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Bis(benzimidazole)amine vanadium catalysts for olefin polymerisation and co-polymerisation: thermally robust, single-site catalysts activated by simple alkylaluminium reagents†

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Vanadium complexes containing bis(benzimidazole)amine ligands, upon activation by simple alkylaluminium reagents, give unusually robust, single-site, catalysts for olefin polymerisation/co-polymerisation.

The past 20 years have seen quite remarkable advances in single-site catalyst technology for the production of polyolefins.[1–3] Facilitated by the serendipitous discovery of methylalumoxane (MAO) as an activator in the late 1970's,[4] a variety of high activity single-site transition metal catalyst systems have since been reported, including commercially relevant Group 4 metallocene systems,[5] half-sandwich (constrained geometry) titanium catalysts,[6] and non-metallocene systems based on a variety of nitrogen and oxygen donor ligands.[1,2] For most of these systems MAO, or modified forms of MAO, are required to achieve the highest activities due to the need to stabilise the highly electrophilic cationic active sites by a weakly-coordinating anion.[7]

Catalyst systems that avoid the need for the costly MAO activator, while retaining high productivity, robustness (*e.g.* high temperature stability and tolerance to poisons) and single-site behaviour, are commercially attractive. Here, we describe a readily available tridentate ligand system containing benzimidazole donor units which, when attached to vanadium, affords an exceptionally active single-site polymerisation system upon activation by simple alkylaluminium reagents rather than MAO and, unusually for vanadium,[8] affords a catalyst system of remarkable thermal stability.

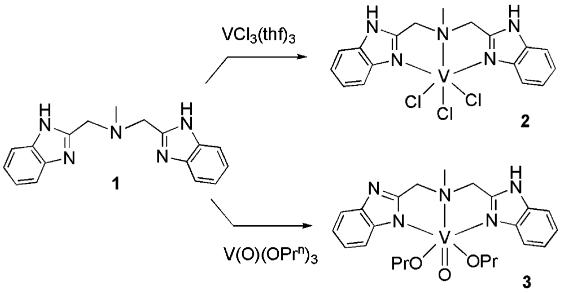
Treatment of bis(benzimidazole)methylamine (BIMA) **1** with $VCl_3(thf)_3$ or $V(O)(OPr^n)_3$ gave the six-coordinate complexes **2** and **3** in high yield according to Scheme 1. In **2**, the ligand retains its two benzimidazole hydrogens and thus acts as a neutral donor, whereas in **3** one of the benzimidazole nitrogen atoms is deprotonated leading to a formally mono-anionic ligand. While **2** is insoluble in common organic solvents, **3** is quite soluble and crystals suitable for an X-ray structure determination‡ were grown from a dichloromethane–pentane (2 : 1) mix. The molecular structure of **3** is shown in Fig. 1; selected bond lengths and angles are given in the caption. The geometry at vanadium is distorted octahedral with the bis(benzimidazole)methylamine ligand binding facially. The distance between the vanadium atom and the central nitrogen donor atom N(3), at 2.4401(13) Å, is *ca.* 0.3 Å longer than the corresponding V(1)–N(1) [2.1005(13) Å] and V(1)–N(4) [2.1315(13) Å] bond lengths, largely a consequence of N(3) lying *trans* to the strongly π-donating oxo [O(1)] ligand. The N(4)–C(10) imine bond is *ca.* 0.02 Å shorter than the other C–N bonds within the imidazole rings (*ca.* 1.34 Å) reflecting the more localized bonding in the protonated imidazole moiety.

Treatment of **2** with dimethylaluminium chloride in toluene afforded a red-brown solution which, when exposed to ethylene in the presence of ethyl trichloroacetate,[11] gave an exceptionally active polymerisation catalyst. Indeed, mass transport problems were encountered due to filling of the reactor with swelled polymer. We found that this could be overcome by carrying out the polymerisation in the presence of hydrogen and at sub-micromole catalyst concentrations. The results of ethylene polymerisations and co-polymerisations are collected in Table 1. It was generally found that the polymerisations are accompanied by large exotherms, affording 30–40 °C temperature rises over the course of 60 min runs. Plots of ethylene uptake *versus* time revealed stable kinetic profiles which demonstrate good thermal robustness for this vanadium catalyst. This contrasts with the typical behaviour of vanadium catalysts which invariably require temperatures below room temperature to maintain their productivity.[12]

For a run at 0.07 μmol catalyst loading at 60 °C (run 2), an activity of 31 550 g PE $mmol^{-1}$ h^{-1} bar^{-1} was recorded.

The resultant polyethylene was highly linear (by ^{13}C NMR) with a molecular weight of *ca.* 400 000 Da and with a polydispersity of *ca.* 2.5, suggestive of single-site behaviour. The use of hydrogen decreases the polymer molecular weight without affecting overall catalyst performance, *cf.* runs 1 and 3 where the molecular weight is lowered from *ca.* 1 000 000 Da in the absence of H_2 to *ca.* 250 000 Da in the presence of H_2 (1 atm).

When hydrocarbon-soluble **3** was activated by dimethylaluminium chloride, a catalyst of comparable activity was obtained (runs 7–9). A comparison of the PE products arising from **2** and **3** revealed close similiarities (*e.g.* compare entries 2 and 8) suggesting that the same active sites are likely being generated from pre-catalysts **2** and **3**. Inspection of the kinetic profile for **3** (from run 9) showed that ethylene uptake remained constant over a 60 min



Scheme 1 Synthesis of vanadium complexes containing bis(benzimidazole)-methylamine ligands (see ESI for procedures†).

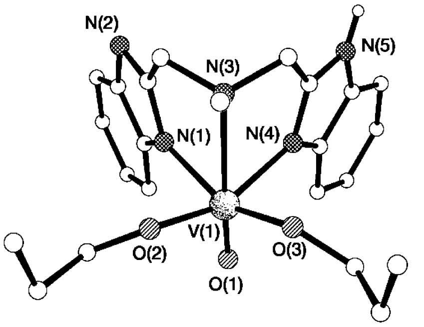


Fig. 1 Molecular structure of **3**; selected bond distances (Å) and angles (°): N(1)–V(1) 2.1005(13), N(3)–V(1) 2.4401(13), N(4)–V(1) 2.1315(13), O(1)–V(1) 1.5959(11), O(2)–V(1) 1.8023(11), O(3)–V(1) 1.7886(11); N(1)–V(1)–N(4) 78.53(5), N(1)–V(1)–N(3) 74.45(5), N(3)–V(1)–N(4) 74.36(5).

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† Electronic supplementary information (ESI) available: experimental procedures for **2** and **3** and polymerisation protocols. See http://www.rsc.org/suppdata/cc/b4/b407065h/

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Table 1 Ethylene homo- and co-polymerizations using **2** and **3**[a]

Run	Pre-cat.	[Cat.]/ µmol	[Me_2AlCl]/ mmol	$p(C_2H_4)$/ bar	Co-M/ mmol[b]	T/°C[c]	t/min	Yield/g	Activity/ g mmol^{-1} h^{-1} bar^{-1}	M_n	M_w	PDI	Co-M incorp. (mol%)
1	**2**	1.00	0.25	4.0	—	50–75	15	5.3	5300	303700	992900	3.3	
2	**2**	0.07	0.50	4.8	—	60–68	60	10.6	31550	165600	411100	2.5	—
3	**2**	0.45	1.00	3.7	—	25–75	60	17.6	10570	100400	248300	2.5	—
4	**2**	0.45	1.00	2.9	—	25–58	60	12.6	9655	134200	338600	2.5	—
5	**2**	0.45	1.00	2.1	—	25–51	60	10.0	10580	140100	338300	2.4	—
6	**2**	0.45	1.00	1.1	—	25–43	60	5.7	11515	127200	595700	2.4	—
7	**3**	0.43	1.00	4.0	—	50–74	15	7.8	18140	313100	984900	3.2	—
8	**3**	0.10	0.05	4.0	—	50–62	30	8.3	41500	172200	579400	3.3	—
9	**3**	0.10	1.00	4.0	—	60	60	14.5	36250	224700	536600	2.4	—
10	**2**	0.08	0.20	3.9	C_3H_6 (57)	60–62	60	5.2	16670	79500	204500	2.6	2.8
11	**2**	0.40	1.60	5.0	NBE (52)	50–75	10	9.0	27000	258700	750300	2.9	10.1
12	**2**	0.40	1.60	5.0	NBE (104)	50–66	20	9.7	11640	301000	879900	2.9	15.5
13	**3**	0.40	0.80	0.5	NBE (60)	50	60	4.5	22500	57100	143700	2.5	32.5

[a] Reaction conditions: runs 2–6, 8, 10–13: Fischer–Porter glass reactor, 220 ml toluene, 1 bar H_2, ethyl trichloroacetate (ECA) promoter; ECA/V = 300 mol/mol; runs 1 and 7: as above but in the absence of H_2; run 9: 1 L stainless steel autoclave, 400 mL heptane, 0.2 bar H_2. [b] C_3H_6 = propylene, NBE = norbornene. [c] Temperature at start and end of run.

run, affording an activity > 36 000 g mmol^{-1} h^{-1} bar^{-1}. These activities are comparable with many MAO-activated metallocene and non-metallocene catalyst systems based on the Group 4 metals[1,2,5] and are exceptional for vanadium-based olefin polymerisation systems.

2 and **3** catalyse the co-polymerisation of ethylene with propylene or norbornene to give the corresponding statistical co-polymers (runs 10–13). In the case of propylene (run 10) an activity of 16 670 g PE mmol^{-1} h^{-1} bar^{-1} was recorded, affording an ethylene–propylene co-polymer of narrow polydispersity, and with 2.4 mol% propylene incorporation. Runs 11–13 show that norbornene is incorporated very efficiently to afford high molecular weight ethylene–norbornene co-polymer products of narrow polydispersity.

In summary, the readily accessible bis(benzimidazole)amine ligand system is found to stabilize highly active olefin polymerisation catalysts based on vanadium. The thermal robustness and single-site behaviour of this system, combined with activation using simple alkylaluminium reagents, provide attractive alternatives to MAO-activated catalyst systems. An important aspect of these new catalysts is the presence of relatively acidic, and therefore reactive, hydrogens within the ligand backbone which will undoubtedly lead to modifications to the ligand upon activation. These effects and their influence on catalyst performance need to be understood more fully and are presently under investigation.

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Notes and references

‡ *Crystal data* for **3**: $C_{23}H_{30}N_5O_3V$, M_r = 475.46, monoclinic, space group $P2_1/n$, orange crystal 0.36 × 0.26 × 0.12 mm³, a = 9.4522(5), b = 24.2311(13), c = 10.2669(6) Å, β = 92.921(2)°, V = 2348.4(2) Å³, T = 150(2) K, Z = 4, ρ_{calcd} = 1.345 g cm^{-3}, $2\theta_{max}$ = 57.98°, Mo–Kα (λ = 0.71073 Å), ω-scans with narrow frames, 20495 data measured on a Bruker SMART 1000 CCD diffractometer,[9] 5678 independent, (R_{int} = 0.023), Lp and absorption corrections applied (based on symmetry equivalent and repeated measurements), μ = 0.456 mm^{-1}, min and max transmission factors: 0.85, 0.95, solved by direct methods,[10] $wR2$ = 0.0932 for all data, $R1$ = 0.0340 for 4551 unique data with $F^2 > 2\sigma(F^2)$ refined on F^2,[10] for 295 parameters with H atoms constrained except for H(5) for which the coordinates were freely refined, largest difference map features within ± 0.41 e Å^{-3}. CCDC 235630. See http://www.rsc.org/suppdata/cc/b4/b407065h/ for crystallographic data in .cif or other electronic format.

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