ti(1)–Cl(1) 2.282(3), Ti(1)–Cl(2) 2.282(2), Ti(1)–N(1) 2.072(6), Ti(1)–N(2) 2.119(6), Ti(1)–N(3) 2.242(6), Ti(1)–O(1) 1.820(5); Cl(1)–Ti(1)–Cl(2) 96.84(10), N(1)–Ti(1)–N(2) 76.4(2), N(2)–Ti(1)–N(3) 84.9(2), O(1)–Ti(1)–N(1) 162.7(2).