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Vanadyl complexes bearing bi- and triphenolate chelate ligands: highly active ethylene polymerisation procatalysts†

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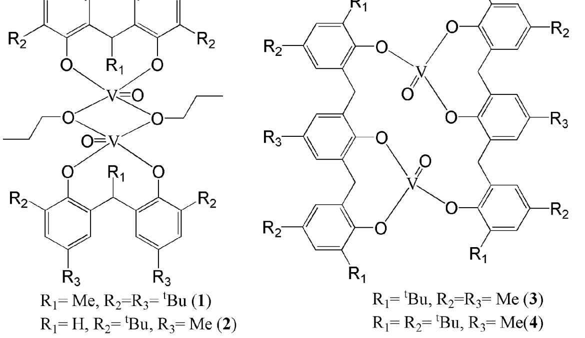
Vanadyl procatalysts bearing chelating aryloxide ligands are found to polymerise ethylene, in the presence of dimethylaluminium chloride, with (for this metal) exceptionally high activities.

Recent literature reflects the continued interest in alternatives to metallocene-type single-site catalysts for α-olefin polymerisation.[1] In contrast to the group IV metals, highly active catalysts of group V are scant,[2] this despite the commercial use of the [V(acac)$_3$] system in the production of ethylene–propylene–diene elastomers.[3] This inactivity is associated with catalyst deactivation typically *via* reduction, in the presence of an alkylaluminium co-catalyst, to the divalent state. Under the elevated temperatures associated with commercial conditions, this catalyst decomposition is more pronounced. Very recently, Fujita and coworkers have prepared the first examples of highly active [up to 65,000 g/mmol (V) h bar], thermally robust [75 °C] vanadium-based olefin polymerisation catalysts.[4] We and others have had some success when using calixarenes as ancillary ligands,[5] whilst a number of groups have used chelating aryloxide complexes of the group IV metals in α-olefin polymerisation.[6] Vanadyl thiobis(phenoxy) complexes have been shown to polymerise propylene with activities up to 2000 g/mmol h bar in liquid monomer.[7] During our studies on chelating aryloxide ligation, we have prepared new, highly active vanadyl complexes of the form [V(O)(μ$_2$-(OPr^n)L^1)]$_2$ (**1**, **2**) and [V(O)L^2]$_2$ (**3**, **4**), where L^1 and L^2 are the deprotonated forms of the di- and triphenols, respectively (see Scheme 1). For **1–4**, preliminary catalytic studies reveal remarkably high activities for these vanadium-based systems (up to 4.5 × 10^6 g/mmol (V) h).

The vanadyl procatalysts used in this study can be prepared, as brown to black crystalline solids, from the reaction of the alkoxide [VO(OPr^n)$_3$] and the parent di- or triphenol, respectively. Alternatively, complexes **3** and **4** are accessible *via* the interaction of [VOCl$_3$] and the parent triphenol. However, similar reaction of diphenols is known to yield four-coordinate oxychloride complexes.[8] Crystals of the procatalyst **1**·MeCN suitable for an X-ray diffraction study were grown from acetonitrile at ambient temperature: they incorporate one diffuse molecule of solvent (modelled at half-weight) per molecule of the complex. The molecule [Fig. 1] is a centrosymmetric dimer, with near symmetric n-propoxide bridges, and in which each vanadium centre possesses a distorted square-based pyramidal geometry. A boat conformation is adopted for both the eight-membered metallocyclic rings, for which the O–V–O η^2 chelate bite angles are *ca.* 94.5°.



R$_1$= Me, R$_2$=R$_3$= ^{t}Bu (**1**)
R$_1$= H, R$_2$= ^{t}Bu, R$_3$= Me (**2**)

R$_1$= ^{t}Bu, R$_2$=R$_3$= Me (**3**)
R$_1$= R$_2$= ^{t}Bu, R$_3$= Me(**4**)

Scheme 1

Crystals of [VO(L)]$_2$·MeCN (**4**·MeCN) grown from a saturated acetonitrile solution, were weakly diffracting requiring the use of a rotating-anode X-ray source. The crystal structure contains both enantiomers of the complex and two diffuse solvent molecules in the asymmetric unit. The triphenolate ligands [see Fig. 2] each bind in an unsymmetrical fashion as seen recently in a series of titanium isopropoxides,[9] *viz* η^2-coordination to one pseudo tetrahedral (angles in the range 107.7(2)–112.4(2)°) vanadium centre. The eight-membered metallocyclic rings, as in **1**, all adopt the boat conformation (bite angle *ca.* 108°).

In the IR spectra, the ν(V=O) stretches for **1–4** occur in the region 994–1024 cm^{-1}. Solution ^{1}H NMR spectra for **3** and **4** are reminiscent of the interconverting isomers observed by Hofmeister *et al.* in the aforementioned titanium isopropoxides.[9] In the presence of dimethylaluminium chloride (DMAC), **1–4** are highly active for the polymerisation of ethylene. High molecular weight, solid polyethylene is obtained in all cases, with a noticeable drop off in molecular weight of the polymer with increasing temperature. All polyethylenes exhibited similar melting points, 131–135 °C by DSC, typical for linear polyethylene. The nature of the co-catalyst is crucial, for example with methylaluminoxane (MAO), the catalysts are best described as poor to moderate (< 100 g/mmol h bar). The activity of the system is a function of the [Al] : [V] molar ratio, increasing with the amount of DMAC used.

In no case has polyethylene been obtained using **1–4** in the absence of aluminium co-catalyst, whilst the use of up to 7000 equivalents of DMAC in the absence of any vanadium species, under the Schlenk-line conditions employed here, afforded only negligible polymer. Complexes **1–4**, in the presence of DMAC, also polymerise propylene, albeit with reduced activities.‡.[10]

Given that the activities of **1–4** start to fall off at temperatures more suited to industrial conditions (80 °C), we revisited our

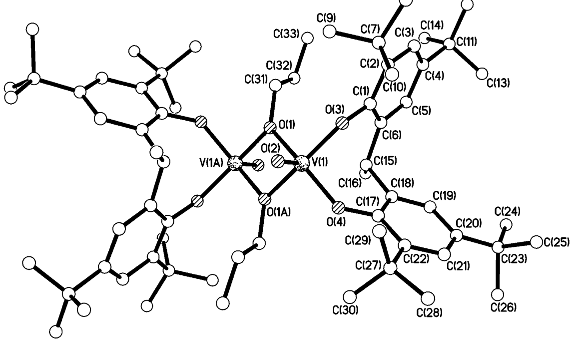


Fig. 1 Selected bond lengths (Å) and angles (°) for **1**: V(1)–O(1A) 1.977(3), V(1)–O(1) 1.973(3), V(1)–O(2) 1.583(3), V(1)–O(3) 1.802(2), V(1)–O(4) 1.815(2), O(3)–V(1)–O(4) 94.49(10), V(1)–O(3)–C(1) 141.3(2), V(1)–O(4)–C(17) 136.6(2), O(1)–V(1)–O(1A) 72.35(12). MeCN molecules of crystallization and H atoms omitted for clarity.

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† Electronic supplementary information (ESI) available: selected spectroscopic and polymerisation data. See http://www.rsc.org/suppdata/cc/b4/b406783e/

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catalytic screening in the presence of the re-activator ethyl trichloroacetate (ETA).[11] For **1–4**, the use of ETA resulted in *ca.* a 7-fold increase in activities, with a concomitant increase in thermal stability (see Table 1). As before, there is an increase in activity with increasing [Al] : [V] molar ratio and activities approaching 100,000 g/mmol h bar are now observed. At higher temperatures, high activities are also possible for much smaller co-catalyst loadings, for example at 55 °C, activities in excess of 3500 g/mmol h bar are readily achievable using [Al] : [V] of 50 : 1 (run 9). At 7 bar in a 1 litre autoclave, activities for **1** and **2** (run 6) in excess of 2×10^6 g/mmol V h (*ca.* 300,000 g/mmol h bar) were readily achievable, whilst for **3** (run 10) and **4** activities of the order of 4.5×10^6 g/mmol V h (*ca.* 640,000 g/mmol h bar) were observed. The values reported here are likely to be limiting as the mass of polymer produced hampers stirring.[12] Lifetime studies indicate that these systems are still highly active ($>$ 16,000 g/mmol h bar) after 25 min. In the absence of ETA, there is a marked decrease in activity after 5 min. Under analogous catalytic conditions, vanadyl procatalysts of the form $[VO(OAr)_3]$[13] containing monodentate aryloxide ligation display comparable activity.[10]

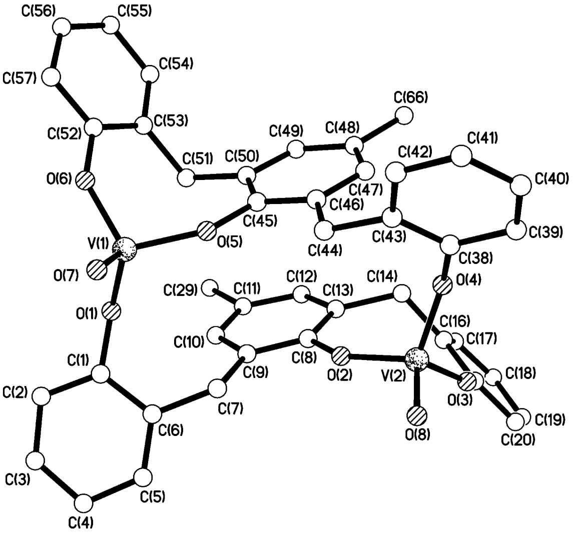

Fig. 2 Selected bond lengths (Å) and angles (°) for one of the two unique molecules in **4**·MeCN: V(1)–O(1) 1.779(5), V(1)–O(5) 1.748(5), V(1)–O(6) 1.772(5), V(1)–O(7) 1.592(6), V(2)–O(4) 1.760(5), V(2)–O(3) 1.754(5), V(2)–O(8) 1.587(6), V(1)–O(1)–C(1) 141.7(5), O(5)–V(1)–O(6) 107.7(2), V(1)–O(5)–C(45) 144.7(5), V(2)–O(4)–C(38) 145.2(5), O(2)–V(2)–O(3) 106.7(2). Bu^t groups, H atoms and MeCN molecules of crystallization omitted for clarity.

Table 1 Ethylene polymerisation results[a]

Run	Procatalyst (μmol)	Temp. (°C)	[Al]/[V]	mp (°C)	Activity[b]
1[c]	**2** (0.5)	55	1000	134	5600
2[c]	**4** (0.2)	55	1000	136	16,500
3	**2** (0.1)	80	5000	—	54,200
4	**2** (0.1)	55	500	131	2900
5	**2** (0.1)	55	1500	—	35,000
6[d]	**2** (0.1)	80	150000	135	300,000
7	**3** (0.1)	25	5000	133	36,400
8	**3** (0.1)	80	5000	133	94,000
9	**3** (2.0)	55	50	—	3600
10[d]	**3** (0.1)	80	150000	135	640,000
11	**3** (0.3)	25	5000[e]	—	< 1

[a] 1 bar ethylene Schlenk test carried out in toluene (40 ml) in the presence of ETA (0.1 ml) over 1 min, reaction quenched with dilute HCl, washed with methanol (50 ml) and dried for 12 h in a vacuum oven at 45 °C. [b] (g/mmol (V) h bar). [c] Without ETA. [d] 7 bar autoclave test carried out in toluene (400 ml) with ETA (1 ml) for 1 min. [e] MAO.

We have demonstrated that exceptionally active vanadyl-based catalysts are accessible using bi- and triphenolate ancillary chelate ligands. Indeed, the systems reported herein have the highest observed activities reported to-date for any vanadium-based ethylene polymerisation system.

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Notes and references

‡ *Crystal data* for **1**·MeCN: $C_{66}H_{102}O_8V_2{\cdot}CH_3CN$, M = 1166.41, triclinic, space group $P\bar{1}$, a = 10.6383(12), b = 12.7094(14), c = 14.6822(16) Å, α = 73.299(2), β = 76.055(2), γ = 70.891(2)°, U = 1772.8(3) Å^3, T = 150(2) K, Z = 1, μ(Mo-Kα) = 0.312 mm^{-1}. 13568 data measured, (R_{int} = 0.024), $wR2$ = 0.2245 for all data, $R1$ = 0.0701 for 5070 unique data with $F^2 > 2\sigma(F^2)$ refined on F^2. *Crystal data* for **4**·MeCN: $C_{74}H_{98}O_8V_2{\cdot}CH_3CN$, M = 1258.46, triclinic, space group $P\bar{1}$, a = 18.2798(4), b = 18.2851(5), c = 22.6903(7) Å, α = 82.9933(10), β = 73.0690(10), γ = 89.9842(13)°, U = 7196.4(3) Å^3, T = 120(2) K, Z = 4, μ(Mo-Kα) = 0.312 mm^{-1}. 41131 data measured, (R_{int} = 0.090) $wR2$ = 0.2733 for all data, $R1$ = 0.1097 for 13847 unique data with $F^2 > 2\sigma(F^2)$ refined on F^2. CCDC 238704–238705. See http://www.rsc.org/suppdata/cc/b4/b406783e/ for crystallographic data in .cif or other electronic format.

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