NJC Letter

Synthesis, X-ray structure, and polymerisation activity of a bis(oxazolinyl)pyridine chromium(III) complex

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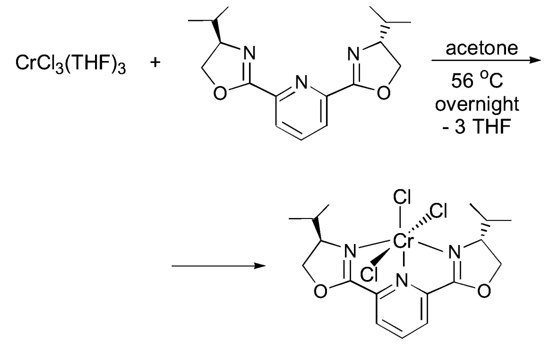
The complex [2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine]-$CrCl_3$, prepared by reaction of $CrCl_3(THF)_3$ with 2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine, catalyses ethylene homopolymerisation and ethylene/1-hexene copolymerisation in the presence of MAO.

Supported chromium catalysts (*i.e.* Phillips or Union Carbide catalysts) have a prominent role in the world-wide production of high density polyethylene.[1,2] A lot of effort has been devoted to model and study the process, but to date there are many aspects that remain obscure.[3] In this context, the development of homogeneous molecular chromium catalysts is an important target, since it could help not only to understand how supported chromium catalysts work but also offer the opportunity of developing new well-defined single-site catalysts. This effort has been focused on half-sandwich chromium species,[4] although recently several non-cyclopentadienyl ligands attached to chromium, such as 1,1-bis-2-naphtholato,[5] salicylaldiminato,[6] β-diketiminato,[7] imido,[8] and triazacyclohexane[9] ligands have been investigated as potential well-defined catalysts for ethylene polymerisation.

Although complexes containing bis(oxazolinyl)pyridine (pybox) ligands have been used as catalysts in a variety of catalytic asymmetric synthesis such as Mukaiyama aldol, cyclopropanation, allylation, hydrosilylation, hydrocyanation, aziridination and Diels–Alder reactions,[10] their potential in olefin polymerisation reactions has been scarcely addressed.[11]

In this letter we report the synthesis, X-ray structure, ethylene and ethylene/1-hexene polymerisation behaviour of a chromium(III) complex bearing a pybox ligand.

The (pybox) chromium(III) complex [2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine]$CrCl_3$ (**1**) is prepared by treatment of $CrCl_3(THF)_3$ with one equivalent of 2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine in acetone at reflux (eqn. 1). It was isolated as a green air stable solid in high yield (82%), and was characterised by elemental analysis, FAB mass spectrometry, IR spectroscopy and by X-ray crystallography.



1

(1)

Fig. 1 shows the molecular structure of complex **1**. The geometry around the chromium atom could be described as a distorted octahedron with the chlorine ligands in *mer* disposition, while the pybox ligand occupies the other three coordination positions. The molecule has almost C_2 symmetry about the axis Cl(1)–Cr–N(2). The Cr–Cl(2) and Cr–Cl(3) bond distances (2.3008(11) and 2.3063(12) Å) are statistically identical, and about 0.02 Å longer than the Cr–Cl(1) bond length (2.2841(11) Å).

Complex **1** catalyses the polymerisation of ethylene in the presence of methylaluminoxane (MAO). The complex was injected into a saturated ethylene–heptane solution with MAO at 4 bar in an autoclave reactor where ethylene was continuously supplied and the consumption monitored by means of a flow-meter.

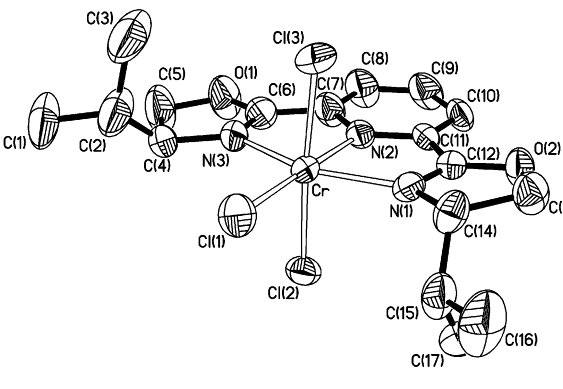


Fig. 1 Molecular diagram of the complex [2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine]$CrCl_3$ (**1**). Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): Cr–N(1) 2.085(3), Cr–N(2) 2.034(3), Cr–N(3) 2.092(3), Cr–Cl(1) 2.2841(11), Cr–Cl(2) 2.3008(11), Cr–Cl(3) 2.3063(12); N(1)–Cr–N(2) 76.42(12), N(1)–Cr–N(3) 153.34(13), N(2)–Cr–N(3) 76.92(13), N(1)–Cr–Cl(1) 102.94(9), N(1)–Cr–Cl(2) 90.98(9), N(1)–Cr–Cl(3) 86.02(9), N(2)–Cr–Cl(1) 178.96(10), N(2)–Cr–Cl(2) 87.89(9), N(2)–Cr–Cl(3) 87.97(9), N(3)–Cr–Cl(1) 103.72(11), N(3)–Cr–Cl(2) 88.23(10), N(3)–Cr–Cl(3) 92.87(10), Cl(1)–Cr–Cl(2) 91.31(4), Cl(1)–Cr–Cl(3) 92.80(5), Cl(2)–Cr–Cl(3) 175.37(5).

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At room temperature 1.27×10^3 g PE (mol Cr)$^{-1}$ bar^{-1} h^{-1} were formed. Increasing the temperature of the reaction gives rise to a significant increase of the activity (6.29×10^3 g PE (mol Cr)$^{-1}$ bar^{-1} h^{-1} at 45 °C). The stability of the catalyst is remarkable and an induction period was not observed. In both cases consumption of ethylene was observed from the beginning. One of the experiments was run for 16 hours, showing no deactivation of the catalytically active species. The resulting polyethylene has high molecular weight ($M_w = 699\,700$) with a wide molecular weight distribution ($M_w/M_n = 86.7$). This molecular weight distribution suggests that this system affords more than one catalytically active species. It is assumed that methylation of the chromium metal centre occurs by action of MAO and possibly cationic unsaturated metal centers are formed in a similar way as has been postulated for many other transition metal single site polymerisation catalysts which are activated by the action of MAO.

The polyethylene obtained with this complex is highly linear. However, as a consequence of the wide molecular weight distribution, the polymer obtained at 45 °C has a calculated degree of crystallinity of just 17% ($T_m = 128.7$ °C, ΔH_m of -48.7 J g^{-1}).

The co-polymerisation ability of complex **1** has been also tested. Co-polymerisation of ethylene with 1-hexene occurs, rendering a branched polyethylene with a slight decrease of the activity in comparison with that of the production of homopolyethylene. At 45 °C and in the presence of 15 mL of 1-hexene (see Experimental), complex **1** co-polymerises 1-hexene and ethylene yielding 1.8 g (activity: 5.17×10^3 g polymer (mol Cr)$^{-1}$ bar^{-1} h^{-1}) of branched polyethylene with 1.20% mol of incorporated 1-hexene. This result, together with those reported for $RuCl_2$(ethylene)(pybox) and $FeCl_2$(pybox),[11b] indicates that the incorporation of 1-hexene in the pybox systems depends on the nature of the metal.

In conclusion, the addition of 2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine to $CrCl_3(THF)_3$ affords [2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine]$CrCl_3$. This complex, which has been characterised by X-ray diffraction analysis, catalyses ethylene homopolymerisation and ethylene/1-hexene copolymerisation in the presence of MAO. The homopolymerisation reaction yields highly linear polyethylene with high molecular weight and a wide molecular weight distribution.

Experimental

All manipulations were conducted with rigorous exclusion of air. The solvents used were dried by known procedures and distilled prior to use. Ethylene (SEO, N35) was further purified by passing it through activated molecular sieve (13 X, 4 Å) and activated alumina beds. ^{13}C NMR polymer analyses were performed in 1,2,4-trichlorobenzene at 378 K. 2,6-Bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine was purchased from Aldrich and used as received. Methylaluminoxane (MAO, 10% in toluene) was purchased from Witco (now Crompton). $CrCl_3(THF)_3$ was prepared by a published procedure.[12]

Preparation of [2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine]$CrCl_3$

A solution of $CrCl_3(THF)_3$ (248 mg, 0.66 mmol) in acetone (10 mL) was treated with the stoichiometric amount of 2,6-bis[(4*S*)-isopropyl-2-oxazolin-2-yl]pyridine (200 mg, 0.66 mmol) and it was heated at 56 °C overnight. The resulting green solution was evaporated to *ca.* 0.5 mL and diethyl ether was added to afford a green solid that was washed repeatedly with diethyl ether (4 × 10 mL) and dried *in vacuo*. Yield: 249 mg (82%). Anal. Calcd. for $C_{17}H_{23}Cl_3CrN_3O_2$: C, 44.41; H, 5.09; N, 9.14. Found: C, 44.74 H, 5.23; N, 8.85%. IR (Nujol, cm^{-1}): 1647, 1622, 1580, 1493, 1409, 1284, 1259, 1210, 1080, 1049, 1033, 961, 922, 830, 755, 398, 364, 355, 314. MS (FAB$^+$): m/z 423 ($M^+ - Cl$), 388 ($M^+ - 2\ Cl$).

Crystallography

Crystals of **1** were grown by layering pentane onto a solution of **1** in dichloromethane and data were collected on a Bruker Smart APEX CCD diffractometer: $C_{17}H_{23}Cl_3CrN_3O_2 \cdot CH_2Cl_2$, $0.30 \times 0.26 \times 0.22$ mm, $T = 173(2)$ K, $M = 544.66$, orthorhombic, space group $P2_12_12_1$, $a = 12.1292(13)$, $b = 12.2378(13)$, $c = 16.3811(18)$ Å; $V = 2431.5(5)$ Å^3, $Z = 4$, μ(Mo-K$_\alpha$) = 1.039 mm^{-1}, 25 438 reflections measured, 5895 unique (R_{int} 0.1009), R_1 (F) = 0.0554, wR_2 (F^2) = 0.1233.

CCDC reference number 191046. See http://www.rsc.org/suppdata/nj/b2/b207093f/ for crystallographic files in CIF or other electronic format.

Polymerisation assays. General procedure

An autoclave glass reactor vessel of 1.3 L was employed for the polymerisation experiments.The reactor was charged with 600 mL of heptane, degassed and saturated with ethylene to a pressure of 4 bar at the set temperature. Polymerisations were effected at constant pressure, the consumption of ethylene being monitored by means of a Tylan Mass Flowmeter Model FM 380. Temperature was measured by means of a PT-100 probe immersed in the reaction solvent. Regulation of the temperature was provided by a combination of heating and cooling systems operating simultaneously by passing two fluids through two external jackets at the walls of the reactor vessel. The heating was effected with oil from a circulating oil-bath (Haake N3). Refrigeration was obtained from cold tap-water controlled by an electro valve connected to a Toho TM-104 controller.

Ethylene polymerisation at room temperature. The polymerisation was performed at room temperature (22–23 °C). First, MAO/toluene (10.0 mL) and, secondly, a solution of complex **1** in dry dichloromethane (5.0 mL, 0.054 mmol) were added to the reactor already filled with ethylene and heptane. Moderate consumption of ethylene was immediately observed, the gas was continuously supplied in order to keep a constant pressure of 4 bar for 16 hours. The polymerisation mixture was then added to a methanol/HCl solution. Filtration, washing with more methanol/HCl and drying of the resulting solid (70 °C/10 mmHg for *ca.* 20 h) gave 4.43 g of a white fibrous solid which was shown to be linear polyethylene according to the ^{13}C NMR spectrum with 2.93 vinyl and 5.75 end methyl groups per 1000 C.[13] GPC analysis showed a broad distribution with $M_w = 699\,700$, $M_w/M_n = 86.7$. Calculated activity = 1.27×10^3 g PE (mol Cr)$^{-1}$ bar^{-1} h^{-1}.

Ethylene polymerisation at 45 °C. First, a MAO/toluene solution (10.0 mL) and, second, a solution of complex **1** in dry dichloromethane (4.0 mL, 0.043 mmol) were added to the reactor already filled with ethylene and heptane. Ethylene was continuously supplied in order to keep a constant pressure of 4 bar. Moderate consumption of ethylene was immediately observed, the gas was continuously supplied in order to keep a constant pressure of 4 bar for 120 min. After venting, the polymerisation mixture was added to a methanol/HCl solution. Filtration, washing with more methanol/HCl and drying of the resulting solid (70 °C/10 mm Hg for *ca.* 20 h) gave 2.19 g of a white fibrous solid which was shown to be linear polyethylene according to the ^{13}C NMR spectrum with 8.33 end methyl groups and 8.95 vinyl groups per 1000 C. The DSC analysis resulted in a T_m of 128.7 °C, and ΔH_m of -48.7 J g^{-1}. Calculated activity = 6.29×10^3 g PE (mol Cr)$^{-1}$ bar^{-1} h^{-1}.

Co-polymerisation assay of ethylene and 1-hexene. Ethylene and 1-hexene were co-polymerised at 45 °C according to the following procedure: 15 mL of freshly dried and distilled 1-hexene, MAO in toluene (10%) (10 mL) and a solution of complex **1** in dry dichloromethane (4.0 mL, 0.043 mmol) were added to the vessel, which was already filled with heptane and saturated with ethylene. Moderate consumption of ethylene was observed, the gas was continuously supplied in order to keep a constant pressure of 4 bar for 120 min. Afterwards, the polymerisation mixture was added to a methanol/HCl solution. Filtration, washing with more methanol/HCl and drying of the resulting solid (70 °C/10 mmHg for *ca.* 20 h) gave 1.8 g of a white fibrous solid which was shown to be a hexene–ethylene co-polymer according to its ^{13}C NMR spectrum with 5.88 butyl branches per 1000 C (corresponding to 1.20% mol of incorporated hexene), 12.94 end methyl groups and 8.07 vinyl groups per 1000 C. Calculated activity = 5.17×10^3 g polymer (mol Cr)$^{-1}$ bar^{-1} h^{-1}.

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