

Communication

Bis(pyrazolyl)pyridine vanadium(III) complexes as highly active ethylene polymerization catalysts

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Abstract

The synthesis, characterization and catalytic activity in ethylene polymerization of novel mononuclear vanadium complexes bearing $N^{\wedge}N^{\wedge}N$ -tridentate (pyrazolyl-pyridine) ligands are described. With $AlEtCl_2$ as co-catalyst, complexes **1** and **2** produce single-site catalysts that polymerized ethylene affording high density polyethylene with fairly narrow molecular weight distribution.

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1. Introduction

Ziegler–Natta olefin polymerization is certainly amongst the most efficient and selective catalytic processes for the large-scale production of olefin polymers [1–3]. Classical Ziegler–Natta vanadium catalyst systems are useful in a number of interesting applications such as: (a) synthesis of high molecular weight polymers with narrow polydispersity [4], (b) synthesis of ethylene- α -olefin copolymers with high α -olefin incorporation [5], (c) synthesis of syndiotactic polypropylene [6]. In view of the performance of these vanadium-based catalysts, the synthetic development of well-defined single-site vanadium catalysts is an extremely desirable industrial goal [7,8].

Studies of the oxidation state of vanadium catalysts for ethylene polymerization have generally revealed that V(III) and V(IV) precursors are often reduced to inactive V(II) species [9–12]. Alkyl vanadium(III) complexes bearing amidinate [13,14] and amide [15,16] ligands produce short-lived ethylene polymerization catalysts and are inactive in propene polymerization. Vanadium(III) complexes bearing α -diimine [17] and diimine-pyridyl ligands, which bind in a

$N^{\wedge}N^{\wedge}N$ -tridentate fashion [18,19] have been shown to polymerize ethylene upon activation with MAO. The electrophilicity of the active site plays a big role in catalyst activity in ethylene polymerization and would suggest that weaker nitrogen donor ligands, such as pyrazoles, are likely to produce more active catalysts than imine analogues. We have therefore used the known bis(pyrazolyl)pyridine ligands to prepare one of few examples of vanadium(III)-based ethylene polymerization catalysts to show relatively long lifetime during the polymerization.

We herein report the synthesis, characterization and ethylene polymerization activity of the precatalysts {2,6-[(3,5-Me₂pz)CO]₂py}VCl₃, **1** and {2,6-[(3,5-Me₂pz)CH₂]₂py}VCl₃, **2**. These catalysts are highly active under fairly mild reaction conditions. This is in contrast to catalysts reported in the literature which are highly active at only high temperatures [18,19]. Furthermore as mentioned earlier, these reported catalysts tend to deactivate after short reaction times.

2. Results and discussion

Complexes **1** and **2** were prepared from the reaction of equimolar amounts of **L1** [20] or **L2** [21] and VCl₃

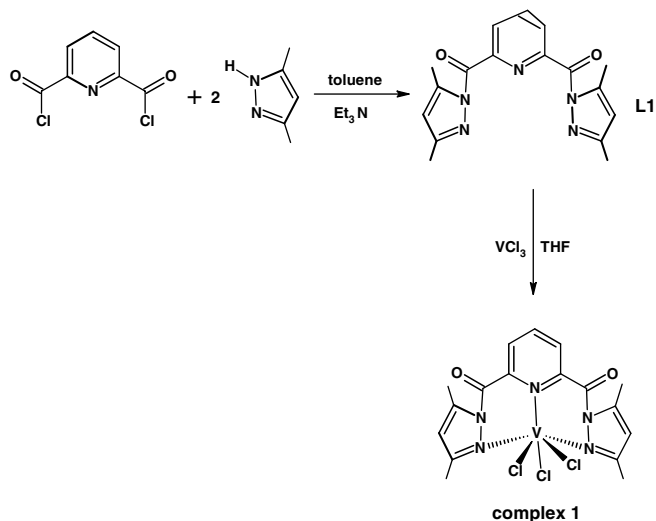
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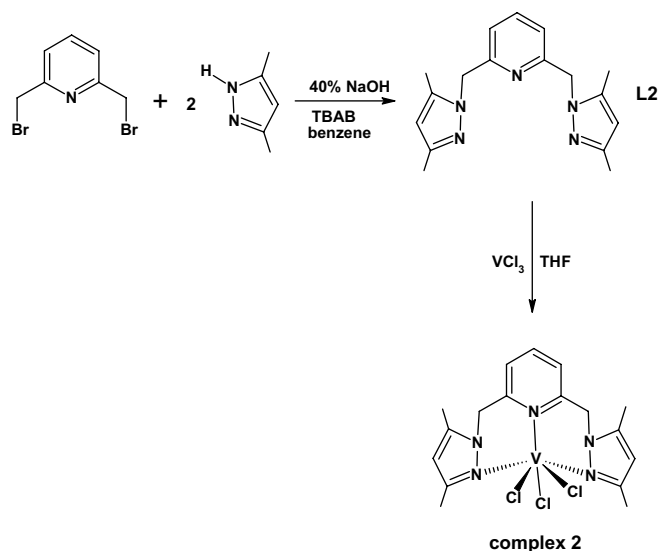
(Schemes 1 and 2). It is assumed that the anhydrous vanadium salt becomes solvated with THF to form the known THF adduct ($\text{VCl}_3 \cdot 3\text{THF}$). Previous workers have actually used the discrete THF adduct in preparing vanadium(III) complexes. Complexes **1** and **2** were characterized by a combination of IR spectroscopy, mass spectrometry and micro analysis. Repeated attempts to obtain single crystals for X-ray analysis to confirm proposed structures of these complexes were unsuccessful.

When complexes **1** and **2** were activated with AlEtCl_2 , they both catalyzed the polymerization of ethylene (Table 1). To study the influence of the catalytic reaction conditions on the productivity of the catalysts employed, we carried out a series of experiments under different reaction times, temperatures, pressures, as well as the ratio of Al:V. Upon activation with small amounts of AlEtCl_2 , complexes **1** and **2** show reasonable to good catalytic activity for ethylene polymerization at 1 and 10 bar of ethylene, producing polyethylene with high molecular weight ($0.6\text{--}1.9 \times 10^6$) g mol^{-1} with relatively narrow molecular weight distributions ($M_w/M_n = 2.4\text{--}3.2$) in all cases. This suggests that the polymerization probably proceed via catalysts which have a single-site nature [22,23].

The catalysts are most active at 25°C , with a productivity of 580 and 940 $\text{kg mol}^{-1} \text{h}^{-1}$ for **1** and **2**, respectively at 10 bar and 160 and 422 $\text{kg mol}^{-1} \text{h}^{-1}$ for **1** and **2**, respectively at 1 bar. At 50°C the overall productivity drops substantially for both catalysts **1** and **2** after 1 h reaction time (entries 5 and 14) at an Al:V ratio of 500:1, indicating a limited thermal stability of the catalysts. At this temperature polyethylene with a significantly higher molecular weight is formed, but it is accompanied by a broadening of the polymer molecular weight distribution. Interestingly, the catalytic activity of **2** decreased only slightly at 50°C at an Al:V ratio of 250 (entry 11) with higher molecular weight of polyethylene, which shows that **2** is more thermally stable than **1** at this molar ratio.



Scheme 1.



Scheme 2.

There is also a marked dependence of the activity on ethylene pressure. Thus for example employing both pre-catalysts **1** and **2** and working at Al:V ratios of 500:1 and 250:1, respectively, at 25°C and 2 h reaction time, an increase in the ethylene pressure from 1 bar to 10 bar resulted in a dramatic increase in polymerization activities (entries 2 and 4) for **1** and (entries 8 and 10) for **2**. Such pressure affects are not unexpected as this is common for many ethylene polymerization catalysts.

Similarly reaction times affected the polymerization rate. Thus at 1 bar ethylene, increasing the reaction time from 30 min to 2 h, the activity for **1** was observed to increase only slightly (entries 1 and 2). The molecular weight in these reactions also shows a marginal increase with time. The activity for **2** on the other hand, decreased by around half when the reaction time is increased to 2 h (entries 7 and 8). At 10 bar pressure of ethylene, increasing reaction time to 2 h, the activity for **1** increased by just over 50% (entries 3 and 4). In the case of catalyst **2** there is a decrease under similar reaction conditions (entries 9 and 10). It would thus appear that catalyst **2** has a lower stability in solution than **1** and that its decomposition is faster than that of catalyst **1**.

However, when comparing the activity of our catalysts to that of vanadium catalysts reported in the literature, it appears that our catalysts when activated with AlEtCl_2 show similar or higher activity than the literature examples [17–19]. Furthermore polymers with higher molecular weight and narrow polydispersities are produced by our catalysts when compared with known vanadium catalysts. In addition the catalyst life-times of our catalysts appear to be superior to other known vanadium systems.

The high temperature NMR spectra of the polyethylene obtained in our experiments were recorded in 1,2,4-trichlorobenzene/benzene- d_6 at 120°C , which verified that all polyethylenes produced by both catalysts (**1** and **2**) are

Table 1
Results of ethylene polymerization using precatalysts **1** and **2**^a

Entry	Catalyst	Al:V ratio	T (°C)	Time (min)	P (bar)	Yield (PE/g)	Activity (kg PE mol ⁻¹ h ⁻¹)	M _w × 10 ⁶	PDI ^b
1	1	500	25	30	1	0.35	140	0.6	3.2
2	1	500	25	120	1	1.6	160	0.78	3.3
3	1	500	25	60	10	1.9	380	0.70	2.8
4	1	500	25	120	10	5.8	580	1.13	3.2
5	1	500	50	60	10	0.5	100	1.87	7.3
6	1	1000	25	60	10	1.6	320	1.20	2.4
7	2	250	25	10	1	0.35	422	0.75	3.2
8	2	250	25	120	1	2.2	220	0.92	2.8
9	2	250	25	60	10	4.7	940	0.68	2.5
10	2	250	25	120	10	5.1	510	0.59	2.5
11	2	250	50	120	10	4.0	400	1.71	2.9
12	2	1000	25	120	10	5.6	560	1.11	2.5
13	2	500	25	60	10	4.3	860	0.68	2.4
14	2	500	50	60	10	0.83	166	n.d. ^c	–

^a Reaction conditions: toluene (50 ml) solvent; [V] = 5 μmol; co-catalyst, AlEtCl₂.

^b PDI = polydispersity index.

^c n.d.: not determined.

essentially linear high density polyethylene. This is based on the observation of only one signal for the methylene group (–CH₂–) in the ¹H and ¹³C NMR spectra. The melting points (*T*_m) of the resulting PEs were determined by differential scanning calorimetry analysis (DSC). For both catalysts under various reaction conditions, the melting point ranges between 129 and 135 °C. These values are in line with known values for high molecular weight linear polyethylene [24].

The GPC results, suggest that activation of catalyst systems based on complexes **1** and **2** afforded single-site active species. This is confirmed by the fact that all GPC traces show monomodal curves. Furthermore the molecular weight distributions as determined from PDI values are fairly narrow, varying between 2.4 and 3.2.

In addition the activated catalysts appear to be relatively stable for extended times. For example **2** is still active after 60 min while **1** shows no sign of deactivation after 120 min at the optimized Al:V molar ratio. This was confirmed by catalyst life time studies. It appears that the ligand system that we're employing is capable of stabilizing the activated metal centre.

3. Experimental

3.1. Instrumentation and materials

All experiments were carried out under dry nitrogen by using Schlenk techniques, or in a nitrogen-purged glove box. Tetrahydrofuran, toluene, and diethyl ether were pre-dried over sodium benzophenone, distilled and stored over 3 Å molecular sieves, 2,6-bis(bromomethyl)pyridine, 3,5-dimethylpyrazole, tetra-butylammonium bromide (98%) and ethylaluminium dichloride as a toluene solution were obtained from Aldrich and used as received. Ethylene of polymerization grade (Afrox) was used without further purification. The ligands 2,6-bis(3,5-dimethylpyrazol-1-ylcarbonyl)pyridine (**L1**) [20] and 2,6-bis(3,5-dimethyl-

pyrazol-1-ylmethyl)pyridine (**L2**) were prepared according to literature methods [21]. The NMR spectra of ligands were recorded at room temperature in CDCl₃ while those of polyethylene were recorded in 1,2,4-trichlorobenzene/benzene-*d*₆ at 120 °C on a Varian Gemini 2000 instrument (¹H at 200 MHz and ¹³C at 50.3 MHz). Elemental analysis was performed by the Micro Analytical Laboratory at the University of Cape Town, South Africa. Polymer molecular weights were performed by high temperature GPC (1,2,4-trichlorobenzene, 160 °C, rate = 1.0 mL/min) on a Polymer Laboratories GPC220 instrument using polystyrene standards at the Institute of Polymer Science at the University of Stellenbosch (South Africa). Electron spray ionization (ESI) mass spectra were recorded on a Waters API Quattro Micro spectrometer at the University of Stellenbosch (South Africa).

3.2. Catalyst preparation and characterization

3.2.1. {2,6-[(3,5-Me₂pz)CO]₂py}VCl₃ (**1**)

To a suspension of VCl₃ (0.073 g, 0.46 mmol) in (15 mL) THF was added a solution of 2,6-[(3,5-Me₂pz-CO)₂-py] **L1** (0.15 g, 0.46 mmol), dropwise at 65 °C (Scheme 1). A dark turquoise precipitate was formed, and the mixture was stirred overnight at the above temperature. The vanadium complex was isolated as a turquoise powder by filtration, washed several times with THF, diethyl ether, and dried in vacuum. Yield: 0.14 g, 57%. Anal. Calc. for C₁₇H₁₇N₅O₂Cl₃V · 2H₂O: C, 39.51; H, 4.07; N, 13.56. Found: C, 39.42; H, 4.32; N, 13.07%. IR (KBr cm⁻¹): (C=O) 1676, (C=N) 1576. ESI mass spectrum: *m/z* 413 [MH⁺–2Cl], 374 [MH⁺–3Cl], 324 [MH⁺–VCl₃], 242 [(3,5-Me₂pz)₂V (base peak)]. Mp > 300 °C.

3.2.2. {2,6-[(3,5-Me₂pz)CH₂]₂py}VCl₃ (**2**)

Complex **2** was prepared in the same manner as **1** using VCl₃ (0.0787 g, 0.5 mmol) in THF (15 mL) and 2,6-[(3,5-Me₂pz-CH₂)₂-py], **L2** (0.148 g, 0.5 mmol). The pure

product (0.155 g, 89%) was obtained as light green powder. Anal. Calc. for $C_{17}H_{21}N_5Cl_3V \cdot 0.25THF$: C, 45.93; H, 4.89; N, 14.88. Found: C, 46.48; H, 4.68; N, 15.01%. IR (KBr cm^{-1}): (C=N) 1554. ESI mass spectrum: m/z 296 $[M^+ - VCl_3]$ (base peak), 96 $[C_5H_8N_2]$. Mp > 300 °C.

3.3. General procedure for ethylene polymerization

Polymerization of ethylene was carried out in a 300 mL stainless steel Parr reactor, which was loaded with the catalyst and co-catalyst, in a glove box. This was done by charging the autoclave with vanadium complex (5 μ mol) in dry toluene (50 mL), and the appropriate amount of $AlEtCl_2$. The reactor was sealed and removed from the glove box and then flushed three times with ethylene after which it was heated to the polymerization temperature. Ethylene was continuously supplied to maintain a constant pressure during the polymerization reaction. After the set reaction time, excess ethylene was vented off and the polymerization quenched by adding excess amounts of acidified (HCl) ethanol. The polymer was filtered, washed extensively with ethanol and dried at 70 °C in vacuo.

4. Conclusions

To our knowledge complexes **1** and **2** are amongst the first examples of vanadium pyrazolyl-pyridine catalyst precursors active for ethylene polymerization under relatively mild conditions. Upon activation with $AlEtCl_2$ these catalysts produced polyethylene with high molecular weight with fairly narrow molecular weight distributions in all cases. In addition these catalysts show extended catalyst life times when compared with known vanadium systems. Further studies on these catalyst systems, including the effect of reaction parameters on the performance of catalysts and the effect of substituents in the pyrazole ring on catalyst activity and polyethylene property, are in progress and will be reported in due course.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.035.

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