

Vanadium(III) phenoxyimine complexes for ethylene or ϵ -caprolactone polymerization: mononuclear versus binuclear pre-catalysts†Cite this: *Catal. Sci. Technol.*,
2013, 3, 152Lucy Clowes,^a Mark Walton,^a Carl Redshaw,^{†*a} Yimin Chao,^a Alex Walton,^b
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The mononuclear $\{[C_6H_4N=CH(ArO)]_2VCl(THF)\}$ (Ar = 2,4-*t*-Bu₂C₆H₂ (**1**), Ar = C₆H₄ (**2**)), $\{O[C_6H_4N=CH(ArO)]_2VCl(THF)\}$ (Ar = 2,4-*t*-Bu₂C₆H₂ (**3**), Ar = C₆H₄ (**4**)) and the binuclear vanadium(III) complexes $\{[C_6H_4N=CH(ArO)]VCl_2(THF)_2\}_2(\mu-CH_2CH_2)$ (Ar = 2,4-*t*-Bu₂C₆H₂ (**5**), Ar = C₆H₄ (**6**)), have been synthesized and fully characterized. The compounds $[C_6H_5N=CH(ArO)]VCl_2(THF)_2$ (Ar = 2,4-*t*-Bu₂C₆H₂ (**7**), Ar = C₆H₄ (**8**)), $[2,4,6-Me_3-C_6H_2N=CH(ArO)]VCl_2$ (Ar = 2,4-*t*-Bu₂C₆H₂ (**9**), Ar = C₆H₄ (**10**)) and $[2,6-*i*-Pr_2-C_6H_3N=CH(ArO)]VCl_2(THF)_2$ (Ar = 2,4-*t*-Bu₂C₆H₂ (**11**), Ar = C₆H₄ (**12**)), $\{\mu-CH_2CH_2[N=CH(C_6H_4O)]_2VCl(THF)\}$ (**14**) and $\{C_6H_4[N=CH(C_6H_4O)]_2VCl(THF)\}$ (**15**) were synthesized for comparative polymerization studies. The dizwitterionic compound $[2,6-*i*-Pr_2-C_6H_3N^+(H)=CH(C_6H_4O)]_2VCl_2O$ (**13**) was also isolated, and presumably formed *via* a fortuitous hydrolysis reaction. The complexes **2**, **5** and **13** have been structurally characterized; the molecular structure of the parent ligand (**L5**) in **5** is also reported. All complexes have been screened for ethylene as well as ϵ -caprolactone polymerization, and results are compared against those for known related mono- and bi-nuclear counterparts to evaluate for possible cooperative effects. The compounds **10** and **12** have been supported on modified SiO₂, analysed by XPS and subjected to homo-polymerization (ethylene) and co-polymerization (1-hexene and ethylene) studies.

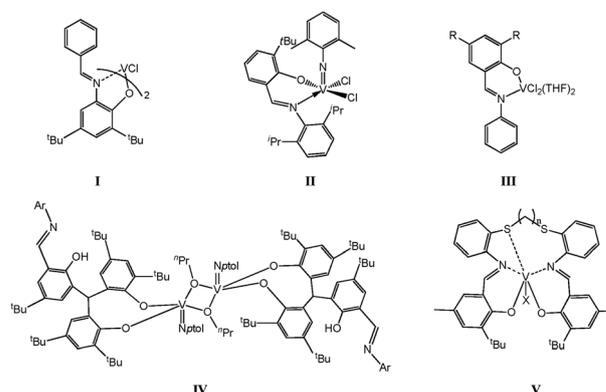
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Introduction

Vanadium catalysts have previously been employed for the production of high molecular weight polyethylene,¹ ethylene/propylene co-polymers or ethylene/propylene/diene elastomers.² However, despite their early commercial importance, it is only in the last few years that highly active α -olefin polymerization catalysts of group V have appeared in the academic literature.³ Of particular note has been the emergence of salicylaldiminato or so-called phenoxyimine-type (FI) ligands as one of the ligand sets of choice for early transition metal catalytic systems. Reports by Fujita *et al.* described highly active (65.1 kg-PE (mmol V h)⁻¹ at 1 bar ethylene pressure) mononuclear pre-catalysts bearing two phenoxyimines at vanadium (see **I**, Scheme 1).⁴ Subsequent



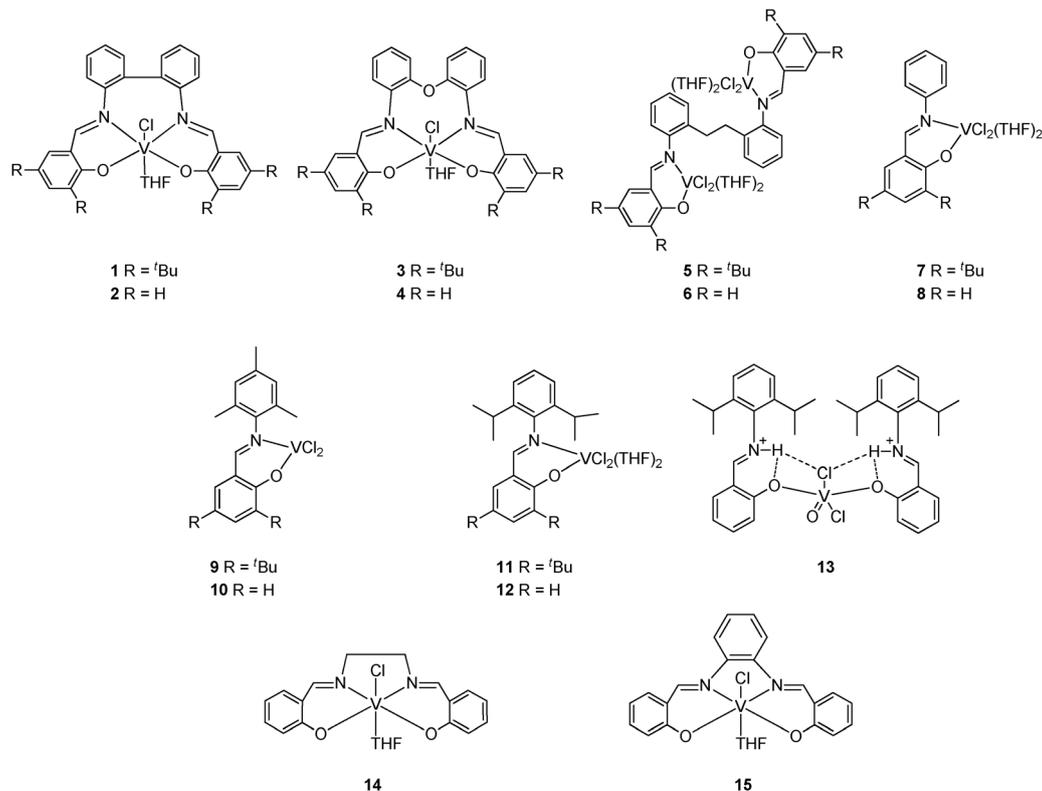
Scheme 1 Known vanadium pre-catalysts I–V.

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studies by Nomura, and by Li *et al.*, led to pre-catalysts of the type **II** and **III**, respectively, both of which also proved to be highly active for ethylene polymerization.⁵ Our laboratory has also recently reported phenoxyimine complexes, where the chelate is either derived from an NO₃ tripodal imine ligand set (**IV**),⁶ or vanadium complexes possessing N₂O₂S₂-based ligands (**V**).⁷ A general feature



Scheme 2 Vanadium pre-catalysts screened in this study.

of this chemistry is the adoption of mononuclear pre-catalysts. However, in a number of other polymerization systems, beneficial cooperative effects are witnessed, leading to either improved catalytic performance or differing polymer properties.⁸ With this in mind, and given the current interest in vanadium, we have embarked upon a program to develop new multi-metallic vanadium-based pre-catalysts. Furthermore, encouraged by recent work on zinc,⁹ we herein report the use of the ligand family $[\text{C}_6\text{H}_4\text{N}=\text{CH}(\text{ArO})]_2(\mu\text{-CH}_2\text{CH}_2)$ (Ar = 2,4-*t*-Bu₂C₆H₂ **L5**, C₆H₄ **L6**), which has previously been shown to act in a tetradentate fashion with either zirconium or zinc centres.^{9,10} Recently, related group IV and V complexes of tetradentate and bidentate Schiff bases have been screened for their ability to polymerise various α -olefins.¹¹ We also note that a number of bimetallic nickel systems have shown increased activities *versus* their mononuclear counterparts.¹² Herein, polymerization screening results for the bimetallic vanadium pre-catalysts are compared under similar conditions with known and novel related mononuclear related vanadium(III) complexes (Scheme 2).

Results and discussion

The ligands **L1**–**L15** required for each of the corresponding vanadium(III) complexes **1**–**15** (Scheme 2) were obtained in good yields *via* standard condensation of the requisite aniline with one or two equivalents of either salicylaldehyde or 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde. Complexes **1**–**6**, **9**–**10** were prepared following methods employed by Li and co-workers in their

syntheses of the mononuclear phenoxyimine complexes **7**, **8**, **11** and **12**.^{5b} Complex **13** was synthesized using the same method as for compound **12** and was presumably formed *via* a fortuitous hydrolysis reaction. The known salicylaldehyde bridged phenoxyimine complexes **14** and **15** were synthesised as benchmark catalytic systems.¹³

Mononuclear vanadium(III) phenoxyimines

Complexes **1** and **2** were prepared by treatment of **L1** or **L2**¹⁴ with excess of $\text{VCl}_3(\text{THF})_3$ in tetrahydrofuran, in the presence of base (triethylamine), to afford, following work up, the dark red complexes $\{[\text{C}_6\text{H}_4\text{N}=\text{CH}(2,4\text{-}t\text{-Bu}_2\text{C}_6\text{H}_2\text{O})]_2\text{VCl}(\text{THF})\}$ (**1**) and $\{[\text{C}_6\text{H}_4\text{N}=\text{CH}(\text{C}_6\text{H}_4\text{O})]_2\text{VCl}(\text{THF})\}$ (**2**) in yields of 47 and 51%, respectively. Crystals of **2** suitable for X-ray crystallography were grown by slow diffusion of the dark red tetrahydrofuran solution into hexane. Compound **2** crystallises with two independent V-complex molecules (together with THF solvent) in the cell. The structure of one of the independent molecules of **2** is depicted in Fig. 1, with selected bond lengths and angles given in the caption; crystallographic data (with those of the other structures reported in this paper) are collated in Table 3.

The two molecules in **2** are very similar in conformation, each with a six-coordinate vanadium atom with an octahedral coordination pattern. Three of the N₂O₂ donor atoms of each **L2**²⁻ ligand are arranged in a meridional mode with the remaining O atom bonding normal to the meridional plane. The two remaining sites are filled by a chloride ion (*trans* to the fourth donor atom) and a THF ligand (*trans* to an imido N atom). In the folding of the **L2**²⁻

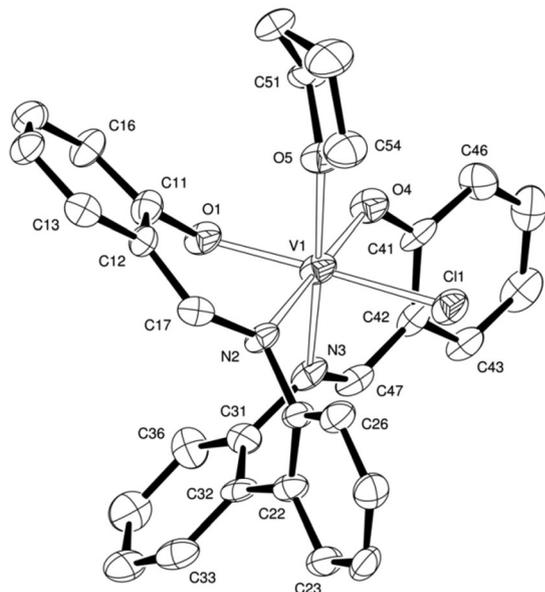


Fig. 1 View of one of the two very similar molecules in crystals of $\{[C_6H_4N=CH(C_6H_4O)]_2VCl(THF)\}_2$ **2** indicating the atom numbering scheme. Hydrogen atoms and solvent molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): V(1)–O(1) 1.926(4), V(1)–N(2) 2.107(5), V(1)–N(3) 2.092(5), V(1)–O(4) 1.917(5), V(1)–O(5) 2.127(4), V(1)–Cl(1) 2.353(2); O(1)–V(1)–N(2) 83.8(2), O(1)–V(1)–O(4) 96.41(19), O(1)–V(1)–Cl(1) 169.19(15), N(2)–V(1)–N(3) 89.7(2), N(2)–V(1)–O(4) 198.8(2), N(3)–V(1)–O(4) 90.2(2), N(3)–V(1)–O(5) 176.12(19), O(5)–V(1)–Cl(1) 88.77(13).

ligand around the metal centre, there is twisting of $ca\ 71.7^\circ$ about the N(2)–C(21) bond (and equivalent N(7)–C(71) bond in the second molecule) and $ca\ 54.5^\circ$ about the N(3)–C(31) and its equivalent bond; the rotation between the two phenyl groups, as about C(22)–C(32), is $ca\ 55^\circ$. In both molecules, the THF ligand rings have ‘twisted’ conformations.

Compound **12** was synthesized using the reported literature method.^{5b} However, the use of ‘wet’ ligand (**L12** that had been dried insufficiently; ligand used for formation of compound **12** had been dried *in vacuo* in excess of 16 hours) resulted in the formation of a dizwitterionic complex **13** in moderate yield ($ca\ 37\%$). Single crystals of **13** were grown from a saturated acetonitrile solution on prolonged standing at ambient temperature. The vanadium atom in complex **13** (Fig. 2) is five-coordinate with an approximately square-pyramidal pattern; the vanadyl oxygen, O(5), is at the apex, with the pairs of chloride ligands and phenolate oxygen atoms in opposite corners of the square base. The two phenolate ligands are arranged with approximate mirror symmetry about the central $VOCl_2$ plane. Both NH groups are donors to bifurcated hydrogen bonds; each is linked to the phenolate O atom of its own ligand and to Cl(3). There are also two solvent (acetonitrile) molecules in the asymmetric unit of the cell.

Binuclear vanadium(III) phenoxyimines

The ethylene-bridged ligands, **L5** and **L6** were prepared in good yields using the literature method.¹⁰ It proved possible to obtain

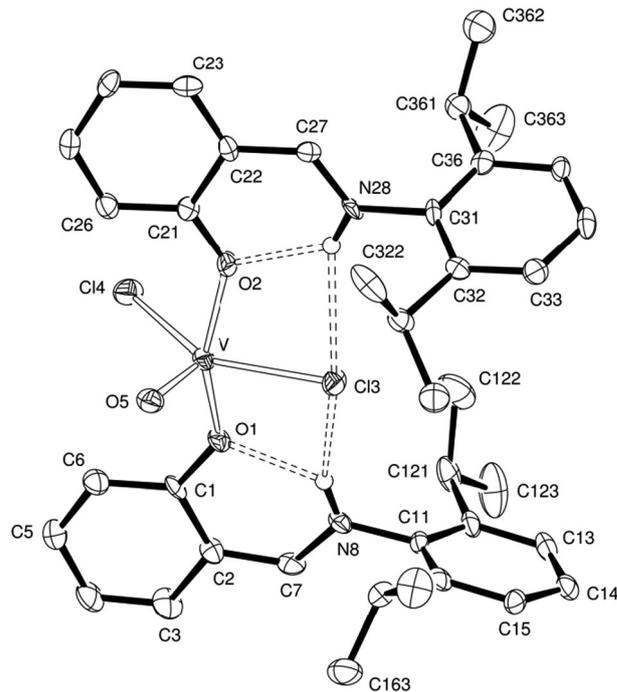


Fig. 2 View of a molecule of the dizwitterionic complex **13**, $[2,6-i-Pr_2-C_6H_3N^+(H)=CH(C_6H_4O)]_2VCl_2O$, indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): V–O(1) 1.987(3), V–O(2) 1.978(3), V–Cl(3) 2.3594(14), V–Cl(4) 2.3265(12), V–O(5) 1.573(3), O(2)–V–O(1) 155.91(14), O(1)–V–Cl(3) 82.08(10), O(1)–V–Cl(4) 90.33(9), O(5)–V–O(1) 101.11(15), O(2)–V–Cl(3) 81.64(9), O(2)–V–Cl(4) 90.26(9), O(5)–V–O(2) 101.43(15), Cl(4)–V–Cl(3) 138.69(5), O(5)–V–Cl(3) 112.20(12), O(5)–V–Cl(4) 109.12(12), C(7)–N(8) 1.312(6), C(27)–N(28) 1.291(6), H(8)···O(1) 1.97, N(8)–H(8)···O(1) 130.0, H(8)···Cl(3) 2.59, N(8)–H(8)···Cl(3) 149.1, H(28)···O(2) 1.95, N(28)–H(28)···O(2) 132.6, H(28)···Cl(3) 2.68, N(28)–H(28)···Cl(3) 153.2.

X-ray quality crystals of the ligand **L5** by crystallization from chloroform/methanol. The molecular structure is shown in Fig. 3, with selected bond lengths and angles in the caption. The molecule lies about a centre of symmetry at the mid-point of the C(27)–C(27') bond, in an anti, staggered conformation, and thus has an ‘S-shape’ rather than curved in a ‘C-shape’ as it would when enfolded a metal centre. The phenolic hydrogen atom (in each half of the molecule) was refined freely and is directed towards the imino nitrogen forming a hydrogen bond, with H(10)···N(20) 1.63 Å.

Complexes **5** and **6** were prepared in the same manner as complex **2**. Treatment of **L5** or **L6** with excess of $VCl_3(THF)_3$ in tetrahydrofuran afforded, following work up, the dark red complexes $\{[C_6H_4N=CH(2,4-t-Bu_2C_6H_2O)]VCl_2(THF)_2\}_2(\mu-CH_2CH_2)$ (**5**) and $\{[C_6H_4N=CH(C_6H_4O)]VCl_2(THF)_2\}_2(\mu-CH_2CH_2)$ (**6**) in yields of 43 and 44%, respectively.

Crystals of **5** suitable for X-ray crystallography were grown by slow diffusion of *n*-hexane into a THF solution of **5** at ambient temperature. The molecular structure is depicted in Fig. 4, with selected bond lengths and angles given in the caption. Regardless of whether the ligands **L5** or **L6** were treated with one or two equivalents of $VCl_3(THF)_3$, the di-nuclear species was always obtained and in yields of about 40–45% and 65%, respectively.

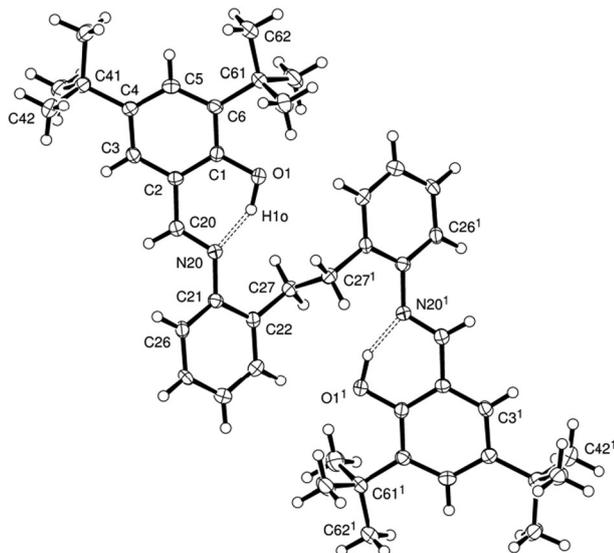


Fig. 3 View of molecule $[\text{C}_6\text{H}_4\text{N}=\text{CH}(2,4\text{-}t\text{-Bu}_2\text{C}_6\text{H}_2\text{OH})]_2(\mu\text{-CH}_2\text{CH}_2)$, **L5**, indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): O(1)–C(1) 1.357(2), O(1)–H(1o) 1.00(3), C(1)–C(2) 1.412(3), C(20)–N(20) 1.283(2), N(20)–C(21) 1.423(2), C(1)–O(1)–H(1o) 105.8(16), O(1)–C(1)–C(6) 119.80(18), C(6)–C(1)–C(2) 120.78(18), N(20)–C(20)–C(2) 122.17(19).

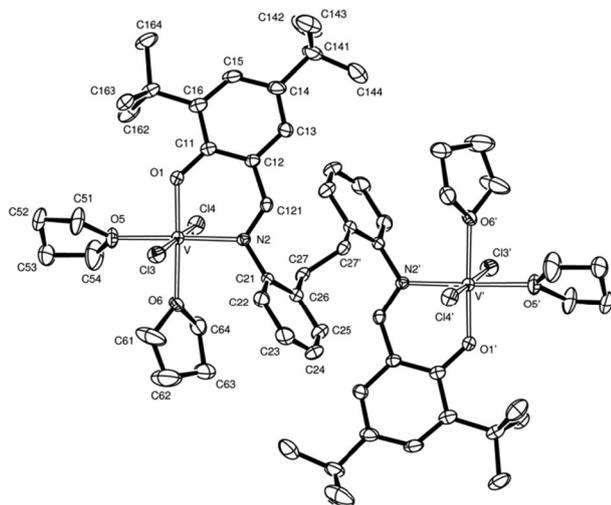


Fig. 4 View of molecule $[\{\text{C}_6\text{H}_4\text{N}=\text{CH}(2,4\text{-}t\text{-Bu}_2\text{C}_6\text{H}_2\text{O})\}\text{VCl}_2(\text{THF})_2]_2(\mu\text{-CH}_2\text{CH}_2)$ **S12** indicating the atom numbering scheme. Hydrogen atoms and the minor disorder component (in one of the THF ligands) have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): V–O(1) 1.870(2), V–N(2) 2.087(2), V–Cl(3) 2.3546(9), V–Cl(4) 2.3581(9), V–O(5) 2.107, V–O(6) 2.117(2), O(1)–V–N(2) 89.56(9), O(1)–V–O(5) 92.12(9), O(1)–V–O(6) 177.31(9), N(2)–V–O(5) 177.87(9), N(2)–V–O(6) 92.60(9), Cl(3)–V–Cl(4) 176.20(4).

Interestingly here, the ligand rather than acting in tetradentate fashion as observed previously,¹⁰ prefers to act as a bis-bidentate ligand, binding to a vanadium centre at either end of the ligand. The centrosymmetry is retained about the C(27)–C(27') bond midpoint and there is rotation about the C(21)–N(2) bond to allow the coordination of the V centres. Six-fold coordination, in

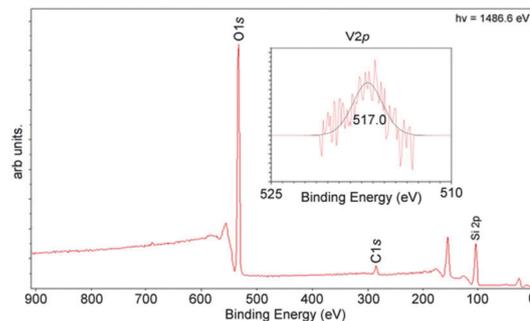


Fig. 5 X-ray photoelectron survey spectrum of **S12**. The vanadium V-2p energy window 525–510 eV is shown inset.

an octahedral pattern, is achieved by the ligation of two chloride ligands (mutually *trans*, Cl(3)–V–Cl(4) 176.20(4) $^\circ$) and two *cis*-THF molecules (opposite the iminophenolate N and O atoms, O(5)–V–O(6) 85.68(9) $^\circ$) at each V centre.

Silica immobilisation

Compounds **10** and **12** were immobilised on pre-treated silica by refluxing in toluene to give supported structures **S10** and **S12**; the SiO₂ had been heated to 350 $^\circ\text{C}$ under dynamic vacuum for 48 h. X-ray photoelectron spectroscopy (XPS) analysis of the silica surface confirmed the percentage coverage of the metal species. Analysis of the resulting photoelectron spectrum of **S12** (Fig. 5) showed a V-2p_{3/2} peak with a single component at 517.0 \pm 0.02 eV. The resulting concentration of vanadium was shown to be 0.054% of the bulk sample. The C-1s peak was used to calibrate the spectrum; however the calculated carbon concentration in the sample is much higher than expected, now assigned to the presence of adventitious carbon. Confirmation that the ligand has not been leached from the system was ascertained from the identification of N-1s and Cl-2p peaks at binding energies of 401.0 eV (0.089%) and 199.7 eV (0.162%).

Ethylene polymerization screening

Complexes **1–10** have been evaluated as pre-catalysts for the polymerization of ethylene, employing DMAC (dimethylaluminium chloride) as co-catalyst, and ETA (ethyltrichloroacetate) as a re-activator.¹⁵ Polymerizations were carried out in toluene (100 mL) using 4000 molar equiv. of co-catalyst at 25 $^\circ\text{C}$ over 30 minutes.

In the presence of DMAC and ETA, the new vanadium(III) bridged phenoximine complexes **1–6** were highly active for the polymerization of ethylene (Table 1, runs 1–6). However, the activities (< 10 000 g mmol⁻¹ h⁻¹ per bar) were disappointing in comparison to other V-based pre-catalyst–DMAC–ETA systems recently reported.^{11,16} The general trend observed in Table 1 is that the *tert*-butyl containing pre-catalysts showed higher activities than did their salicylaldehyde counterparts (*e.g.* runs 1 vs 2); the exception was 3 *cf.* 4, whose activities were of the same magnitude. The enhanced performance suggests that the steric hindrance of the *tert*-butyl group did not hinder the approach of the monomer, or this was possibly

Table 1 Ethylene polymerization results^a

Pre-catalyst/run ^b	Polymer ^c	Activity ^d	M_w^e	M_n^f	PDI ^g	M_p^h
1	2.1	8400	217 000	49 300	4.4	143.3
2	0.64	2560	—	—	—	141.9
3	0.34	1360	536 000	136 000	3.9	144.2
4	0.42	1680	404 000	288 000	1.4	145.6
5	2.38	9520	445 000	181 000	2.5	140.6
6	1.2	4800	170 000	30 500	5.6	143.1
7	0.98	3920	273 000	47 600	5.7	143.7
8	1.31	5240	168 000	39 200	4.3	142.6
9	0.55	2210	—	—	—	—
10	0.80	3190	—	—	—	—
11	0.48	1920	—	—	—	—
12	0.71	2850	—	—	—	—
13	0.41	1640	—	—	—	—
14	1.14	4560	—	—	—	—
15	0.25	1000	—	—	—	—

^a Conditions: 1 bar ethylene; toluene (100 mL); ETA (0.1 mL); reaction quenched with dilute HCl, washed with methanol (20 mL) and dried for 12 h in a vacuum oven at 80 °C. ^b 0.5 μmol. ^c Grams of polymer.

^d Grams of polymer mmol⁻¹ h⁻¹ per bar. ^e Weight average molecular weight. ^f Number average molecular weight. ^g Polydispersity index.

^h °C determined by DSC. All runs carried out at 25 °C, 30 min and Al/V (molar ratio) 4000.

simply due to the improved solubility of the *tert*-butylated pre-catalyst.

Only in the case of **1** (run 1) does the tetra-dentate nature of the ligand appear to be beneficial compared with its bi-dentate counterpart **7** (run 7), though the situation is reversed for the non-*tert*-butylated species (runs 2 vs 8). These tetra-dentate systems must undergo a rearrangement of the *trans* disposed chlorines to afford a system which is more catalytically favorable. Bialek *et al.* have observed enhanced activity in *tert*-butylated tetra-dentate vanadium(IV) systems compared to their bi-dentate counterparts.^{11a}

In terms of polymer properties, the presence of an oxygen bridge in **3** and **4** led to increased molecular weight (M_w), and in the case of the non-*tert*-butylated complex **4**, better control ($M_w/M_n = 1.4$, run 4).

When comparing the bi-metallic (5–6) versus the mono-metallic (1–4 and 7–15) vanadium complexes in Table 1, it was evident that in the case of the tetra-dentate ligand sets, activities for the bi-metallic systems were somewhat higher, whilst the molecular weight (M_w) of the polyethylene obtained from **6** was at the lower end of those observed herein.

On comparing complexes **9** and **10** with the bi-metallic complexes **5** and **6**, it is evident that for the *tert*-butyl derivatives (**5** and **9**), there is evidence of a co-operative effect in **5**; observed activities for **11** and **12** suggest that this is not simply a steric effect. In the case of R=H (**6** and **10**), the beneficial cooperative effect in **6** is far less pronounced.

Comparison with the bi-dentate systems **7** and **8** reveals increased activity and molecular weight (M_w) only in the case of the *tert*-butylated derivative **5** (run 5); the values for **6** closely resemble those of **8**. In the case of complexes **14** and **15**, the presence of the phenylene backbone was found to be detrimental to activity. Bialek and Liboska have previously observed enhanced activity when using cyclohexylene bridged ligand sets.^{11c}

Table 2 ε-Caprolactone screening results for complexes 1–15^a

Pre-catalyst/run	Conversion ^b	M_n calculated	M_n measured ^c	PDI
1	57	26 024	10 751	1.4
2	47	21 458	8640	1.4
3	24	10 960	7977	1.2
4	33	15 070	9249	1.2
5	48	21 900	10 080	1.4
6	70	31 960	11 010	2.3
7	72	32 870	4973	1.2
8	100	45 660	4060	1.1
9	87	39 720	13 670	1.3
10	93	42 460	14 260	1.1
11	97	44 290	21 340	1.1
12	19	8670	—	—
13	93	42 460	13 290	1.2
14	94	42 920	4790	1.1
15	3	1370	4560	1.4

^a Conditions: monomer/metal = 400; 72 h; 80 °C; 20 mL of toluene; 2.5 mL of ε-caprolactone; 1 equivalent of benzyl alcohol (from a 0.97 M solution in toluene). ^b Calculated by ¹H NMR. ^c M_n measured = 0.58 × M_n GPC.¹⁷

ε-Caprolactone screening

Complexes **1–15** were also screened, in the presence of benzyl alcohol, for their ability to polymerize ε-caprolactone. Complex **6** was subjected to time, temperature and co-initiator screening to obtain the optimum conditions. The subsequent ε-caprolactone screening of complexes **1–15** were completed using these conditions (Table 2). All complexes, except **6**, formed only oligomers with low polydispersity (≤ 1.4), which suggested that these 'polymerizations' occurred without side reactions and, interestingly, only low molecular weight oligomers were obtained under these conditions. Complex **6** deviated, in relation to polydispersity, from the other pre-catalysts screened herein and as such was subjected to lifetime studies which showed an almost linear increase in conversion over time.

The above results might be described as disappointing; however, they should be put into context by comparison with recent work carried out by Mahha *et al.*¹⁸ who noted that the heteropolyacids HPA-2 produced lower activities under an inert atmosphere; this was attributed to the reduction of the metal centres to V(IV) and/or Mo(V). However, when dioxygen was added, the reduced species were re-oxidized to the active vanadium(V) and Mo(VI). Unlike these heteropolyacid systems, our phenoxyimine complexes show similar conversion rates without the need to re-oxidise the deactivated species.

Table 3 Homogenous PPR ethylene polymerization results^a

Run	Catalyst ^b	Temp. ^c	Yield ^d	Activity ^e
1	5 (0.10)	60	0.0436	65
2	5 (0.15)	60	0.0382	38
3	5 (0.20)	60	0.0408	31
4	5 (0.25)	60	0.0455	27
5	5 (0.10)	80	0.0363	54
6	5 (0.20)	80	0.0475	36
7	5 (0.25)	80	0.0461	28

^a Conditions: 6.67 bar ethylene, 1 h reaction time, Al/V (molar ratio) 4000. ^b mmol. ^c °C. ^d Grams of polymer. ^e g mmol⁻¹ h⁻¹ per bar.

Generally, the salicylaldiminato complexes **2**, **4**, **6**, **8** and **10** slightly out-performed their *tert*-butylated counterparts; exceptionally, pre-catalyst **11** outperformed complex **12**. We note that pre-catalysts **8**, **11** and **14** exhibited the best conversion rates and provide excellent control of the molecular weight distribution (PDI = 1.1) of all those reported herein.

Homogenous parallel pressure reactor ethylene screening

Homogenous screening of pre-catalyst **5**, in combination with methylaluminoxane (MAO), produced moderate catalysts for the polymerization of ethylene (Table 3). Increasing the amount of catalyst loading was found to be detrimental to the activity. The varying activity in co-catalyst was explored by Nomura *et al.*,¹⁹ who showed that the size of MAO forces the catalyst to form discrete ions, whereas DMAC can form a chloro-bridged species.

Heterogenous parallel pressure reactor ethylene screening

S10 and **S12** were subjected to homo-polymerization (ethylene) and co-polymerization (1-hexene and ethylene), over a one hour period. Triisobutyl aluminium (TIBA) and ethylaluminium dichloride (EADC) were used separately as co-catalysts, with the addition of ethyl trichloroacetate (ETA) where required. The metal content contained in the bulk sample was determined by XPS and this value was used to determine the catalytic activity of the supported catalysts (Tables S1–S3).

The results of the polymerization experiments and conditions are shown in the ESI.† Homo-polymerization has shown

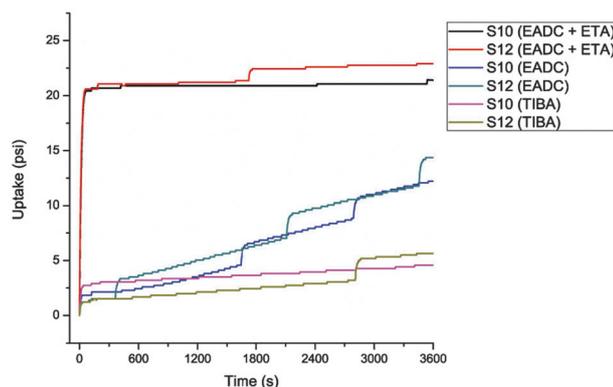


Fig. 6 Consumption profiles of **S10** and **S12**.

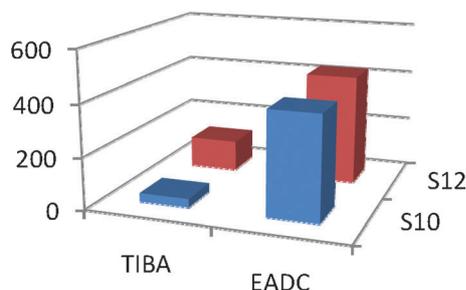


Chart 1 TIBA vs EADC as co-catalyst for co-polymerization.

the two pre-catalysts to be inactive for the polymerization of ethylene using TIBA (Table S1, ESI† runs 1–6); the resulting uptake of ethylene (psi) was due to saturation of heptane rather than polymerisation. Co-polymerization was more successful, where **S12** outperformed **S10** with peak activities of 1744 and 757 g mmol⁻¹ h⁻¹ bar⁻¹ respectively (Table S3, ESI† runs 25 and 19), using EADC as co-catalyst and the addition of ETA. Use of ETA indeed gave higher activities on a number of runs, but also led to a large divergence of resulting activities (Tables S2 and S3, ESI† runs 7–28).

The problems with repeatability seem to stem from the rapid deactivation of the metal centres; the consumption profiles when using EDAC and ETA show that the active site was dead soon after the polymerization run has commenced (Fig. 6). Co-polymerization using TIBA as co-catalyst was detrimental, lowering the activity by 60–90% (Chart 1), although the active site remained active for a much longer period.

Conclusions

In conclusion, a series of new vanadium(III) complexes bearing bridged phenoxyimines (**1–6**) have been synthesized and shown to be highly active (<10 000 g mmol⁻¹ h⁻¹ per bar) for polyethylene production when used in combination with ETA and DMAC.

For ethylene polymerization, observed activity values for the *tert*-butylated systems **5** and **7** were suggestive of a cooperative effect operating between the two metal centres in **5**; no such effect was observed for the *de-tert*-butylated systems (runs **6** and **8**). Comparatively high activity was also observed when employing the *tert*-butylated tetra-dentate mono-metallic pre-catalyst **1**. The presence of the *tert*-butyl groups in such systems was thought to play a crucial role by enhancing solubility. Mounting vanadium complexes **10** and **12** upon silica (forming **S10** and **S12**) was detrimental to the polymerization activity.

Screening for ϵ -caprolactone polymerization revealed that the mononuclear species (complexes **8–14**) generally exhibited higher conversions ($\geq 87\%$) than did the binuclear species (**5** and **6**) ($\leq 70\%$), with compounds **7** and **15** exceptions to this rule. Extending the bridge between ligand binding sites in tetra-dentate compounds led to decreased conversion rates (compounds **1–4**, **14** and **15**). A relationship between the size of the peripheral substituent and percentage conversion was observed, indicating a need for consideration of steric effects when designing pre-catalysts for ϵ -caprolactone polymerization.

Experimental

All manipulations involving vanadium were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the London Metropolitan University. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400 MHz or a Gemini at

300 MHz (^1H); chemical shifts are referenced to the residual protio impurity of the deuterated solvent; IR spectra (nujol mulls, KBr windows) were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers. Solution state magnetic susceptibility was measured by Evans' method on a Varian VXR 400 S spectrometer using a 5% d_{12} -cyclohexane–95% d_2 -dichloromethane solution. Polymer melting point measurements were carried out using a TA Instruments DSC 2920.

Synthesis of ligands

Ligands **L1**–**L15** were synthesised by the standard condensation of the corresponding amine with one or two equivalents as required of either salicylaldehyde or 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde in ethanol.

Synthesis of vanadium complexes

Complexes **1**–**6** and **9**–**10**, were synthesised following analogous methods to that utilised by Li *et al.* to synthesise known complexes **7** and **8**.^{5b} Complexes **11**, **12**, **14** and **15** were synthesised by the literature procedures.¹¹ Complex **13** was synthesized using the same method as that for compound **12**, however use of 'wet' ligand (**L12**, which had been dried insufficiently) led to a fortuitous hydrolysis reaction.

Pre-catalyst 1

To a solution of **L1** (0.5 g, 0.8 mmol) in THF (20 ml), $\text{VCl}_3(\text{THF})_3$ (0.67 g, 1.8 mmol) was added and this solution was stirred for 10 minutes before adding Et_3N (0.25 ml, 1.8 mmol). The solution was stirred at room temperature for 4 hours and then concentrated to approximately 15 mL. The mixture was filtered and recrystallised by diffusion of *n*-hexane (10 mL) to yield complex **1** as a brown powder (0.42 g, 47%). IR/ cm^{-1} 1610 (s) (C=N). Elemental analysis for $\text{VClC}_4\text{H}_5\text{N}_2\text{O}_3$ found (calculated): %C = 71.39 (71.44), H = 7.34 (7.56), N = 3.52 (3.62). MS (EI, m/z): 758 $[\text{M-Me}]^+$. Magnetic moment $\mu = 2.70\mu_{\text{B}}$.

Pre-catalyst 2

Procedure as described for complex **1** using **L2** (0.5 g, 1.2 mmol), $\text{VCl}_3(\text{THF})_3$ (0.97 g, 2.6 mmol) and Et_3N (0.36 ml, 2.6 mmol). Complex **2** was obtained as maroon crystals (0.56 g, 51%). IR/ cm^{-1} 1605(s) (C=N). Elemental analysis for $\text{VClC}_2\text{H}_8\text{N}_2\text{O}_2$ (bake dried 24 h –THF) found (calculated): %C = 65.40 (65.49), H = 3.87 (3.80), N = 5.78 (5.87). MS (EI, m/z): 476 $[\text{M-THF}]^+$. Magnetic moment $\mu = 2.23\mu_{\text{B}}$.

Pre-catalyst 3

Procedure as described for complex **1** using **L3** (0.5 g, 0.8 mmol), $\text{VCl}_3(\text{THF})_3$ (0.34 g, 0.9 mmol) and Et_3N (0.13 ml, 0.9 mmol). Complex **3** was obtained as a dark brown powder (0.34 g, 54%). IR/ cm^{-1} 1609(s) (C=N). Elemental analysis for $\text{VClC}_4\text{H}_5\text{N}_2\text{O}_4$ found (calculated): %C = 69.81 (69.99), H = 7.55 (7.41), N = 3.35 (3.55). MS (EI, m/z): 716 $[\text{M-THF}]^+$. Magnetic moment $\mu = 1.91\mu_{\text{B}}$.

Pre-catalyst 4

Procedure as described for complex **1** using **L4** (0.5 g, 1.2 mmol), $\text{VCl}_3(\text{THF})_3$ (0.97 g, 2.6 mmol) and Et_3N (0.36 ml, 2.6 mmol).

Complex **4** was obtained as a dark brown powder (0.43 g, 63%). IR/ cm^{-1} 1606(s) (C=N). Elemental analysis for $\text{VClC}_3\text{H}_6\text{N}_2\text{O}_4$ found (calculated): %C = 63.37 (63.78), H = 4.85 (4.64), N = 4.83 (4.96). MS (EI, m/z): 492 $[\text{M-THF}]^+$. Magnetic moment $\mu = 1.79\mu_{\text{B}}$.

Pre-catalyst 5^{5b}

Procedure as described for complex **1** using **L5** (0.25 g, 0.6 mmol), $\text{VCl}_3(\text{THF})_3$ (0.33 g, 0.9 mmol) and Et_3N (0.12 ml, 0.9 mmol). Complex **5** was obtained as dark red crystals (0.57 g, 65%). Mp: 110 °C. IR/ cm^{-1} 1609(s) (C=N). Elemental analysis for $\text{V}_2\text{Cl}_4\text{C}_6\text{H}_8\text{N}_2\text{O}_6$ found (calculated): %C = 61.19 (61.33), H = 7.23 (7.38), N = 2.38 (2.38). MS (EI, m/z): 693 $[\text{M-V-4Cl-4THF}]^+$. Magnetic moment $\mu = 1.90\mu_{\text{B}}$.

Pre-catalyst 6^{5b}

Procedure as described for complex **1** using **L6** (0.25 g, 0.6 mmol), $\text{VCl}_3(\text{THF})_3$ (0.49 g, 1.3 mmol) and Et_3N (0.18 ml, 1.3 mmol). Complex **6** was obtained as a red powder (0.34 g, 61%). IR/ cm^{-1} 1608(s) (C=N). Elemental analysis for $\text{V}_2\text{Cl}_4\text{C}_{44}\text{H}_{54}\text{N}_2\text{O}_6$ found (calculated): %C = 55.65 (55.59), H = 5.60 (5.73), N = 3.07 (2.95). MS (EI, m/z): 468 $[\text{M-V-4Cl-4THF}]^+$. Magnetic moment $\mu = 2.18\mu_{\text{B}}$.

Pre-catalyst 9

To a solution of **L9** (0.5 g, 1.4 mmol) in THF (20 ml), $\text{VCl}_3(\text{THF})_3$ (0.57 g, 1.54 mmol) was added and this solution was stirred for 10 minutes before adding Et_3N (0.21 ml, 1.54 mmol). The solution was stirred at room temperature for 4 hours and then concentrated to approximately 15 mL. The mixture was filtered and recrystallised by diffusion of *n*-hexane (10 mL) to yield complex **9** as a brown powder (0.38 g, 57%). IR/ cm^{-1} 1612 (s) (C=N). Elemental analysis for $\text{VCl}_2\text{C}_2\text{H}_3\text{NO}$ found (calculated): %C = 61.15 (61.02), H = 6.70 (6.83), N = 3.08 (2.97). MS (EI, m/z): 452.2 $[\text{M-Cl}^t\text{Bu+H}]^+$. Magnetic moment $\mu = 1.69\mu_{\text{B}}$.

Pre-catalyst 10

To a solution of **L10** (0.5 g, 1.4 mmol) in THF (20 ml), $\text{VCl}_3(\text{THF})_3$ (0.57 g, 1.54 mmol) was added and this solution was stirred for 10 minutes before adding Et_3N (0.21 ml, 1.54 mmol). The solution was stirred at room temperature for 4 hours and then concentrated to approximately 15 mL. The mixture was filtered and recrystallised by diffusion of *n*-hexane (10 mL) to yield complex **10** as a red powder (0.29 g, 36%). IR/ cm^{-1} 1631 (s) (C=N). Elemental analysis for $\text{VCl}_2\text{C}_{16}\text{H}_{16}\text{NO}$ (sample dried *in vacuo* for 12 h, loss of THF) found (calculated): %C = 61.15 (61.02), H = 6.70 (6.83), N = 3.08 (2.97). MS (EI, m/z): 359 $[\text{M}]^+$. Magnetic moment $\mu = 2.05\mu_{\text{B}}$.

Pre-catalyst 13

To a solution of **L12** (0.5 g, 1.7 mmol), which had been held under dynamic vacuum for 5 hours, in toluene (40 ml), $\text{VCl}_3(\text{THF})_3$ (0.29 g, 1.0 mmol) was added and this solution was refluxed for 12 hours. The solvents were removed *in vacuo* and the residue was extracted into hot acetonitrile (35 mL) affording dark orange needles on cooling. (0.49 g, 37%). IR/ cm^{-1} 1605 (s) (C=N),

927 (V=O). Elemental analysis for $\text{VCl}_2\text{C}_{38}\text{H}_{46}\text{N}_2\text{O}_3$ (sample dried *in vacuo* for 12 h, loss of MeCN) found (calculated): %C = 65.00 (65.14), H = 6.70 (6.62), N = 4.12 (4.00). MS (EI, *m/z*, sample dried *in vacuo* 12 h, loss of MeCN): 646.2 $[\text{M}-\text{MeH}-\text{HCl}]^+$ 627.3 $[\text{M}-2\text{HCl}]^+$. Magnetic moment $\mu = 0.982\mu_{\text{B}}$.

Typical homogenous ethylene polymerization procedure

A flame dried (250 mL) pyrex flask was purged several times with ethylene gas at 1 bar pressure. This pressure was maintained throughout the polymerization run. Dry, degassed toluene (100 mL) and ethyltrichloroacetate (ETA, 0.1 mL, 0.72 mmol) were added and stirred for 10 minutes. The required temperature was achieved *via* a water bath, and the co-catalyst was added; the pre-catalyst was then injected as a toluene solution. The polymerization time was recorded from injection of pre-catalyst and left for the required time. The polymerization solution was quenched by addition of methanol and acidified water. The solid polyethylene was then filtered and dried.

Typical ϵ -caprolactone ROP procedure

A Schlenk flask (250 mL) previously baked at 160 °C overnight was charged with the required quantity of pre-catalyst under glove box conditions. Dry, degassed toluene (20 mL) was added, the required temperature was achieved, and one equivalent of benzyl alcohol was then added. The polymerization was initiated by addition of the ϵ -caprolactone and was stirred for the allotted time. Conversion of monomer was determined by ^1H NMR, and the polymerization was quenched by addition of methanol.

Typical parallel pressure reactor polymerization run

A pre-weighed glass vial with stirring paddles was sealed and purged with ethylene. 5 μmol of co-catalyst from a 100 mM heptane solution was added along with co-monomer (if required). Heptane was then added to reach a volume of 4000 μL in the reaction vessel and heated to 80 °C. The ethylene pressure was set to 92 psi (6.34 bar) and the catalyst (along with ETA) was added as a heptane slurry. The run was left stirring for 60 minutes and quenched with CO_2 (35% in N_2). The glass vial was dried by vacuum centrifuge and weighed.

X-ray photoelectron spectroscopy analysis

A small amount ($\sim\text{mg}$) of powdered sample was pressed onto adhesive carbon tape. High resolution XPS core level measurements were performed with a VG Escalab 250 in LENNF, Leeds University, equipped with a conventional hemispherical sector analyser and controlled by a VGX900 data system. XPS experiments were carried out using a high intensity monochromated Al-K α source (1486.6 eV) operated at 15 kV and 20 mA. V-2p, C-1s, Cl-2p and N-1s spectra were recorded using a pass energy of 20 eV. The energy scale of the spectrometer was calibrated to the Ag-3d $_{5/2}$ peak at 368.3 eV. The binding energy scale was calibrated to the C-1s at 284.5 eV. High-resolution peak fitting was performed using CasaXPS software (version 2.3.15).

Crystallographic analyses

Single-crystal X-ray diffraction intensities for compound **2** were measured at 120 K on a Bruker-Nonius Apex II Kappa-CCD diffractometer (at the EPSRC National Crystallography Service), for **L5** and **5** at 140 K on an Oxford Diffraction Xcalibur-3 CCD

Table 4 Summary of the crystal data and structure determination results for compounds **2**, **L5**, **5** and **13**

Compound	2	L5	5	13
Formula	$2(\text{C}_{30}\text{H}_{26}\text{ClN}_2\text{O}_3\text{V}), 1.5\text{THF}$	$\text{C}_{44}\text{H}_{56}\text{N}_2\text{O}_2$	$\text{C}_{60}\text{H}_{86}\text{Cl}_4\text{N}_2\text{O}_6\text{V}_2$	$\text{C}_{38}\text{H}_{46}\text{Cl}_2\text{N}_2\text{O}_3\text{V}, 2 \text{ MeCN}$
Formula weight	1205.99	644.9	1175.0	782.72
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/a$	$P2_1/a$	$Pbca$	$P2_1nb$
Unit cell dimensions				
a (Å)	17.8598(14)	9.6297(3)	15.4851(3)	11.0873(5)
b (Å)	10.7750(8)	12.1792(4)	12.3449(2)	17.9157(8)
c (Å)	31.054(2)	16.2276(6)	33.0323(6)	20.6832(14)
α (°)	90	90	90	90
β (°)	101.730(4)	100.851(4)	90	90
γ (°)	90	90	90	90
V (Å 3)	5851.2(7)	1869.18(11)	6314.5(2)	4108.4(4)
Z	4	2	4	4
Temperature (K)	120(2)	140(1)	140(1)	100
D_{calcd} (Mg m $^{-3}$)	1.369	1.146	1.236	1.262
Absorption coefficient, μ (mm $^{-1}$)	0.470	0.069	0.512	0.414
Crystal size (mm 3)	$0.2 \times 0.16 \times 0.08$	$0.41 \times 0.30 \times 0.09$	$0.43 \times 0.41 \times 0.09$	$0.22 \times 0.01 \times 0.01$
$2\theta_{\text{max}}$ (°)	20	25	25	25
Reflections measured	27 495	19 826	104 961	9744
Unique reflections, R_{int}	5438, 0.111	3295, 0.106	5557, 0.072	5871, 0.048
Reflections with $F^2 > 2\sigma(F^2)$	3866	1981	4572	4516
Transmission factors (max, min.)	0.746, 0.604	1.118, 0.904	1.020, 0.982	1.000, 0.480
Number of parameters	737	221	339	471
R_1, wR_2 [$F^2 > 2\sigma(F^2)$]	0.065, 0.116	0.050, 0.083	0.061, 0.105	0.051, 0.090
R_1, wR_2 (all data)	0.101, 0.127	0.106, 0.096	0.087, 0.113	0.078, 0.098
Largest difference peak and hole (e Å $^{-3}$)	0.39 and -0.30	0.16 and -0.15	0.39 and -0.31	0.31 and -0.29

diffractometer, and for 13 at 100 K on a Rigaku AFC12 Kappa-3-circle, Saturn724 + CCD diffractometer (at the EPSRC National Crystallography Service); all machines were equipped with Mo-K α radiation and graphite monochromator. Intensity data were measured by thin-slice ω - and ϕ -scans.

The Apex data for 2 were processed with the DENZO/SCALEPACK²⁰ programs and SADABS,²¹ the Xcalibur data were processed (including correcting for absorption) using the CrysAlis-CCD and -RED programs,²² and the Rigaku data were processed with CrystalClear-SM.²³ Structures were determined by the direct methods routines in the SHELXS program²⁴ and refined by full-matrix least-squares methods, on F²'s, in SHELXL.²⁴

In compound 2, there is disorder in one of the THF ligands, and one of the THF solvent molecules lies disordered about a centre of symmetry. The non-hydrogen atoms (except the minor component C atom in the disordered ligand, and the half-atoms in the disordered THF molecule) were refined with anisotropic thermal parameters. The phenolic hydrogen atom in L5 was located in a difference map and was refined freely. In 5, there is disorder of a methylene group in one of the THF ligands; the minor occupancy carbon atom was refined isotropically. Except for the phenolic hydrogen atom in L5, all hydrogen atoms were included in idealised positions and their U_{iso} values were set to ride on the U_{eq} values of the parent carbon atoms. Scattering factors for neutral atoms in all samples were taken from reference.²⁵ Computer programs used in this analysis have been noted above, and were run through WinGX²⁶ on a Dell Precision 370 PC at the University of East Anglia.

Crystal data and refinement results for the four complexes are collated in Table 4. CCDC 837291–837293 and 895725.†

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