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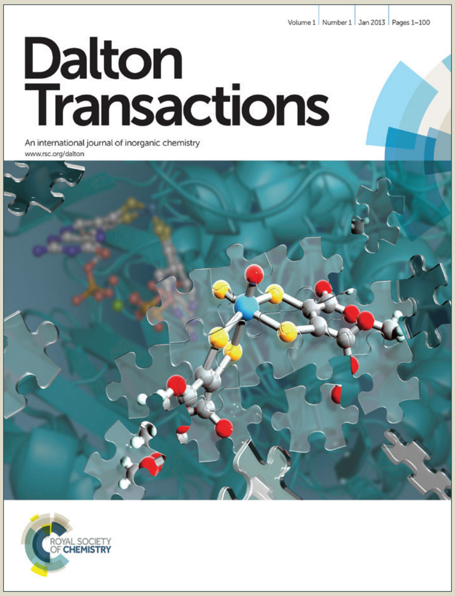

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ARTICLE TYPE

Vanadyl complexes bearing bi-dentate phenoxyimine ligands: Synthesis, structural studies and ethylene polymerization capability

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Reaction of $[VO(O\textit{n}Pr)_3]$ with the Schiff bases 3,5-(*t*Bu)2-2-OH-C_6H_2CH(N(x-OR-C_6H_4) (R = Me; x = 2, **L**^{1}H; x = 3, **L**^{2}H; x = 4, **L**^{3}H; R = Et (**L**^{4}H), CF_3 (**L**^{5}H), Ph (**L**^{6}H)) or 4-methyl-3-(R)-2-(OH)-C_6H_4C=N($2'$-($2''$-(OR_1)C_6H_4)C_6H_4) (R = adamantyl, R_1 = Ph (**L**^{7}H) or R = C(Me)$_2$Ph, R_1 = Ph (**L**^{8}H)) afforded the bis(chelate) vanadium(IV) complexes [VO(**L**^{n})$_2$] (n = 1 (**1**); n = 2 (**2**); n = 3 (**3**); n = 4 (**4**); n = 5 (**5**); n = 6 (**6**); n = 6, (**7**·1.5MeCN); n = 7, (**8**); n = 8, (**9**)); in the case of **L**^{6}H, the oxo-bridged vanadium(V) complexes [VO(μ-O)(**L**^{6})]$_2$ (**10**) was also isolated. By contrast, interaction of 4-methyl-3-(R)-2-(OH)-C_6H_4C=N($2'$-($2''$-(OR_1)C_6H_4)C_6H_4) (R = adamantyl, R_1 = Me (**L**^{9}H); R = *t*Bu, R_1 = Me (**L**^{10}H); R = C(Me)$_2$Ph, R_1 = Me (**L**^{11}H)) with $[VO(O\textit{n}Pr)_3]$ led to the isolation of the dinuclear complexes [VO(μ-OH)(μ-O*n*Pr)(**L**^{n})]$_2$ (n = 9, (**11**); 10, (**12**); 11, (**13**)), respectively. The molecular structures of **1** to **13** are reported. All complexes have been screened as pre-catalysts for the polymerization of ethylene in the presence of the co-catalyst diethylaluminium chloride (DEAC) with or without ethyltrichloroacetate (ETA) present at 1 or 10 bar of ethylene. Under high pressure, all pre-catalysts exhibited high activity and afforded high molecular weight (*M*w ≈ 200,000 to 675,000), linear polyethylene with activities (in the presence of ETA) in the range 4,960 – 16,400 g/mmol.h; at one bar, the products were generally of lower molecular weight. The use of methylaluminoxane (MAO) or modified MAO (MMAO) as co-catalyst led to trace or poor (≤ 110 g/mmol.h) activity, respectively.

1. Introduction

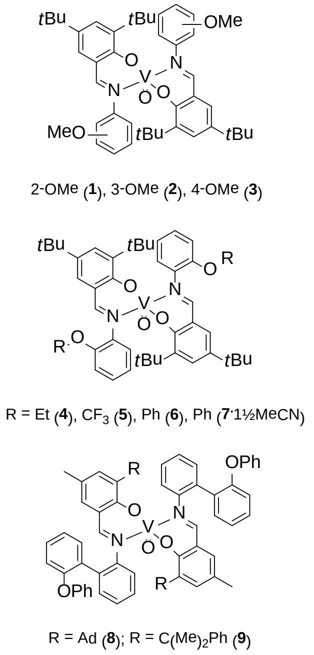
In recent years, there has been considerable interest in the use of vanadium-based pre-catalysts for olefin polymerization catalysis, in both academic [1] and industrial circles. [2] This interest stems from encouraging catalytic activities and thermal stability observed for a number of vanadium systems, as well as their ability to perform desirable co- and ter-polymerizations. [3] As in other catalyst systems, the ancillary ligands present at the metal play a pivotal role in controlling the behaviour of the polymerization process. Indeed, in the case of the phenoxyimine ligand set, Fujita has noted that a bulky imine-bound group and that at the *ortho* position of the phenoxide are a prerequisite for forming cis oriented halide ligands (in group IV systems). Furthermore, the use of a bulky group at the *ortho* position of the phenoxide enhances catalytic activity; bulky imine-bound substituents generally favour high molecular weight products. [4] With this in mind, we note that imine-based ligands have been shown to impart stability at vanadium, [5] and we [6] and others [4] have investigated the use of phenoxyimine-based ligand sets in combination with vanadium centres. The use of tridentate ligands sets has proved particularly fruitful with group IV metals, as highlighted by the work of Tang *et al*, [7] and the Mitsui group, [8] whilst the Li group have also done some work with group V (vanadium). [9] More recently, McGuinness *et al* extended the Mitsui work on titanium to include a number of related donor functionalized ligands. [10] Encouraged by these findings, we have prepared a series of bi-dentate ligands bearing additional functionality and the vanadium complexes thereof (see schemes 1 and 2). 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) activities in the range 2,990 – 7,700 at 1 bar and 3,000 – 12,000 g/mmol.h at 10 bar ethylene were achievable over a 20 or 30 minute period, respectively. [11] The polymer products were mostly linear polyethylene, with higher molecular weights favoured at higher ethylene pressure. Use of other co-catalysts such as MAO or MMAO led to no or poor activity.

2. Results and Discussion

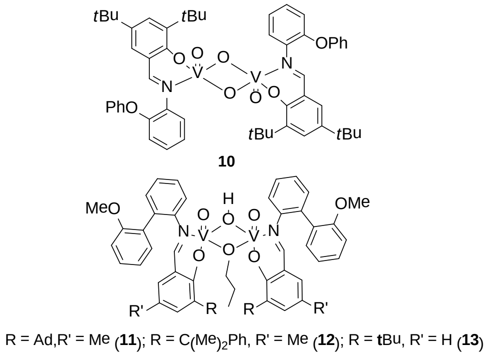
Mononuclear complexes

Reaction of the vanadyl complex $[VO(O\textit{n}Pr)_3]$ with the Schiff bases 3,5-(*t*Bu)$_2$-2-OH-C_6H_2CH(N(x-OR-C_6H_4) (R = Me; x = 2, **L**^{1}H; x = 3, **L**^{2}H; x = 4, **L**^{3}H; R = Et (**L**^{4}H), CF_3 (**L**^{5}H), Ph (**L**^{6}H)) or 4-methyl,3-(R)-2-(OH)-C_6H_4C=N($2'$-($2''$-(OR^1)C_6H_4)C_6H_4) (R = adamantyl, R^1 = Ph (**L**^{7}H) or R = C(Me)$_2$Ph, R^1 = Ph (**L**^{8}H)) in refluxing toluene afforded, following work-up, dark crystals of the respective bis(chelate) vanadium(IV) complexes [VO(**L**^{n})$_2$] (n = 1 (**1**); n = 2 (**2**); n = 3 (**3**); n = 4 (**4**); n = 5 (**5**); n = 6 (**6**); n = 6, (**7**·1.5MeCN); n = 7, (**8**); n = 8, (**9**)) in isolated yields of 26 to 75 % (see experimental and Scheme 1). During the reaction, the vanadium centre is reduced from V(V) to V(IV), as observed previously. [5b] Oxidation reactions (of alcohols) catalyzed by vanadyl complexes are well established, including those bearing additional alkoxide ligands. [12] A proposed mechanism has been reported by Velusamy and Punniyamurthy [13], and we envisaged that the propanol formed herein on addition of the phenoxyimine ligands is subject to a related oxidation process with the concomitant reduction of the vanadium centre.

These vanadium(IV) complexes were characterized by X-band EPR measurements at 150 K and 298 K and, as expected, each gave an 8 line spectrum characteristic of V(IV) (d^1, I = $^7/_2$) – see Table 1 (and ESI, Figures S2 and S3 for representative spectra). Anisotropic parameters were collected from frozen toluene solutions, and analysis was performed using simulations using EasySpin. [14] Values for $g_{\parallel}$ and $g_{\perp}$ compare favourably with previously reported vanadyl(IV) systems, [15] and particularly with those adopting a $VO[N_2O_2]$ coordination environment. [6b, 16]



Scheme 1. Mono-vanadium complexes screened in this study



Scheme 2. Oxo-bridged di-vanadium complexes screened in this study

Crystals of **1** – **9** suitable for single crystal X-ray diffraction studies were grown from saturated acetonitrile solutions on prolonged standing (1 - 2 days) at ambient temperature. The molecular structures of **1** , **3** and **5** (for others see ESI) are presented in Figure 1, and selected bond lengths and angles are given in Table 2; crystallographic data are collated in Table 7.

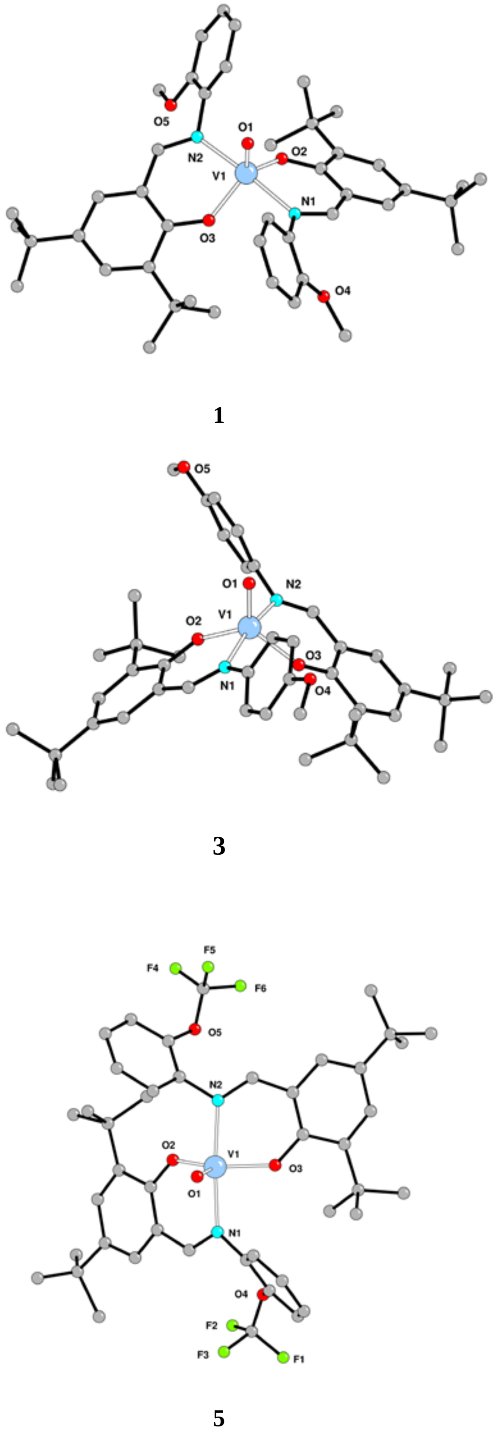


Figure 1: CAMERON representations of the structures of **1**, **3** and **5** (for **2**, **4**, **6** - **9**, see the ESI). Hydrogen atoms and molecules of acetonitrile have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (º) for complexes **1** – **9**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
V(1)-O(1)	1.596(3)	1.597(2)	1.596(2)	1.603(3)	1.605(4)	1.596(2)	1.596(2)	1.593(2)	1.595(2)
V(1)-O(2)	1.915(3)	1.905(2)	1.9165(19)	1.925(3)	1.904(4)	1.907(2)	1.916(2)	1.911(2)	1.912(2)
V(1)-O(3)	1.904(3)	1.905(2)	1.9109(19)	1.908(3)	1.913(4)	1.897(2)	1.903(2)	1.903(2)	1.915(2)
V(1)-N(1)	2.129(3)	2.118(3)	2.126(2)	2.139(3)	2.134(5)	2.134(2)	2.121(3)	2.113(2)	2.093(3)
V(1)-N(2)	2.135(4)	2.126(3)	2.119(2)	2.138(3)	2.125(5)	2.126(2)	2.122(3)	2.113(2)	2.113(3)
O(1)-V(1)-O(3)	118.06(16)	118.77(11)	115.50(10)	117.76(15)	118.20(19)	120.01(11)	116.48(12)	125.65(11)	123.94(12)
O(1)-V(1)-O(2)	118.87(16)	119.60(10)	120.63(9)	119.99(14)	114.7(2)	116.39(11)	121.00(12)	122.19(11)	123.33(12)
O(3)-V(1)-O(2)	123.06(13)	121.64(10)	123.87(9)	122.24(13)	127.08(17)	123.58(9)	122.49(11)	112.15(10)	112.73(10)
O(1)-V(1)-N(1)	92.77(15)	95.17(10)	95.74(9)	93.90(14)	92.5(2)	93.31(10)	95.51(11)	95.34(10)	92.93(11)
O(3)-V(1)-N(1)	88.99(13)	87.50(9)	88.28(8)	89.31(12)	87.77(18)	87.90(9)	89.75(10)	86.07(9)	89.74(10)
O(2)-V(1)-N(1)	87.75(13)	87.66(9)	86.54(9)	87.03(12)	88.27(18)	87.65(9)	86.91(10)	87.07(9)	86.76(10)
O(1)-V(1)-N(2)	93.59(16)	93.78(10)	96.22(9)	93.58(14)	96.4(2)	94.01(10)	93.06(12)	95.16(10)	92.14(11)
O(3)-V(1)-N(2)	88.53(13)	87.02(9)	88.61(8)	87.58(12)	86.87(17)	86.73(9)	87.38(11)	87.79(9)	86.90(10)
O(2)-V(1)-N(2)	88.66(13)	89.09(9)	85.43(9)	88.87(12)	89.19(17)	90.86(9)	87.77(10)	87.37(9)	90.98(10)
N(1)-V(1)-N(2)	173.60(14)	170.94(9)	167.82(9)	172.50(13)	170.99(18)	172.41(9)	171.37(12)	169.50(9)	174.89(10)

All complexes **1** – **9** adopted distorted trigonal bipyramidal geometry at the metal centre with the N atoms axial and the O atoms equatorial, the latter being approximately co-planar. The distortion is best illustrated by the variation of the N(1) – V(1) – N(2) angles [167.82(9) – 174.89(10) º] from linearity. The vanadyl bond lengths are all similar and are in the range 1.593(2) – 1.605(4) Å, which are typical. [6, 17]

The other geometrical parameters associated with **1** - **9** are similar (see Table 2), particularly the bond lengths, though there is some variation of the angle between the vanadyl and the chelate [115.50(10) – 125.54(11) Å]; the larger angles being associated with those complexes (**8** and **9**) containing the bulky adamantyl and CMe_2Ph substituents. The bite angle of the chelating ligand falls in the range 86.54(9) - 88.61(8) º. Complexes **1** – **9** all possess non-crystallographic C_2 symmetry with the 2-fold axis parallel to the V=O bond.

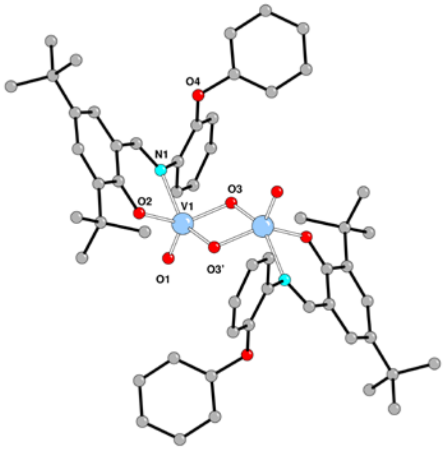
Table 1. EPR data for complexes **1** to **13**.

Complex	g_{iso}	A_{iso}	$g_{\perp}$	$A_{\perp}$	$g_{\parallel}$	$A_{\parallel}$
1	1.99485	97.76	2.00577	61.60	1.88861	176.83
2	1.99504	96.00	2.00649	60.62	1.97776	178.73
3	1.99643	97.56	2.00806	61.13	1.97845	178.35
4	1.99452	94.83	2.00701	61.46	1.97955	178.01
5	1.99442	95.22	2.00513	59.78	1.97867	176.67
6	1.99552	97.18	2.00553	61.13	1.97617	181.37
8	1.99286	89.74	2.00158	63.98	1.96095	168.27
9	1.98756	89.74	2.00083	64.82	1.95741	173.98
11	1.99047	96.49	2.00120	66.34	1.96314	171.29
12	1.98748	92.09	2.00734	63.27	1.96528	171.30
13	2.05984	105.46	2.02799	62.48	2.00238	110.50

Conditions: g_{iso} and A_{iso} were recorded at 298 K in toluene using X-band; $g_{\perp}$, $A_{\perp}$, $g_{\parallel}$ and $A_{\parallel}$ were recorded at 120 K in toluene using X-band.

Dinuclear complexes

In the case of the ligands $\mathbf{L^6}$H, changing the ratio of metal to ligand led to the isolation of the dark red oxo-bridged centrosymmetric vanadyl(V) complex [VO(μ-O)(μ-O*n*Pr)($\mathbf{L^6}$)]$_2$ (**10**). Contrastingly, use of the ligands 4-methyl,3-(R)-2-(OH)-C_6H_4C=N(2$^{/}$-(2$^{//}$-(OR^1)C_6H_4)C_6H_4) (R = adamantyl, R^1 = Me ($\mathbf{L^9}$H); R = *t*Bu, R^1 = Me ($\mathbf{L^{10}}$H); R = C(Me)$_2$Ph, R^1 = Me ($\mathbf{L^{11}}$H)) with [VO(O*n*Pr)$_3$] led to the isolation of the dinuclear hydroxyl/*n*-propoxide-bridged complexes [VO(μ-OH)(μ-O*n*Pr)(L^n)]$_2$ (n = 9, (**11**); 10, (**12**); 11, (**13**)). The IR spectra contain a strong band at 982 (**10**), 991 (**11**), 991 (**12**) and 993 (**13**) cm^{-1} assigned to the *v*(V=O) group, and for **11** - **13**, a broader band assigned to *v*(OH) at 3611 (**11**) 3617 (**12**), and 3620 (**13**) cm^{-1}. The crystal structure of **10** is shown in Figure 2, with selected bond lengths and angles given in table 3; crystallographic data are presented in table 5. Complex **10** is a centrosymmetric molecule, in which each vanadium centre adopts a distorted square pyramidal geometry; the centres are linked via oxo bridges. The source of the oxo bridges is most likely adventitious hydrolysis. The angle subtended at each bridging oxygen is 96.75(4) º, with V(1) – O(3) at 1.8247(9) Å. The chelating rings form a six-membered ring adopting an envelope conformation with the V atom as the tip of the flap and with a bite angle of 82.30(4) º, which is somewhat smaller than those observed in the bis(chelate) complexes **1** - **9**. Crystal structures of **11** - **13** are shown in Figure 3, with selected bond lengths and angles given in Table 4; crystallographic data are presented in Table 5. Complexes **11** - **13** lie on a pseudo 2- fold symmetry axis

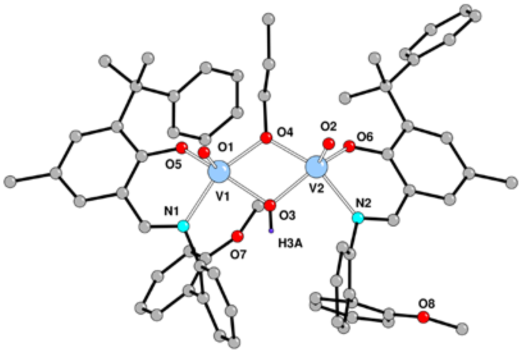


10

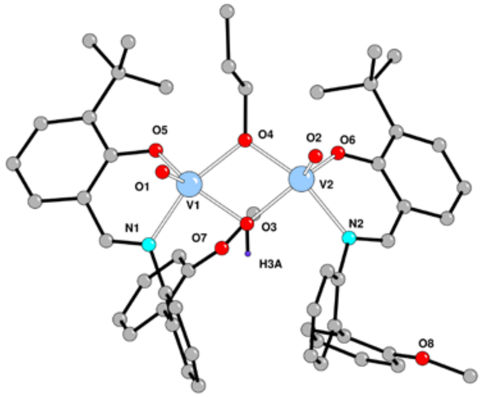
Figure 2. CAMERON representation of the dinuclear μ-oxo complex **10** showing the atom numbering scheme. Hydrogen atoms and solvent (MeCN) molecules have been omitted for clarity.

Table 3. Selected lengths (Å) and angles (º) for complexes **10**.

	10
V(1)-O(1)	1.5952(10)
V(1)-O(3')	1.8084(10)
V(1)-O(3)	1.8247(9)
V(1)-O(2)	1.8334(9)
V(1)-N(1)	2.1371(11)
V(1)···V(1')	2.7157(4)
O(1)-V(1)-O(3')	107.30(5)
O(1)-V(1)-O(3)	109.76(5)
O(3')-V(1)-O(3)	83.25(4)
O(1)-V(1)-O(2)	107.13(5)
O(3')-V(1)-O(2)	95.93(4)
O(3)-V(1)-O(2)	141.55(5)
O(1)-V(1)-N(1)	99.71(5)
O(3')-V(1)-N(1)	152.13(5)
O(3)-V(1)-N(1)	81.27(4)
O(2)-V(1)-N(1)	82.30(4)
O(1)-V(1)-V(1')	115.16(4)
O(3')-V(1)-V(1')	41.86(3)
O(3)-V(1)-V(1')	41.40(3)
O(2)-V(1)-V(1')	126.52(3)
N(1)-V(1)-V(1')	119.12(3)



12



13

Figure 3. CAMERON representation of the dinuclear complexes **12** and **13**, showing the atom numbering scheme (for **11**, see ESI). Hydrogen atoms, except OH, and solvent (MeCN) molecules have been omitted for clarity.

which runs through O(3), H(3) and O(4) and the attached *n*-propyl group (there is no disorder). The geometry at each vanadium is best described as distorted squared-based pyramidal, and the centres are linked via slightly asymmetric OH/O*n*-Pr bridging. The difference in the bridging ligands is best highlighted by the angles subtended at each respective oxygen, *viz* V(1) - O(3) - V(2) 107.5(2) (**11**), 105.08(15) (**12**), 105.77(7) (**13**) *cf* V(1) - O(4) - V(2) 105.8(2) (**11**), 103.75(15) (**12**), 104.41(7) (**13**) º. The chelate ligand forms a bite angle of 88.3(2)/86.8(2) (**11**), 87.32(15)/86.58(15) (**12**) and 86.40(7)/86.55(7) (**13**) º. This type of OH/OR bridging has been observed previously in our studies of chelating aryloxides, [5b], whilst Cornman *et al*., and Chaudhuri *et al*. have also reported (μ-OR)$_2$ and (μ-OH)$_2$ bridged vanadyl complexes. [18]

Polymerization studies

1 bar studies

Firstly, complex **9** was screened to ascertain the optimum polymerization conditions for the polymerization of ethylene at 1 bar; the results are collated in table S1 (ESI). Diethylaluminium chloride (DEAC) was used as co-catalyst and ethyltrichloroacetate (ETA) as re-activator. The polymerization screening indicated that the best conditions were 16,000 equivalents of DEAC to vanadium. The activity of complex **9** increased with temperature and peaked at 80 °C, however the polymer molecular weight dropped by an order of magnitude above 30 °C (~ 135,600 at 20 °C, table S1 run 4 *versus* ~ 15,800 g/mol at 30 °C, table S1 run 7).

Table 4. Selected bond lengths (Å) and angles (º) for complexes **11**, **12** and **13**.

	11	**12**	**13**
V(1)-O(1)	1.600(6)	1.595(4)	1.5841(17)
V(1)-O(5)	1.936(5)	1.956(3)	1.9267(17)
V(1)-O(3)	1.964(5)	1.985(3)	1.9717(16)
V(1)-O(4)	1.996(5)	1.970(3)	1.9751(16)
V(1)-N(1)	2.077(6)	2.087(4)	2.0803(18)
V(2)-O(2)	1.599(6)	1.593(4)	1.5909(16)
V(2)-O(6)	1.947(5)	1.924(3)	1.8977(17)
V(2)-O(3)	1.974(5)	1.950(4)	1.9479(16)
V(2)-O(4)	1.986(6)	2.001(3)	1.9803(16)
V(2)-N(2)	2.086(7)	2.105(4)	2.0943(19)
O(1)-V(1)-O(5)	109.1(3)	105.90(16)	107.44(8)
O(1)-V(1)-O(3)	111.3(3)	107.36(16)	108.54(8)
O(5)-V(1)-O(3)	139.3(2)	146.46(15)	143.72(7)
O(1)-V(1)-O(4)	106.8(3)	108.47(18)	108.48(8)
O(5)-V(1)-O(4)	91.2(2)	91.36(14)	89.99(7)
O(3)-V(1)-O(4)	72.7(2)	74.17(14)	74.41(7)
O(1)-V(1)-N(1)	101.3(3)	101.45(18)	98.89(8)
O(5)-V(1)-N(1)	88.3(2)	87.32(15)	86.40(7)
O(3)-V(1)-N(1)	88.6(2)	90.28(15)	92.56(7)
O(4)-V(1)-N(1)	150.4(2)	149.20(15)	152.19(7)
O(2)-V(2)-O(6)	108.1(3)	111.05(18)	113.14(8)
O(2)-V(2)-O(3)	109.6(3)	111.39(17)	115.96(8)
O(6)-V(2)-O(3)	142.1(2)	137.40(15)	130.65(7)
O(2)-V(2)-O(4)	108.4(3)	107.73(16)	104.33(8)
O(6)-V(2)-O(4)	91.6(2)	89.69(14)	88.88(7)
O(3)-V(2)-O(4)	72.7(2)	74.22(14)	74.82(7)
O(2)-V(2)-N(2)	99.1(3)	100.32(17)	100.36(8)
O(6)-V(2)-N(2)	86.8(2)	86.58(15)	86.55(7)
O(3)-V(2)-N(2)	91.2(2)	89.41(15)	89.27(7)
O(4)-V(2)-N(2)	151.5(2)	151.11(15)	154.68(7)
V(1)-O(3)-V(2)	107.5(2)	105.08(15)	105.77(7)

The catalyst system was short-lived with the activity dropping to below 50 % after 60 minutes. Complexes **1-13** (not **7**) and the benchmark pre-catalyst **14** [VO(FI)$_2$] (FI = 2-O-C_6H_4CH=NC_6H_5) [2a] were screened using the optimum conditions for activity determined by the screening of complex **9**, *ie* 16,000 equivalents DEAC, 0.1 mL ETA, 80 °C; the results are presented in table 5. Given that **6** and **7** differ only in the degree of solvation, complex **7** was not screened. All of the complexes were found to be highly active for the polymerization of ethylene. The polymer molecular weights (M_w) were in the range 2,400 – 11,700 with PDI values of between 2.6 and 5.6. In the series of OMe substituted complexes (**1**, *o*-OMe, **2**, *m*-OMe, **3**, *p*-OMe), the *ortho* derivative gave the highest activity (table 5, runs 1-3), and also possessed the smallest PDI (3.0). Replacement of the *o*-OMe group by the more electron withdrawing *o*-OCF_3 group led to a reduction in activity (table 5, run 1 *versus* run 5) indicating an electronic influence on the observed catalytic activity. The order of activity for catalysts bearing *o*-OR groups is OMe > OPh > OEt > OCF_3. The best activities were found with systems using complexes **8** and **9** for which activities were 7,700 and 7,170 g/mmol.h, respectively over a 20 minute period. Compound **8** achieved slightly higher conversion than complex **9** (table 5, run 8 *vs.* 9), where the *ortho* substituent on the phenolate has been changed from an adamantyl to a -CMe_2Ph group. In the OH/O*n*Pr bridged di-vanadium compounds (**11** – **13**) the size of the *ortho* phenolate substituent (**11**, Ad; **12**, CMe_2Ph; **13**, *t*Bu) led to only small changes in the observed catalytic activity. The benchmark catalyst **14** (run 13) afforded an activity of 3,850 g/mmol.h under the conditions employed here.

10 bar studies

Complex **10** was used to obtain the optimum conditions for the polymerization of ethylene at 10 bar and the results are presented in Table S2 (ESI). Complex **10** was found to be active for the polymerization of ethylene using diethylaluminium chloride (DEAC) as co-catalyst, with or without ethyltrichloroacetate (ETA) present as re-activator. As expected, best results were obtained in the presence of ETA (see runs 1 – 7 *versus* 8 – 17 in Table S2) as noted for other vanadium-based systems. [11] From the catalytic observations, it was determined that the best conditions for conducting further screening were again the use of 16,000 equivalents of DEAC, however the operating temperature required at 10 bar was 20 °C rather than 80 °C (as used at 1 bar). In the absence of ETA, and using an Al:V ratio of 1000:1, the activity peaked at 20 ^{o}C; the use of either MAO or MMAO as co-catalyst led to negligible or poor (≤ 110 g/mmol.h) activity, respectively. Interestingly, in the absence of ETA, higher molecular weight polyethylene was obtained (~790,000 *versus* ~430,000 g/mol, table S2 runs 4 and 8). The activity of the system was rather short-lived dropping by more than 50 % over 30 min.

Molecular weights in the range of ~200,000 to ~670,000 can be obtained on addition of ETA, PDI values were in the range 2.4 – 3.9 (2.0 - 8.6 in the absence of ETA) and the melting points of the polymers were *ca.* 134-136 °C, consistent with the formation of linear polyethylene. Using the optimum conditions determined for pre-catalyst **10**, the complexes **1 – 13** (not **7**) and the benchmark pre-catalyst **14** [VO(FI)$_2$] (FI = 2-O-C_6H_4CH=NC_6H_5) [2a] were also screened for their ability to polymerize ethylene (see Table 6). Pre-catalysts **1-13** were found to be highly active, and similarly to the 1 bar screening, the best activities were again achieved by the pre-catalysts **8** and **9** (11,790 and 10,060, table 6, runs 7 and 8), which bear the bulky adamantyl and CMe_2Ph substituents. Unexpectedly, the benchmark catalyst **14** afforded a lower activity (~ 200 g/mmol.h) under these conditions.

Within the mini-series of *o*, *m* or *p*- OMe-containing pre-catalysts, that bearing an *ortho* OMe group performed best, whilst replacing the Me group with a more electron withdrawing group (CF_3) led to lower activities. Comparison of 1 bar and 10 bar ethylene screening shows that although approximately the same order of magnitude activity can be achieved using lower pressure, use of higher pressure leads to a pronounced increase in polymer molecular weight. However, it should be noted that at 10 bar, the nature of the polymer being formed hampered stirring, and so it is likely that the actual catalytic activities at 10 bar are somewhat

Table 5. Catalysis runs using pre-catalysts **1** to **14** (not **7**) under optimized conditions at 1 bar.[a]

Run	Complex	PE (g)	Activity (g/mmol.h)	M_w /10^4	M_n /10^4	PDI	T_m (℃)
1	**1**	1.134	6800	0.45	0.15	3.00	124.9
2	**2**	0.868	5210	0.99	0.20	4.95	127.2
3	**3**	0.956	5740	0.84	0.20	4.20	126.7
4	**4**	0.871	5230	0.34	0.11	3.09	123.8
5	**5**	0.801	4810	0.58	0.16	3.63	125.7
6	**6**	1.006	6030	1.17	0.21	5.57	128.0
7	**8**	1.284	7700	0.71	0.18	3.94	126.3
8	**9**	1.195	7170	0.36	0.13	2.77	124.2
9	**10**	0.640	3840	0.78	0.18	4.33	126.2
10	**11**	0.498	2990	0.51	0.13	3.92	125.2
11	**12**	0.551	3300	0.24	0.09	2.67	122.6
12	**13**	0.608	3650	0.50	0.14	3.57	124.9
13	**14**	0.642	3850	0.58	0.16	3.63	126.6

[a] Conditions: 0.5 μmol of [V] per run, 30 mL of toluene, 80 °C, 16,000 equivalents of Et_2AlCl, 0.1 mL of ETA, 20 min, 1 bar of ethylene. GPC analysis was conducted in 1,2,4-trichlorobenzene.

higher; mass transport problems have been noted in other vanadium-based ethylene polymerization systems. [19a] At both pressures, polyethylene melting points at high temperatures are lower (≤ 128 °C), and this is thought to be due to the lower molecular weight of the products rather than branching; for representative ^{13}C NMR spectra of the polymers see ESI. We have previously conducted EPR studies on the interaction of a vanadyl phenoxyimine with AlR_3 and AlR_2Cl (R = Me, Et), with and without ETA present. [20] In the case of the most active systems (using $AlMe_2Cl$), a species of the form $[L^{/}V^{IV}(O)(Me)(AlMe_2Cl)]$ ($L^{/}$ = modified initial phenoxyimine ligand) was invoked. However, such V^{IV} species wee in the minority and most of the vanadium was present as EPR silent V(III) species. Monitoring the concentrations of V(IV) and V(III) species indicated that the V(IV) species were active rather than the V(III) species. These mono(phenoxyimine) species were thought to have lost a phenoxyimine ligand via transfer to the alkylaluminium co-catalysts in much the same way as previously reported for the group IV systems. [4]

The catalytic results observed for the systems herein are on a par with those observed (~ 1,000 – 7,000 g/mol.h.bar) for the vanadyl complexes bearing phenoxyimine ligands derived from the *C*-capped ligand set {3-[2,2$^{/}$-methylenebis(4,6-di-*tert*-butylphenol)-5-*tert*-butylsalicylidene-R-imine]} (R = Ph, *p*-tolyl, 2,4,6-$Me_3C_6H_2$). [6a] However, when compared to the majority of other vanadium systems bearing chelating phenoxide type ligation, screened in the presence of DEAC/ETA, the activities observed herein are somewhat low. [19] We note that the activity can drop by two orders of magnitude by simply changing the geometrical parameters of the ligands associated with the metal centre, such as in the tripodal system $\{VO([N(CH_2C_6H_4O\text{-}2)_3]\}$ (*ca*. 100,000 g/mmol.h.bar) *versus* $\{VO(L)[N(C_6H_4O\text{-}2)_3]\}$ (L = MeCN, *n*PrOH, *p*-tolylNH_2; *ca*. 1000 g/mmol.h.bar), and access to the metal centre can be impaired. [19b] A number of the ligands employed herein are certainly bulky enough to impede access to the vanadium centre, which might also account for the reduced catalytic activity.

Conclusions

In conclusion, we have used a number of bi-dentate Schiff base ligands **L** bearing a variety of substituents to form new bis(chelate) complexes of vanadyl(IV), namely $[VO(\mathbf{L})_2]$ via the precursor $[VO(O\textit{n}Pr)_3]$. All these bis(chelate) complexes possessed non-crystallographic C_2 symmetry with the 2-fold axis parallel to the V=O bond. During the course of these studies, a number of dinuclear dioxo or OH/O*n*-Pr bridged complexes were also structurally characterized. Although the vanadyl complexes isolated herein did not attain the very high activities noted for a number of chelating phenoxide vanadium systems for the polymerization of ethylene, they are on a par with other reported vanadium systems bearing phenoxyimine ligation. Best activities herein were observed when the procedure was conducted in the presence of diethylaluminium chloride (DEAC) and ethyltrichloroacetate (ETA). In particular, ligands featuring a bulky substituent *ortho* to the hydroxyl moiety led to more active pre-catalysts (complexes **8** and **9**), whilst increasing the ethylene pressure led to an increase in polymer molecular weight.

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, whilst 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; ^1H 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 Advance DPX-300 spectrometer at 300 MHz. The ^1H 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.

Table 6. Polymerization screening of pre-catalysts **1** to **14**.[a]

Run	Complex	PE(g)	Activity (g/mmol.h)	M_w /10^4	M_n /10^4	PDI	T_m(°C)
1	**1**	2.662	7990	22.61	7.26	3.12	135.4
2	**2**	1.283	3850	20.14	4.76	4.23	135.4
3	**3**	1.633	4900	22.66	2.81	8.08	134.8
4	**4**	1.811	5430	44.86	16.15	2.78	135.0
5	**5**	1.486	4460	50.41	22.06	2.29	134.9
6	**6**	1.580	4740	54.46	20.41	2.67	136.1
7	**8**	3.930	11790	35.61	11.71	3.04	135.8
8	**9**	3.353	10060	32.78	8.89	3.69	135.9
9	**10**	4.421	8840	31.08	10.93	2.84	135.9
10	**11**	1.979	5940	21.54	8.43	2.56	135.9
11	**12**	2.289	6870	53.21	17.95	2.96	135.4
12	**13**	3.023	9070	28.48	10.35	2.75	135.1
13	**14**	0.078	230	118.20	15.49	7.63	135.1

[a] Conditions: 1 μmol of [V] per run, 100 mL of toluene, 20 °C, 16,000 equivalents of Et_2AlCl, 0.1 mL of ETA, 20 min, 10 bar of ethylene.

GPC analysis was conducted in 1,2,4-trichlorobenzene

Molecular weights (M_w) and molecular weight distribution of polyethylenes were determined by a PL-GPC220 at 150 °C using 1,2,4-trichlorobenzene as solvent. The ligands **L$^{1-13}$H** were prepared using standard condensation chemistry as described in the literature. [21] The vanadium precursor was purchased from Sigma Aldrich and used as received (and stored under argon).

Preparation of [VO(**L^1**)$_2$] (**1**)

A toluene solution (20 mL) of **L**^{1}H (0.42 g, 1.2 mmol) and vanadium oxytripropoxide (0.15mL, 0.68 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, green needles of **1** formed in an isolated yield of 0.20 g, 44 %. MS (MALDI-TOF) 743.3 [M]$^+$. Anal Found: C, 70.84; H, 7.65; N, 3.62 %. $C_{44}H_{56}N_2O_5V$ requires C, 71.04; H, 7.59; N, 3.77 %. IR (cm^{-1}): 2956m, 2905w, 1609s, 1535w, 1492m, 1460w, 1391w, 1253s, 1167m, 1087s, 1019s, 963.6m, 875w, 840m, 795s, 752s, 732s, 694m. EPR (toluene, 298 K): g_{iso}= 1.99485, A_{iso}= 97.76 G; (toluene, 120 K): $g_{\perp}$= 2.00577, $A_{\perp}$= 61.60 G, $g_{|}$ = 1.88861, $A_{|}$ = 176.83 G.

Preparation of [VO(**L^2**)$_2$] (**2**)

A toluene solution (20 mL) of **L**^{2}H (0.40 g, 1.2 mmol) and vanadium oxytripropoxide (0.16 mL, 0.71 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, brown needles of **2** formed in an isolated yield of 0.33 g, 37 %. MS (MALDI-TOF) 743.3 [M]$^+$. Anal Found: C, 70.49; H, 7.74; N, 3.63 %. $C_{44}H_{56}N_2O_5V$ requires C, 71.04; H, 7.59; N, 3.77 %. IR (cm^{-1}): 2951m, 2906w, 2862w, 1609s, 1586s, 1538s, 1483s, 1457m, 1433s,1388s, 1361m, 1307m, 1254s, 1206w, 1175s, 1142s, 1090w, 1046m, 966s, 889w, 869w, 844s, 779s, 751m, 694s. EPR (toluene, 298 K): g_{iso}= 1.99504, A_{iso}= 96.00 G; (toluene, 120 K): $g_{\perp}$= 2.00649, $A_{\perp}$= 60.62 G, $g_{|}$ = 1.97776, $A_{|}$ = 178.73 G.

Preparation of [VO(**L^3**)$_2$] (**3**)

A toluene solution (20 mL) of **L**^{3}H (0.40 g, 1.2 mmol) and vanadium oxytripropoxide (0.16 mL, 0.71 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, dark red needles of **3** formed in an isolated yield of 0.18 g, 40 %. MS (MALDI-TOF) 743.2 [M]$^+$. Anal Found: C, 70.73; H, 7.74; N, 3.66 %. $C_{44}H_{56}N_2O_5V$ requires C, 71.04; H, 7.59; N, 3.77 %. IR (cm^{-1}): 2956m, 2905w, 1612s, 1502,s 1431w, 1387w, 1252s, 1169m, 1087s, 1017s, 970s, 874w, 790s, 751m, 687m. EPR (toluene, 298 K): g_{iso}= 1.99643, A_{iso}= 97.56 G; (toluene, 120 K): $g_{\perp}$= 2.00806, $A_{\perp}$= 61.13 G, $g_{|}$ = 1.97845, $A_{|}$ = 178.35 G.

Preparation of [VO(**L^4**)$_2$] (**4**)

A toluene solution (20 mL) of **L**^{4}H (0.40 g, 0.85 mmol) and vanadium oxytripropoxide (0.12 mL, 0.51 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, brown needles of **4** formed in an isolated yield of 0.17 g, 50 %. Anal Found: C, 71.50; H, 7.76; N, 3.53 %. $C_{46}H_{60}N_2O_5V$ requires C, 71.57; H, 7.83; N, 3.63 %. MS (MALDI-TOF) 771.3 [M]$^+$. IR (cm^{-1}): 2949m, 2362m, 2161m, 2027m, 1608s, 1536s, 1486s, 1432w, 1389s, 1359s, 1302w, 1248s, 1170s, 1118m, 968s, 928m, 874w, 839s, 745s. EPR (toluene, 298 K): g_{iso}= 1.99452, A_{iso}= 94.83 G; (toluene, 120 K): $g_{\perp}$= 2.00701, $A_{\perp}$= 61.46 G, $g_{|}$ = 1.97955, $A_{|}$ = 178.01 G.

Preparation of [VO(**L^5**)$_2$] (**5**)

A toluene solution (20 mL) of **L**^{5}H (0.10 g, 0.27 mmol) and vanadium oxytripropoxide (0.04 mL, 0.16 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, dark red needles of **5** formed isolated yield 0.03 g, 26 %. Anal Found: C, 62.21; H, 6.04; N, 3.89 %. $C_{44}H_{50}F_6N_2O_5V$ requires C, 62.04; H, 5.92; N, 3.29 %. IR (cm^{-1}): 2954m, 1611s, 1593s, 1540m, 1488m, 1458w, 1434w, 1392m, 1361m, 1248s, 1206s, 1158s, 1109s, 1045w, 968s, 927m, 876m, 839s, 756s, 686w. EPR (toluene, 298 K): g_{iso}= 1.99442, A_{iso}= 95.22 G; (toluene, 120 K): $g_{\perp}$= 2.00513, $A_{\perp}$= 59.78 G, $g_{|}$ = 1.97867, $A_{|}$ = 176.67 G.

Preparation of [VO(**L^6**)$_2$] (**6**)

A toluene solution (30 mL) of **L**^{6}H (1.0 g, 2.5 mmol) and vanadium oxytripropoxide (0.32 mL, 1.5 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, orange needles of **6** formed. (0.73 g, 67 % isolated yield). MS (E.I.) 867.3 [M]$^+$. IR (cm^{-1}): 2952m, 2867w, 1605s, 1540m, 1483s, 1453m, 1390m, 1357w, 1303w, 1232s, 1203m, 1171s, 1105m, 1070w, 1000m, 968s, 887m, 846s, 785m, 749s, 688s. Found: C, 74.53; H, 7.05; N, 3.35 %. $C_{54}H_{60}N_2O_5V$ requires C, 74.72; H, 6.97; N, 3.23 %. EPR (toluene, 298 K): g_{iso}= 1.99552, A_{iso}= 97.18 G; (toluene, 120 K): $g_{\perp}$= 2.00553, $A_{\perp}$= 61.13 G, $g_{|}$ = 1.97617, $A_{|}$ = 181.37 G.

Complex **7** was made in the same way as for **6**, but following prolonged standing at ambient temperature (1 - 2 days) was found to be a different solvate, containing $1^1/_2$ MeCN per vanadium complex.

Preparation of [VO(**L^7**)$_2$] (**8**)

A toluene solution (20 mL) of **L**^{7}H (0.20 g, 0.39 mmol) and vanadium oxytripropoxide (0.06 mL, 0.23 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, dark red needles of **8** formed isolated yield 0.06 g, 30 %. MS (MALDI-TOF) 1091.4 [M]$^+$. Anal Found: C, 79.22; H, 6.21; N, 2.67 %. $C_{72}H_{68}N_2O_5V$ requires C, 79.17; H, 6.28; N, 2.56 %. IR (cm^{-1}) 2897m, 2871m, 2845m, 2030w 1599s, 1539m, 1475s, 1432s, 1384w, 1289m, 1230s, 1191m, 1163m, 1103w, 973s, 874w, 831s, 747s, 688s. EPR (toluene, 298 K):

g_{iso}= 1.99286, A_{iso}= 89.74 G; (toluene, 120 K): $g_{\perp}$= 2.00158, $A_{\perp}$= 63.98 G, $g_{\parallel}$ = 1.96095, $A_{\parallel}$ = 168.27 G.

Preparation of [VO(**L**^{8})$_2$] (**9**)

A toluene solution (20 mL) of **L**^{8}H (0.26 g, 0.52 mmol) and vanadium oxytripropoxide (0.07 mL, 0.08 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, dark red needles of **9** formed; isolated yield 0.19 g, 69 %. Anal Found: C, 79.3; H, 5.79; N, 2.66 %. $C_{70}H_{60}N_2O_5V$ requires C, 79.3; H, 5.70; N, 2.64 %. MS (MALDI-TOF) 1059.4 [M]$^+$. IR (cm^{-1}) 3025w, 2948w, 2168w, 2031w, 1615s, 1595s, 1545s, 1489s, 1471s, 1433s, 1382m, 1293m, 1221s, 1162s, 1125m, 969s, 866m, 825s, 747s, 693s. EPR (toluene, 298 K): g_{iso}= 1.98756, A_{iso}= 89.74 G; (toluene, 120 K): $g_{\perp}$= 2.00083, $A_{\perp}$= 64.82 G, $g_{\parallel}$ = 1.95741, $A_{\parallel}$ = 173.98 G.

Preparation of [VO(μ-O)(**L**^{6})]$_2$ (**10**)

A toluene solution (30 mL) of **L**^{6}H (1.0 g, 2.5 mmol) and vanadium oxytripropoxide (0.6 mL, 2.7 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, dark red needles of **10** formed. (0.65 g, 27 % isolated yield). MS (E.I.) 966.5 [M]$^+$. Anal Found: C, 67.24; H, 6.37; N, 2.82 %. $C_{54}H_{60}N_2O_8V_2$ requires C, 67.07; H, 6.25; N, 2.90 %. IR (cm^{-1}): 2958m, 1610s, 1588m, 1547m, 1485s, 1458m, 1433m, 1360w, 1302w, 1237s, 1203s, 1179s 1108m, 1022m, 982s, 857m, 797m, 752s. ^{1}H NMR ($CDCl_3$): δ = 8.67 (s, 1H, C*H*=N), 7.61 (d, 1H, *J* = 2.55, Ar*H*), 7.57 (dd, 1H, *J* = 1.61, 7.97, Ar-*H*), 7.29 (d, 1H, *J* = 2.45, Ar*H*), 7.25-7.24 (overlapping m, 2H, Ar*H*), 7.20-7.16 (m, 2H, Ar*H*), 7.09-7.07 (m, 2H, Ar*H*), 7.00-6.97 (m, 2H, Ar*H*), 1.33 (s, 9H, *t*Bu), 1.28 (s, 9 H, *t*Bu). ^{13}C NMR ($CDCl_3$), 169.5 (H*C*=N), 157.7 (Ar*C*), 156.7 (Ar*C*), 149.5 (Ar*C*), 143.1 (Ar*C*), 142.5 (Ar*C*), 137.9 (Ar*C*), 131.4 (Ar*C*), 129.6 (Ar*C*), 128.1 (Ar*C*), 127.7 (Ar*C*), 127.5 (Ar*C*), 124.7 (Ar*C*), 123.3 (Ar*C*), 123.2 (Ar*C*), 120.0 (Ar*C*), 119.3 (Ar*C*) 35.1 (*C*(CH$_3$)$_3$), 34.4(*C*(C*H*$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 29.5 (C(*CH*$_3$)$_3$). ^{51}V NMR (C_6D_6): δ = -532.56.

Preparation of [VO(μ-OH)(μ-O*n*Pr)(**L**^{9})]$_2$ (**11**)

A toluene solution (20 mL) of **L**^{9}H (0.35 g, 0.78 mmol) and vanadium oxytripropoxide (0.11 mL, 0.47 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, blue needles of **11** formed in a 25 % isolated yield (0.13 g). Anal Found: C, 70.70; H, 6.67; N, 2.38 %. $C_{54}H_{60}N_2O_5V$ requires C, 70.26; H, 6.53; N, 2.52 %. IR (cm^{-1}): 3611w, 2902m, 2848m, 1610s, 1542s, 1499w, 1475m, 1432s, 1398m, 1295m, 1231s, 1172m, 1109w, 1072w, 991s, 8550s, 754s. EPR (toluene, 298 K): g_{iso}= 1.99047, A_{iso}= 96.49 G; (toluene, 120 K): $g_{\perp}$= 2.00120, $A_{\perp}$= 66.34 G, $g_{\parallel}$ = 1.96314, $A_{\parallel}$ = 171.29 G.

Preparation of [VO(μ-OH)(μ-O*n*Pr)(**L**^{10})]$_2$ (**12**)

A toluene solution (20 mL) of **L**^{10}H (0.42 g, 0.96 mmol) and vanadium oxytripropoxide (0.13 mL, 0.58 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, green needles of **12** formed in 27 % isolated yield (0.14 g). Anal Found: C, 69.70; H, 6.06; N, 3.06 %. $C_{63}H_{63}N_2O_8V_2$ requires C, 70.19; H, 5.89; N, 2.60 %. IR (cm^{-1}) 3617w, 2967w,1605s, 1542s, 1498m, 1430s, 1351w, 1300m, 1246s, 1164m, 1125w, 1101w, 1056w, 991s, 837s, 748s, 700s. EPR (toluene, 298 K): g_{iso}= 1.98748, A_{iso}= 92.09 G; (toluene, 120 K): $g_{\perp}$= 2.00734, $A_{\perp}$= 63.27 G, $g_{\parallel}$ = 1.96528, $A_{\parallel}$ = 171.30 G.

Preparation of [VO(μ-OH)(μ-O*n*Pr)(**L**^{11})]$_2$ (**13**)

A toluene solution (20 mL) of **L**^{11}H (0.35 g, 0.96 mmol) and vanadium oxytripropoxide (0.24 mL, 1.1 mmol) was refluxed for 12 h. The solution was cooled to room temperature and volatiles were removed *in vacuo*. The residue was extracted into hot acetonitrile. After 24 h, dark red needles of **13** formed in 63 % isolated yield (0.28 g). Anal Found: C, 66.10; H, 6.13; N, 3.21 %. $C_{51}H_{56}N_2O_8V_2$ requires C, 66.09; H, 6.09; N, 3.02 %. IR (cm^{-1}) 3620m, 2945m, 1603s, 1543s, 1497m, 1472m, 1434w, 1417s, 1368m, 1304m, 1246m, 1180s, 1146m, 1120w, 1087w, 1054m, 1021m, 993s, 837s, 745s, 690w. EPR (toluene, 298 K): g_{iso}= 2.05984, A_{iso}= 105.46 G; (toluene, 120 K): $g_{\perp}$= 2.02799, $A_{\perp}$= 62.48 G, $g_{\parallel}$ = 2.00238, $A_{\parallel}$ = 110.50 G.

Ethylene polymerization

At 1 bar of ethylene pressure: Ethylene polymerization 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 via the use of an oil bath, and then the co-catalyst and the reactivating agent ETA was added (0.1 mL, 0.72 mmol); 10ml toluene which dissolved complex was also added. The polymerization time was measured from pre-catalyst injection; the polymerization 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 in vacuum overnight.

At 10 bar of ethylene pressure: A 250 ml stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was employed for the reaction. Firstly, the autoclave was heated in vacuum at 80 °C and recharged with ethylene three times, and then 50 ml toluene (freshly distilled) were injected to the clave which was full of ethylene. When the required temperature was reached, another 30 ml of toluene, which dissolved the complex, and the required amount of co-catalyst DEAC, ETA, and the residual toluene were added by syringe, successively. The reaction mixture was intensely stirred for the desired time under the corresponding pressure of ethylene throughout the entire experiment. The reaction was terminated and the resulting polymer was analyzed using the same procedure as described above for the procedure conducted at ambient pressure.

Table 7. Crystallographic data for complexes

Compound	**1·2CH$_3$CN**	**2**	**3·2CH$_3$CN**	**4**	**5**	**6**	**7·1.5CH$_3$CN**	**8**	**9**	**10**	**11·4MeCN**	**12**	**13**
Formula	$C_{44}H_{56}N_2O_5V.2CH_3CN$	$C_{44}H_{56}N_2O_5V$	$C_{44}H_{56}N_2O_5V.2CH_3CN$	$C_{46}H_{60}N_2O_5V$	$C_{44}H_{50}F_6N_2O_5V$	$C_{54}H_{60}N_2O_5V$	$C_{54}H_{60}N_2O_5V\cdot1.5CH_3CN$	$C_{72}H_{68}N_2O_5V$	$C_{70}H_{60}N_2O_5V$	$C_{54}H_{60}N_2O_8V_2$	$C_{65}H_{71}N_2O_8V_2\cdot4C_2H_3N$	$C_{63}H_{63}N_2O_8V_2$	$C_{51}H_{56}N_2O_8V_2$
Formula weight	825.96	743.85	825.96	771.90	851.80	867.98	929.56	1092.22	1060.14	966.92	1274.33	1078.03	926.86
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions													
a (Å)	17.946(4)	15.165(3)	10.979(2)	13.997(3)	14.096(3)	11.896(2)	15.3075(16)	13.457(3)	12.286(3)	11.9699(5)	13.547(3)	9.830(2)	10.169(2)
b (Å)	9.2015(18)	18.182(4)	13.256(3)	18.580(4)	15.274(3)	14.224(3)	18.0329(18)	15.049(3)	13.190(3)	15.6408(6)	13.980(3)	13.423(3)	12.960(3)
c (Å)	28.165(6)	19.034(4)	15.575(3)	17.898(4)	24.527(5)	15.568(3)	20.191(2)	16.071(3)	19.728(4)	13.9536(5)	21.040(4)	21.429(4)	20.218(4)
α (º)	90	66.33(3)	101.47(3)	90	87.65(3)	108.49(3)	76.0289(15)	70.73(3)	70.80(3)	90.00	105.21(3)	92.36(3)	71.25(3)
β (º)	95.87(3)	67.40(3)	91.71(3)	104.38(3)	75.73(3)	90.94(3)	81.7168(15)	68.07(3)	74.35(3)	99.3405(6)	90.24(3)	100.78(3)	71.42(3)
γ (º)	90	67.40(3)	92.44(3)	90	64.15(3)	109.43(3)	78.9101(15)	79.53(3)	87.75(3)	90.00	117.26(3)	98.46(3)	74.94(3)
V (Å^3)	4626.6(16)	4433.0(15)	2217.7(8)	4508.7(16)	4592.1(16)	2334.2(8)	5279.7(9)	2843.8(10)	2902.9(11)	2577.74(17)	3381.7(12)	2740.7(10)	2354.6(8)
Z	4	4	2	4	4	2	*4*	2	2	2	2	2	2
Temperature (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	150(2)	173(2)	173(2)	150(2)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Calculated density (g.cm^{-3})	1.186	1.115	1.237	1.137	1.232	1.235	1.169	1.276	1.213	1.246	1.251	1.306	1.307
Absorption coefficient (mm^{-1})	0.262	0.266	0.273	0.263	0.283	0.262	0.237	0.230	0.224	0.416	0.335	0.399	0.452
Transmission factors (min./max.)	0.9870 and 0.9255	0.9330 and 0.8998	0.9345 and 0.8759	0.9128 and 0.8794	0.9615 and 0.9149	0.9727 and 0.9031	0.9813 and 0.8670	0.9498 and 0.9087	1.0000 and 0.5983	0.9518 and 0.7945	0.9360 and 0.9360		0.8939 and 0.8249
Crystal size (mm^3)	0.30 × 0.27 × 0.05	0.41 × 0.33 × 0.26	0.50 × 0.44 × 0.25	0.50 × 0.46 × 0.35	0.32 × 0.18 × 0.14	0.40 × 0.17 × 0.11	0.62 × 0.38 × 0.08	0.42 × 0.27 × 0.23	0.536 × 0.422 × 0.254	0.58 × 0.20 × 0.12	0.20 × 0.20 × 0.20	0.288 × 0.252 × 0.159	0.44 × 0.28 × 0.25
θ(max) (°)	25.00	25.00	27.52	25.00	25.00	25.00	22.50	27.50	25.00	30.56	25.00	25.00	25.00
Reflections measured	25257	32972	28054	25974	35870	25233	44050	25484	30994	29752	24375	21355	17326
Unique reflections	8083	15504	10097	7916	16108	8209	13810	10190	15504	7812	11669	9547	8194
R_{int}	0.0639	0.0497	0.0576	0.0619	0.0739	0.0692	0.0659	0.0465	0.0497	0.0315	0.0826	0.0699	0.0574
Number of parameters	570	996	539	532	1069	559	1250	723	831	304	811	685	577
R_1 [$F^2 > 2\sigma(F^2)$]	0.0830	0.0661	0.0642	0.0857	0.1081	0.0590	0.0485	0.0731	0.0782	0.0378	0.1386	0.0894	0.0464
wR_2 (all data)	0.2740	0.1833	0.2105	0.2769	0.3372	0.2345	0.1303	0.2590	0.2527	0.1069	0.3335	0.2840	0.1164
GOOF, *S*	1.218	1.069	1.040	1.222	1.111	1.023	1.049	0.984	1.092	1.024	1.110	1.228	1.072
Largest difference peak and hole (e Å^{-3})	0.714 and -0.773	0.353 and -0.293	0.461 and -0.579	0.882 and -0.717	1.095 and -0.679	0.827 and -0.801	0.445 and -0.276	0.729 and -0.946	1.197 and -0.677	0.440 and -0.399	1.181 and -0.516	0.702 and -1.320	0.508 and -0.298

Crystallography

For each sample, a crystal was mounted in oil on a glass fiber and fixed in the cold nitrogen stream on the diffractometer. A Rigaku R-AXIS Rapid IP diffractometer was used for **1-6**, **8**, **9**, **11-13**, and a Bruker APEX 2 CCD diffractometer was used for **7**·1.5MeCN and **10**, with both equipped with graphite-monochromated MoKα radiation (λ = 0.71073 Å) at 173(2) K (150 K for **7**·1.5MeCN and **10**). [22] Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Using the SHELXS-97 and SHELXL-97 packages respectively, structure solution and refinement were performed. [23-25] Crystal data and processing parameters for complexes **1-13** are summarized in Table 7. For **1**, there is disorder in the *t*Bu at C33 with major component 65.0(7) %, and there are two molecules of acetonitrile in the unit. There are two similar complex molecules in the asymmetric unit of **2**, whilst for **3**, two molecules of acetonitrile are also in the unit. In the case of **5**, there are two molecules of the vanadium complex in the asymmetric unit. For **7**·1.5MeCN there are two similar vanadium complex molecules and three molecules of acetonitrile in the asymmetric unit. The methyl groups in one *t*Bu group at C(65) were modelled as two-fold disordered with major component 66(3) %. In **10** the molecule lies on a centre of symmetry, so half is unique. For **9**, the group bearing C42, which is located at the *ortho* position of one ligand N atom was modelled with two–fold disorder with a component of 51.3(5) %. There are four molecules of acetonitrile in the asymmetric unit of **11**. 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. CCDC numbers 980001-980013.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of compounds **1** – **13**. Example EPR spectrum (of **5**) and ^{13}C NMR spectrum of polyethylene (from run 7 of table S1 and run 11 of table 5). Tables of the catalytic optimization runs conducted at 1 bar and 10 bar.

Notes and references

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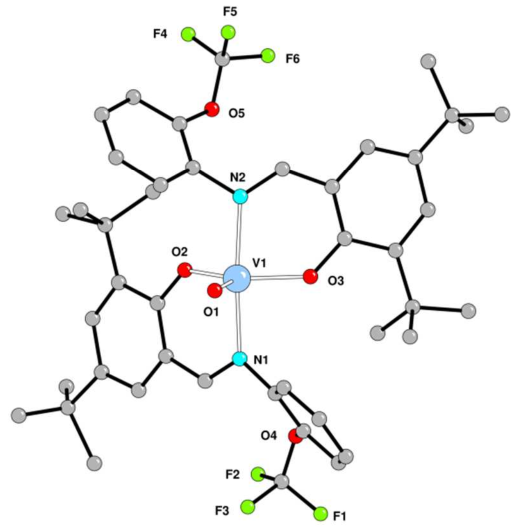
Graphical Abstract



A number of mono- and di-vanadium complexes bearing bi-dentate phenoxyimine ligands have been structurally characterized and shown to exhibit high catalytic activity for ethylene polymerization in the presence of diethylaluminum chloride and ethyltrichloroacetate.