

# Tri- and tetra-dentate imine vanadyl complexes: Synthesis, structure and ethylene polymerization/ring opening polymerization capability

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

**ABSTRACT:** Reaction of the ligand 2,4-*tert*-butyl-6-[(2-methylquinolin-8-ylimino)methyl]phenol (L<sup>1</sup>H) with [VOCl<sub>3</sub>] in the presence of triethylamine afforded the complex [VOCl<sub>2</sub>L<sup>1</sup>] (1), whereas use of [VO(OnPr)<sub>3</sub>] led to the isolation of [VO<sub>2</sub>L<sup>1</sup>] (2) or [VO<sub>2</sub>L<sup>1</sup>]•MeCN (2•MeCN). Reaction of 2-((2-(1H-10 benzo[d]imidazol-2-yl)quinolin-8-ylimino)methyl)-4,6-R<sup>1</sup>,R<sup>2</sup>-phenols (R<sup>1</sup> = R<sup>2</sup> = *t*Bu; L<sup>2</sup>H), (R<sup>1</sup> = R<sup>2</sup> = Me; L<sup>3</sup>H) and (R<sup>1</sup> = Me, R<sup>2</sup> = Ad; L<sup>4</sup>H) with [VO(OnPr)<sub>3</sub>] afforded complexes of the type [L<sup>2-4</sup>VO] (using L<sup>2</sup> = 3, L<sup>3</sup> = 4, L<sup>4</sup> = 5). The molecular structures of 1 to 3 are reported; the metal centre adopts a distorted octahedral, trigonal bipyramidal or square-based pyramid, respectively. All complexes have been screened as pre-catalysts for the polymerization of ethylene using diethylaluminium chloride 15 (DEAC) as co-catalyst in the presence of ethyltrichloroacetate (ETA), and for the ring opening polymerization (ROP) of  $\epsilon$ -caprolactone in the presence of benzyl alcohol. All pre-catalyst/DEAC/ETA systems are highly active ethylene polymerization catalysts affording linear polyethylene with activities in the range 3,000 – 10,700 g/mol.h.bar; the use of methylaluminoxane (MAO) or modified MAO as co-catalyst led to poor or no activity. In the case of the ring opening polymerization (ROP) of  $\epsilon$ -caprolactone, 20 systems employing complexes 1 - 5 were virtually inactive at temperatures < 110 °C; on increasing the Cl:V ratio at 110 °C, conversions of the order of 80 % were achievable.

## Introduction

The high activity and thermal stability exhibited by a number of recent vanadium-based systems for olefin polymerization 25 catalysis has attracted both academic and industrial interest.<sup>1</sup> This has also led to investigations into their potential use as catalysts for ring opening polymerizations (ROP) of lactones and/or lactides.<sup>2</sup> In our laboratory, vanadyl species bearing phenoxide-type ligand sets as well as the use of imine-based ligand systems 30 have been investigated, and some notable successes have been achieved.<sup>1c,3</sup> In more recent work, we found that by combining these two functionalities in the form of bi-dentate phenoxyimines, similar to those employed in the Mitsui FI catalyst system,<sup>4</sup> reasonably high activities for ethylene polymerization ( $\leq 10,000$  35 g/mmol.h.bar) were achievable.<sup>5</sup> Meanwhile, in other studies, it has been noted that titanium complexes bearing the quinoline containing ligand 2,4-*tert*-butyl-6-[(2-methylquinolin-8-ylimino)methyl]phenol (L<sup>1</sup>H), were capable of both ethylene and propylene polymerization, though the active species involved 40 appeared not to be simple.<sup>6</sup>

In general, the use of tridentate ligand sets has proved

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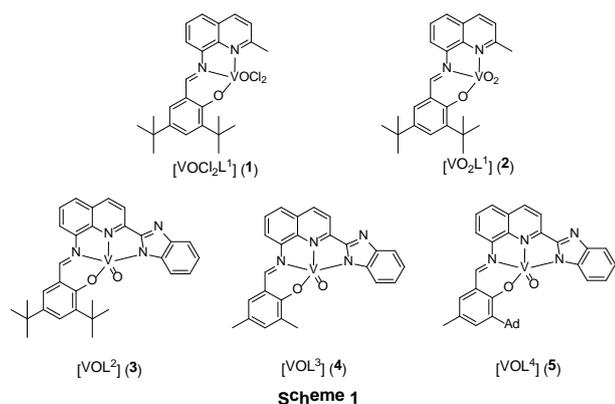
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particularly fruitful with group IV metals, as highlighted by the work of Tang *et al.*,<sup>7</sup> whilst Li and coworkers have investigated a number of vanadium systems.<sup>8</sup> Interestingly, the potentially tetra-45 dentate ligands L<sup>2</sup>H – L<sup>4</sup>H have previously been used to form organoaluminium complexes, though they were shown by Sun *et al* to be incapable of the ROP of  $\epsilon$ -caprolactone under a variety of conditions.<sup>9</sup>

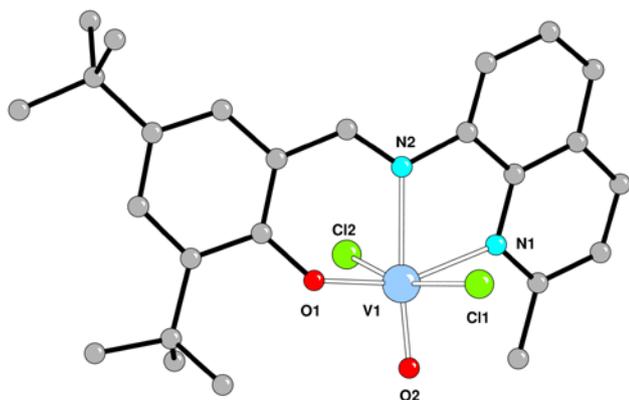
Encouraged by these findings, we have prepared and fully 50 characterized a number of vanadyl complexes bearing tri- and tetra-dentate ligands (see scheme 1). Investigations into their ability to polymerize ethylene revealed that, in the presence of the co-catalyst diethylaluminium chloride (DEAC) and the re-activator ethyltrichloroacetate (ETA),<sup>10</sup> activities of the order of 55 10,500 g/mol.h.bar were achievable. The operating temperature for optimum catalytic activity was found to be 60 °C; many previous vanadium systems have suffered from thermal instability, primarily as a result of reduction to inactive species.<sup>11</sup> The polymer products were mostly linear polyethylene of 60 relatively high molecular weight ( $M_w$ ) ( $\leq 32,400$ ) at 30 °C, however the  $M_w$  values dropped rapidly on increasing the temperature. In contrast to the previous work on aluminium complexes,<sup>9</sup> use of the ligands L<sup>2</sup>H – L<sup>4</sup>H herein provided 65 of  $\epsilon$ -caprolactone with good control, albeit requiring the use of high temperatures (110 °C) to achieve reasonable conversions.



## Results and Discussion

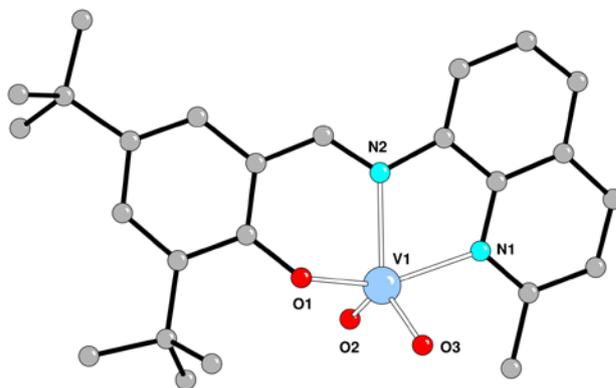
### Tri-dentate imine vanadyl complexes

Reaction of 2,4-*tert*-butyl-6-[(2-methylquinolin-8-ylimino)methyl]phenol (**L<sup>1</sup>H**) with [VOCl<sub>3</sub>] in the presence of triethylamine in tetrahydrofuran (THF) afforded, following work-up (extraction into acetonitrile), the brown complex [VOCl<sub>2</sub>L<sup>1</sup>] (**1**) in 68 % isolated yield. Single crystals of the **1** were grown from a saturated acetonitrile solution at ambient temperature. The molecular structure is shown in Figure 1, with selected bond lengths and angles given in the caption; crystallographic data for **1** (and compounds **2**, **2'** and **3**) are collected in Table 4. In **1**, the metal centre possesses a pseudo octahedral geometry with the tridentate ligand binding in *mer* fashion, and with the vanadyl group *trans* to the imino nitrogen. The V1 – N1 bond to the quinolone nitrogen is slightly longer than that to the ‘central’ nitrogen N2, which suggests that former forms a stronger bond; both V – N bonds are dative. The vanadyl bond length at 1.5911(14) Å is at the lower end of the range [1.593(2) – 1.605(4) Å] typically observed for this function.<sup>2c,3,11</sup>



**Figure 1.** CAMERON representation of **1** showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): V1 – O1 1.8105(14), V1 – O2 1.5911(14), V1 – N1 2.1669(17), V1 – N2 2.2090(16), V1 – C11 2.3610(6), V1 – C12 2.3147(6); O1 – V1 – N1 158.23(6), O2 – V1 – N2 173.64(7), C11 – V1 – C12 162.72(2).

By contrast, interaction of **L<sup>1</sup>H** with [VO(OnPr)<sub>3</sub>] in refluxing toluene afforded, after work-up (extraction into acetonitrile), the yellow complex [VO<sub>2</sub>L<sup>1</sup>] (**2**) in 64 % isolated yield. Single crystals of **2** were grown from a saturated acetonitrile solution at ambient temperature. The molecular structure is shown in Figure 2, with selected bond lengths and angles given in the caption. There are three vanadium complexes and two molecules of acetonitrile in the asymmetric unit. The metal adopts a distorted trigonal bipyramidal geometry with the phenoxide oxygen and quinoline nitrogen atom occupying axial positions, and with *cis* oxo groups. The vanadyl bond lengths of 1.624(3) and 1.628(4) Å (and for **2'**, see below, 1.629(2) and 1.623(2) Å) are longer than that observed in **1**. Presumably the presence of the second oxo group arises *via* fortuitous hydrolysis, with two propoxide ligands of the vanadium precursor eliminated in the form of propanol. The mutual twist between the quinolinyl group and the C<sub>6</sub>H<sub>2</sub> aromatic rings in **2** varies somewhat between the three unique complexes, *viz* 39.94(9)° for that containing V1, 31.07(9)° for V2 and 30.96(9)° for V3, respectively. The molecules pack parallel to the *b* axis *via* π – π interactions (see ESI, Figure S1). The centroid – centroid separations are all close to 3.5 Å, with the closest atom – atom contacts at about 3.35 Å. There is a weak interaction C40 – H40 ⋯ O7' between stacks at 2.43 Å.



**Figure 2.** CAMERON representation **2**:2/3(MeCN) showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): V1 – O1 1.913(3), V1 – O2 1.624(3), V1 – O3 1.628(4), V1 – N1 2.139(4), V1 – N2 2.164(4); O1 – V1 – N1 134.67(17), O2 – V1 – N2 98.21(15), O3 – V1 – N2 152.79(14).

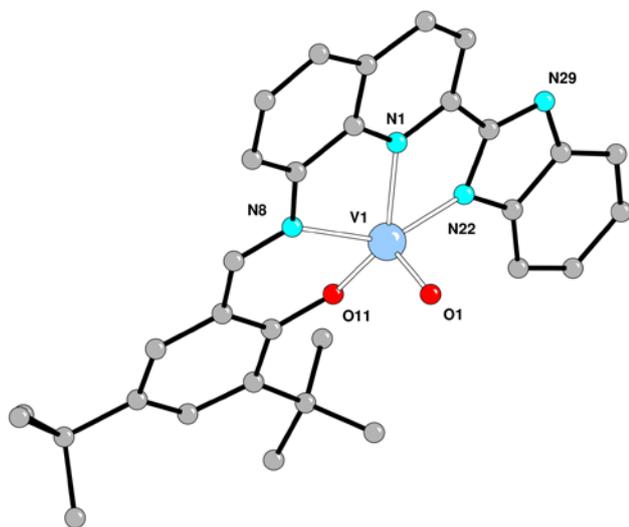
The reaction was repeated in an attempt to avoid the hydrolysis reaction; however, again, a dioxo complex was formed, which differed from **2** in the degree of solvation. This alternative crystalline form **2'** does not feature the stacking arrangement seen in **2** (see ESI, Figure S2 and geometrical parameters of **2'** and Table 4).

### Tetra-dentate imine vanadyl complexes

Reaction of the ligands 2-((2-(1H-benzo[*d*]imidazol-2-yl)quinolin-8-ylimino)methyl)-4,6-*R*<sup>1</sup>,*R*<sup>2</sup>-phenols (*R*<sup>1</sup> = *R*<sup>2</sup> = *t*Bu; **L<sup>2</sup>H**), (*R*<sup>1</sup> = *R*<sup>2</sup> = Me; **L<sup>3</sup>H**) and (*R*<sup>1</sup> = Me, *R*<sup>2</sup> = Ad; **L<sup>4</sup>H**) with [VO(OnPr)<sub>3</sub>] in refluxing toluene afforded, after work-up (extraction into acetonitrile), complexes of the type [L<sup>2-4</sup>VO] (*R*<sup>1</sup> = *R*<sup>2</sup> = *t*Bu **3**, *R*<sup>1</sup> = *R*<sup>2</sup> = Me **4**, *R*<sup>1</sup> = Me, *R*<sup>2</sup> = Ad **5**) in good yield (> 70 %). During the reaction, the vanadium centre was reduced from V(V) to V(IV), and we have attributed this to an oxidation reaction (of propanol) catalyzed by the vanadyl complex. Such reactions are well established for vanadyl complexes, including

those bearing additional alkoxide ligands;<sup>12</sup> a mechanism has been proposed by Velusamy and Punniyamurthy.<sup>13</sup> These vanadium(IV) complexes were characterized by X-band EPR measurements where possible at 298 K and, as expected, in the case of **3**, gave an 8-line spectrum characteristic of V(IV) ( $d^1$ ,  $I = 7/2$ ). Given the poor solubility of **4** and **5**, the EPR spectra were recorded on solid samples only;  $g$  values compare favorably with previously reported vanadyl(IV) systems,<sup>14</sup> and particularly with those adopting a  $VO[N_2O_2]$  coordination environment.<sup>3b,15</sup>

Crystals of **3**·MeCN suitable for an X-ray structure determination were grown from a saturated solution in acetonitrile on prolonged standing (1–2 days) at ambient temperature. The molecular structure is shown in Figure 3, with selected bond lengths and angles given in the caption. The metal centre adopts a distorted square-based pyramid with the oxo group at the apex and the ( $L^2$ ) ligand wrapped around the four base sites. There is rotation about the C8–N8 bond so that the normals to the phenolate ring of C11–16 and the quinoline system, N1–C10, are *ca* 15° apart; the quinolone and benzimidazole ring systems are more coplanar with rotation about the C2–C21 bond *ca* 1.7° from planarity. Molecules of **3** stack such that adjacent vanadyl groups align along the crystallographic *a* axis (see ESI, Figure S3) and the quinolinyl-benzimidazole unit overlaps a centrosymmetrically-related unit with an inter-planar distance of *ca.* 3.35 Å.



**Figure 3.** CAMERON representation of **3**·MeCN showing the atom numbering scheme. Selected bond lengths (Å) and angles (°): V1 – O1 1.589(3), V1 – O11 1.906(3), V1 – N1 2.036(3), V1 – N8 2.088(3), V1 – N22 2.071(4); O11 – V1 – N1 141.89(13), O11 – V1 – N8 87.89(13), N1 – V1 – N22 76.69(15).

## Catalytic screening

### Ethylene polymerization

Complexes **1** – **5** were found to be active for the polymerization of ethylene using diethylaluminium chloride (DEAC) as co-catalyst, with ethyltrichloroacetate (ETA) present as re-activator. Complex **3** was used to obtain the optimum polymerization conditions and the results are presented in Table 1. Over 15 min., at 30 °C and 1 bar ethylene, on changing the molar ratio of Al:V from 10,000 to 30,000 (runs 1 to 5), the highest activity was observed for Al:V at 20,000. Notably, the higher the Al:V ratio employed, the lower the molecular weight of the polyethylene obtained. At this temperature (30 °C), the products formed

possessed relatively narrow molecular weight distributions ( $< 3$ ). At an Al:V ratio of 20,000, the temperature was varied from 30 to 80 °C (runs 3 and 6 – 10), and the highest activity, namely 7,480 g/mmol.h.bar, was achieved at 60 °C. As observed in other vanadium-based systems, increasing the temperature led to a rapid decrease in the molecular weight of the product. <sup>13</sup>C NMR spectral analysis of the polymers indicated that there was no branching present (see ESI, Figures S4 – S6); the lower melting points ( $\leq 128$  °C) observed for some runs were thought to be due to the lower molecular weights of the products obtained as opposed to the presence of branching.

Given the results in Table 1, the optimum conditions for screening of **1** – **5** were set at 60 °C and an Al:V ratio of 20,000; results under these conditions are presented in Table 2. For the tridentate systems (runs 1 and 2), the oxydichloride **1** exhibited superior activity, whereas for the dioxo complex **2**, the molecular weight of the isolated polymer was somewhat greater; molecular weight distributions were similar for the two systems. In the case of the complexes bearing tetra-dentate ligand sets, complex **5** possessing the *ortho* adamantyl substituent exhibited the highest activity; this system also produced polyethylene possessing highest molecular weight.

Comparison with the recently reported vanadyl complexes bearing bi-dentate phenoximine ligands reveals similar observed activities, molecular weights ( $M_w$ ) and range of PDIs, although for the bi-dentate systems, the optimum operating temperature was found to be 80 °C.<sup>5</sup>

### Ring opening of $\epsilon$ -caprolactone

The use of **1** – **5**, in the presence of benzyl alcohol, for the ROP of  $\epsilon$ -caprolactone was evaluated. The results are presented in Table 3; complex **1** was used to determine the conditions required for best results, and this revealed that only low conversions ( $< ca$  22 %) were observed at temperatures below 90 °C. Increasing the temperature led to better conversions, which peaked at *ca* 73 % when using a CL:V ratio of 800 at 110 °C. All systems were well behaved (good control) with PDI values generally of about 1.1 to 1.2, with the corrected average molecular mass of the polymers obtained close to the calculated values. Higher molecular weight products ( $M_w$ ) were isolated using complex **2** ( $\sim 50,000$  g mol<sup>-1</sup>) as well as **3** and **4** (both about  $\sim 33,000$  g mol<sup>-1</sup>), though conversion rates for these systems were disappointing ( $< 30$  %). Interestingly, within the family of complexes bearing tetra-dentate ligands, complex **5** bearing the adamantyl substituent exhibited highest conversion, but afforded the product of lowest molecular weight ( $M_w$ ). We note that aluminium complexes bearing related tetra-dentate ligand sets were found to be poor initiators.<sup>9</sup> In the MALDI-TOF spectra (see ESI, Figures S7 – S9), only one population of peaks, which possess the spacing of 114 mass unit (the molecular weight of the monomer), was detected. The peaks are assigned to the sodium adducts of the polymer chains with benzyloxy end groups. The <sup>1</sup>H NMR spectrum of the polymer was obtained (see ESI, Figures S10 and S11) to verify the molecular weight of the polymer and identify the end chain group of the PCL. Typically, peaks at 7.29, 5.04 and 3.57 ppm (5:2:2) indicated that the polymer chains were capped by one benzyl ester and a hydroxyl group, consistent with insertion of a benzyloxy group during polymerization; <sup>13</sup>C NMR data (ESI, Figures S12 and S13) also revealed peaks ( $\delta$  127.5, 127.2, 127.1 and 50.1) due to the benzyl group. The polymer molecular weight ( $M_n$ ) was calculated from the ratio of the peaks at 5.12 and 4.06 ppm (see Table 3).

## ARTICLE TYPE

**Table 1.** Polymerization screening using pre-catalyst **3**.<sup>a</sup>

Run	Al/V	T (°C)	T (min)	PE (g)	Activity (g/mmol.h.bar)	$M_w$ (x $10^3$ )	$M_n$ (x $10^3$ )	PDI	$T_m$ (°C)
1	10000	30	15	0.0751	3000	64.6	32.4	1.99	134.10
2	15000	30	15	0.1038	4150	46.8	17.0	2.75	133.49
3	20000	30	15	0.1421	5680	44.3	19.7	2.25	133.26
4	25000	30	15	0.1335	5340	41.0	18.2	2.25	133.12
5	30000	30	15	0.0998	3990	40.7	13.9	2.93	132.52
6	20000	40	15	0.1594	6380	17.7	3.8	4.68	130.13
7	20000	50	15	0.1766	7060	9.6	2.4	4.09	128.00
8	20000	60	15	0.1871	7480	7.6	2.2	3.52	126.79
9	20000	70	15	0.1803	7210	6.9	1.9	3.68	126.71
10	20000	80	15	0.1612	6450	6.1	1.9	3.18	127.46
11	20000	60	30	0.2911	5820	13.8	2.5	5.54	128.05

<sup>a</sup> Conditions: 0.1  $\mu$ mol of [V] per run, 30 mL of toluene, 0.1ml ETA per run, 1 atm of ethylene. GPC analysis was conducted in 1,2,4-trichlorobenzene.

**Table 2.** Catalysis runs using pre-catalysts **1 - 5** under optimized conditions at 1 bar.

Run	Complex	PE (g)	Activity (g/mmol.h.bar)	$M_w$ (x10 <sup>3</sup> )	$M_n$ (x10 <sup>3</sup> )	PDI	$T_m$ (°C)
1	<b>1</b>	0.2173	8690	7.6	2.5	3.03	127.91
2	<b>2</b>	0.1410	5640	10.9	3.7	2.98	129.73
3	<b>3</b>	0.1871	7480	7.6	2.2	3.5	126.79
4	<b>4</b>	0.1362	5450	11.2	5.9	1.91	130.15
5	<b>5</b>	0.2673	10690	20.0	6.8	2.94	129.04

<sup>a</sup> Conditions: 0.1  $\mu$ mol of [V] per run, 30 mL of toluene, 60 °C, 20,000 equivalents of Et<sub>2</sub>AlCl, 0.1 mL of ETA, 15 min, 1 atm of ethylene. GPC analysis was conducted in 1,2,4-trichlorobenzene.

In conclusion, a series vanadyl complexes bearing tri- or tetra-  
dentate ligand sets has been synthesized and characterized  
by <sup>1</sup>H, <sup>13</sup>C, <sup>51</sup>V NMR or EPR spectroscopy, elemental analysis,  
IR spectroscopy and where possible by single crystal X-ray  
diffraction. Complexes **1 - 5** exhibited high activity (ca. 5,500 -  
10,700 g/mmol.h.bar) when using 20,000 equivalents of DEAC  
as co-catalyst in the presence of the re-activator ETA at 60 °C  
and 1 bar ethylene. The products were moderate to high

molecular weight ( $M_w$ ), linear polyethylenes. In the ROP of  $\epsilon$ -  
caprolactone, moderate to good conversion was achieved at 110  
°C, with molecular weights ( $M_w$ ) in the range ~3,000 to 50,000 g  
mol<sup>-1</sup>; the systems were generally well-behaved with PDIs  
typically less than 1.2.

**Table 3.**  $\epsilon$ -Caprolactone screening results for complexes **1-5**.<sup>a</sup>

Run	Complex	Ratio (CL:V)	T (°C)	Conversion <sup>b</sup> (%)	$M_w$	$M_n$ GPC	$M_n$ NMR	PDI
1	<b>1</b>	400	110	27.3	9704	6646		1.4
2	<b>1</b>	600	110	76.9	7558	6137	7734	1.2
3	<b>1</b>	800	110	81.3	6868	5788	5682	1.1
4	<b>1</b>	1000	110	26.4	6215	5560		
5	<b>1</b>	800	90	21.9	7858	7025		1.1
6	<b>1</b>	800	70	9.9	8100	7085		1.1
7	<b>1</b>	800	50	0				
8	<b>2</b>	800	110	10.7	7635	6817	7747	1.1
9	<b>3</b>	800	110	30.1	7518	6876	6151	1.1
10	<b>4</b>	800	110	24.2	7632	6923	11167	1.1
11	<b>5</b>	800	110	47.1	7672	6828	9685	1.1

<sup>a</sup> Conditions: 5 mL of toluene; 1 mL of  $\epsilon$ -caprolactone; 1 equivalent of benzyl alcohol; 24 h. <sup>b</sup> Calculated by <sup>1</sup>H NMR spectroscopy. GPC analysis was conducted in THF.

**Experimental**

*General:* All manipulations were carried out under an atmosphere

of dry nitrogen using conventional Schlenk and cannula  
techniques or in a conventional nitrogen-filled glove box.  
Toluene was refluxed over sodium. Acetonitrile was refluxed

over calcium hydride. All solvents were distilled and degassed prior to use. IR spectra (nujol mulls, KBr windows) were recorded on a Nicolet Avatar 360 FT IR spectrometer;  $^1\text{H}$  NMR spectra were recorded at room temperature on a Varian VXR 400 S spectrometer at 400 MHz or a Gemini 300 NMR spectrometer or a Bruker Avance DPX-300 spectrometer at 300 MHz. The  $^1\text{H}$  NMR spectra were calibrated against the residual protio impurity of the deuterated solvent. EPR spectra were recorded on a JES-FA200 spectrometer at Tsinghua University. Elemental analyses were performed by the elemental analysis service at the London Metropolitan University. Magnetic moments were measured on a Johnson Matthey magnetic susceptibility balance. The ligands  $\text{L}^1$ - $^3\text{H}$  were prepared as described in the literature.<sup>6,9</sup> The vanadium precursors were purchased from Sigma Aldrich and were used as received.

*Synthesis of (E)-2-(2-methylquinolin-8-ylimino)-4,6-di-tert-butyl-phenolate oxovanadium dichloride (1)*

$\text{L}^1\text{H}$  (0.5 g, 1.33 mmol) was dissolved in tetrahydrofuran (40 mL). Triethylamine (0.2 mL, 1.44 mmol) and vanadium oxytrichloride (0.14 mL, 1.46 mmol) were added *via* syringe and the solution stirred at ambient temperature for 6 h. The volatiles were removed *in vacuo*. Crystallization using hot acetonitrile gave brown plates of the vanadium compound **1**. (0.46 g, 68 % yield). MS (E.I.) 475.1  $[\text{M}-\text{Cl}]^+$ . IR (nujol): 1610m, 1588s, 1566m, 1538w, 1505m, 1431m, 1311m, 1232w, 1213m, 1199m, 1170m, 1146s, 972s, 886w, 796s, 764m, 694m. Found: C, 58.82; H, 5.87; N, 5.57.  $\text{C}_{25}\text{H}_{29}\text{Cl}_2\text{N}_2\text{O}_2\text{V}$  requires C, 58.72; H, 5.72; N, 5.48 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 8.94 (s, 1H,  $\text{CH}=\text{N}$ ), 8.24 (d, 1H,  $J = 8.40$ ,  $\text{ArH}$ ), 7.94 (d, 1H,  $J = 7.36$ ,  $\text{ArH}$ ), 7.81 (d, 1H,  $J = 7.84$ ,  $\text{ArH}$ ), 7.66 (d, 1H,  $J = 2.36$ ,  $\text{ArH}$ ), 7.61 (m, 2H,  $\text{ArH}$ ), 7.48 (d, 1H,  $J = 2.36$ ,  $\text{ArH}$ ), 3.58 (s, 3H,  $\text{Ar-Me}$ ), 1.63 (s, 9H, 'Bu), 1.38 (s, 9H, 'Bu).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 161.0, 157.4, 152.7, 141.3, 138.9, 136.4, 130.7, 129.5, 128.6, 128.1, 127.1, 126.8, 126.1, 125.9, 115.3, 35.6, 35.1, 35.0, 30.9, 30.8, 30.1, 29.2, 28.7.  $^{51}\text{V}$  NMR ( $\text{CDCl}_3$ ): -261.47 ( $w_{1/2} = 256$  Hz).

*Synthesis of (E)-2-(2-methylquinolin-8-ylimino)-4,6-di-tert-butyl-phenolate dioxovanadium(V) (2)*

$\text{L}^1\text{H}$  (0.5 g, 1.33 mmol) was dissolved in toluene (40 mL), and vanadyl tri-*n*-propoxide (0.34 mL, 1.46 mmol) was added *via* syringe and the solution refluxed for 16 h. The solution was allowed to cool to room temperature and the volatiles were removed *in vacuo*. Crystallization using hot acetonitrile gave yellow needles of the vanadium compound **2**. (0.39 g, 64 % yield). MS (E.I.) 456.1  $[\text{M}]^+$ , 441.0  $[\text{M}-\text{Me}]^+$ . IR (nujol): 1613s, 1587s, 1556m, 1538s, 1508m, 1323m, 1253s, 1200m, 1181s, 1171s, 1149m, 1134w, 987w, 969w, 942s, 895w, 843s, 792s, 754m. Found: C, 65.63; H, 6.46; N, 6.23.  $\text{C}_{25}\text{H}_{29}\text{N}_2\text{O}_3\text{V}$  requires C, 65.78; H, 6.40; N, 6.14 %.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 9.17 (s, 1H,  $\text{CH}=\text{N}$ ), 8.30 (d, 1H,  $J = 8.35$ ,  $\text{ArH}$ ), 7.93 (d, 1H,  $J = 7.60$ ,  $\text{ArH}$ ), 7.81 (d, 1H,  $J = 7.95$ ,  $\text{ArH}$ ), 7.68 (ABq, 2H,  $\Delta\nu_{\text{AB}} = 5.72$ ,  $J = 6.70$ ,  $\text{ArH}$ ), 7.60 (d, 1H,  $J = 8.35$ ,  $\text{ArH}$ ), 7.36 (d, 1H,  $J = 2.40$ ,  $\text{ArH}$ ), 3.82 (s, 3H,  $\text{Ar-Me}$ ), 1.50 (s, 9H, 'Bu), 1.36 (s, 9H, 'Bu).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 166.3, 165.7, 163.5, 144.2, 140.9, 140.8, 140.4, 138.9, 134.0, 128.2, 127.6, 127.4, 126.2, 120.8, 115.6, 35.5, 34.3, 31.3, 29.6, 27.5.  $^{51}\text{V}$  NMR ( $\text{CDCl}_3$ ): -535.93 ( $w_{1/2} = 535$ ).

*Synthesis of 2-((2-(1H-benzo[d]imidazol-2-yl)quinolin-8-ylimino)methyl)-4,6-di-tert-butyl-phenolate oxovanadium(IV) (3)*

$\text{L}^2\text{H}$  (0.8 g, 1.7 mmol) was dissolved in toluene (40 mL), and vanadyl tri-*n*-propoxide (0.41 mL, 1.8 mmol) was added *via* syringe and the solution refluxed for 16 h. The solution was allowed to cool to room temperature and the volatiles were removed *in vacuo*. Crystallization from hot acetonitrile gave yellow needles of the vanadium compound **3** (0.73 g, 79 % yield). MS (E.I.) 541  $[\text{M}]^+$ . IR (Nujol): 1600m, 1585w, 1529w, 1261m, 1094s, 1020s, 865w, 800s, 749w, 737w. Found: C, 68.68; H, 5.57; N, 10.19.  $\text{C}_{31}\text{H}_{31}\text{N}_4\text{O}_2\text{V}$  requires C, 68.75; H, 5.58; N, 10.34. EPR (toluene, 298K): giso = 1.99, Aiso = 90 G.

*Synthesis of 2-((2-(1H-benzo[d]imidazol-2-yl)quinolin-8-ylimino)methyl)-4,6-dimethyl-phenolate oxovanadium(IV) (4)*

$\text{L}^3\text{H}$  (0.17 g, 0.43 mmol) was dissolved in toluene (20 mL), and vanadyl tri-*n*-propoxide (0.11 mL, 0.44 mmol) was added *via* syringe and the solution refluxed for 16 h. The solution was allowed to cool to room temperature and the volatiles were removed *in vacuo*. Crystallization from either acetonitrile or dichloromethane gave yellow needles of the vanadium compound **4** (0.15 g, 76 % yield). MS (E.I.) 457  $[\text{M}]^+$ . IR: 1606m, 1587m, 1547m, 1516w, 1425w, 1374m, 1322w, 1301m, 1258s, 1218m, 1012s, 980s, 861m, 794s, 748s. Found: C, 41.8; H, 3.5; N, 6.8 %.  $\text{C}_{25}\text{H}_{18}\text{N}_4\text{O}_2\text{V}\cdot 4\frac{1}{2}\text{CH}_2\text{Cl}_2$  requires C, 41.9; H, 3.2; N, 6.6. EPR (solid, 298K): giso = 2.00

*Synthesis of 2-((2-(1H-benzo[d]imidazol-2-yl)quinolin-8-ylimino)methyl)-4-methyl,6-adamantyl-phenolate oxovanadium(IV) (5)*

$\text{L}^4\text{H}$  (0.10 g, 0.19 mmol) was dissolved in toluene (20 mL), and vanadyl tri-*n*-propoxide (0.05 mL, 0.21 mmol) was added *via* syringe and the solution refluxed for 16 h. The solution was allowed to cool to room temperature and the volatiles were removed *in vacuo*. Crystallization from hot acetonitrile or dichloromethane gave brown needles of the vanadium compound **5** (0.06 g, 55 % yield). MS (E.I.) 577.17  $[\text{M}]^+$ . IR: 1643w, 1610s, 1540s, 1445w, 1406m, 1338m, 1294s, 1226s, 1166m, 1093w, 1040m, 1018m, 957s, 839s, 767m, 709w, 676m. Found: C, 57.86; H, 4.47; N, 7.49 %.  $\text{C}_{34}\text{H}_{30}\text{N}_4\text{O}_2\text{V}\cdot 1\frac{1}{2}\text{CH}_2\text{Cl}_2$  requires C, 57.91; H, 4.26; N, 7.95 %. EPR (solid, 298K): giso = 1.98.

*Ethylene polymerization*

Ethylene polymerisation reactions were performed in a dried Schlenk glass flask (250 mL) equipped with a magnetic stirrer bar. The flask was evacuated and recharged 3 times with ethylene, and then 20 mL of dry, degassed toluene was added *via* a glass syringe. The solution was then stirred for 10 min to allow ethylene saturation, and the correct temperature was acquired using an oil bath. The co-catalyst and the reactivating agent ETA were added (0.1 mL, 0.72 mmol); 10ml toluene, which dissolved the complex, was also added. The polymerisation time was measured from pre-catalyst injection; the polymerisation was quenched by the injection of 5 mL of ethanol. The resulting polymer was transferred into a 500 mL beaker containing acidified ethanol, and the polyethylene was collected by filtration and dried at 50 °C under vacuum overnight.

*$\epsilon$ -Caprolactone procedure*

Typical polymerization procedures in the presence of one equivalent of benzyl alcohol (Table 3, run 1) were as follows. A toluene solution of **3** (0.025 mmol, 1.0 mL toluene) and BnOH (0.025 mmol) were added into a Schlenk tube in the glove-box at

room temperature. The solution was stirred for 2 min, and then  $\epsilon$ -caprolactone (2.5 mmol) along with 1.5 mL toluene was added to the solution. The reaction mixture was then placed into an oil bath pre-heated at 110 °C, and the solution was stirred for the prescribed time (24 h). The polymerization mixture was then quenched by addition of an excess of glacial acetic acid (0.2 mL) into the solution, and the resultant solution was then poured into methanol (200 mL). The resultant polymer was then collected on filter paper and was dried *in vacuo*.

#### Crystallography

Intensity data were collected on a Rigaku R-AXIS Rapid IP diffractometer (**1**), a Rigaku Saturn724+ with a rotating anode X-ray source (**2**), an Oxford Diffraction Xcalibur-3/Sapphire3-CCD (**2'**), or a Bruker SMART 1000 CCD diffractometer using narrow slice 0.3°  $\omega$ -scans (**3**). All data were measured with monochromated Mo-K $\alpha$  radiation. Structures were determined by the direct methods routines in SHELXS-97<sup>17</sup> or Superflip<sup>18</sup> and were refined by full-matrix least-squares methods on  $F^2$  in SHELXL-97 or SHELXL-2013.<sup>19</sup> Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions and their  $U_{\text{iso}}$  values were set

to ride on the  $U_{\text{eq}}$  values of the parent carbon atoms except for **2** where H atoms were freely refined.

Crystal data and refinement results for all samples are collated in Table 4. CCDC 998655-998658 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### Acknowledgements

We thank Sichuan Normal University for financial support. The EPSRC X-ray service at Southampton is thanked for the data collection for complex **2**.

**Supporting Information Available:** X-ray crystallographic files, in CIF format, from the structure determinations of compounds **1** – **3**. Stacking diagrams for complexes **2** and **3**, and CAMERON representation of **2'**. Selected spectra (<sup>1</sup>H, <sup>13</sup>C NMR and MALDI TOF of polymer samples).

**Table 4.** Crystallographic data for complexes **1**, **2**·**2**/3(MeCN), **2'** and **3**·MeCN.

Compound	<b>1</b>	<b>2</b>	<b>2'</b>	<b>3</b> ·MeCN
Formula	C <sub>25</sub> H <sub>29</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> V	C <sub>25</sub> H <sub>29</sub> N <sub>2</sub> O <sub>3</sub> V 0.67(C <sub>2</sub> H <sub>3</sub> N)	C <sub>25</sub> H <sub>29</sub> N <sub>2</sub> O <sub>3</sub> V	C <sub>31</sub> H <sub>30</sub> N <sub>4</sub> O <sub>2</sub> V C <sub>2</sub> H <sub>3</sub> N
Formula weight	511.34	483.81	456.44	582.58
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	8.9979(4)	26.127(17)	11.9806(4)	11.8130(4)
<i>b</i> (Å)	12.6300(6)	10.845(8)	10.2865(4)	14.8706(4)
<i>c</i> (Å)	13.0073(9)	26.44(2)	17.9031(12)	17.5707(7)
$\alpha$ (°)	61.214(4)	90	90	90
$\beta$ (°)	78.851(6)	91.646(12)	98.769(7)	103.120(3)
$\gamma$ (°)	70.715(5)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1221.78(12)	7489(9)	2180.56(18)	3006.01(18)
<i>Z</i>	2	12	4	4
Temperature (K)	100(2)	100(2)	100(2)	140(1)
Wavelength (Å)	0.71075	0.71073	0.71075	0.71073
Calculated density (g.cm <sup>-3</sup> )	1.390	1.287	1.390	1.287
Absorption coefficient (mm <sup>-1</sup> )	0.649	0.428	0.485	0.368
Transmission factors (min./max.)	0.872 and 1.000	0.931 and 0.996	0.718 and 1.000	0.981 and 1.022
Crystal size (mm)	0.10 × 0.40 × 0.01	0.17 × 0.05 × 0.01	0.10 × 0.40 × 0.01	0.15 × 0.14 × 0.02
$\theta$ (max) (°)	27.47	31.48	27.48	21.3
Reflections measured	16140	60185	15333	36680
Unique reflections	5555	22162	4999	3330
$R_{\text{int}}$	0.0385	0.0892	0.0353	0.154
Reflections with $F^2 > 2\sigma(F^2)$	5555	15014	4998	2217
Number of parameters	296	1265	287	371
$R_1 [F^2 > 2\sigma(F^2)]$	0.0389	0.1250	0.0535	0.056
$wR_2$ (all data)	0.0966	0.1893	0.1586	0.084
GOOF, <i>S</i>	1.062	1.194	1.075	1.017
Largest difference peak and hole (e Å <sup>-3</sup> )	0.718 and -0.488	0.508 and -0.839	0.567 and -1.175	0.26 and -0.25

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