Vanadium aminophenolate complexes and their catalytic activity in aerobic and H_2O_2-mediated oxidation reactions

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Abstract

Vanadium compounds supported by tetradentate amino-bis(phenolate) ligands, [VO(OMe)($O_2NO^{BuMeMeth}$)] (**1**), [VO(OMe)(ON_2O^{BuMe})] (**2**), [VO(OMe)(O_2NN^{BuBuPy})] (**3**), and [VO(OMe)($O_2NO^{BuBuFurf}$)] (**4**) (where ($O_2NO^{BuMeMeth}$) = $MeOCH_2CH_2N(CH_2ArOH)_2$, Ar = 3,5-C_6H_2-Me, *t*-Bu]; (ON_2O^{BuMe}) = $HOArCH_2NMeCH_2CH_2NMeCH_2ArOH$, Ar = 3,5-$C_6H_2$-Me, *t*-Bu; ($O_2NN^{BuBuPy}$) = $C_5H_4NCH_2N(CH_2ArOH)_2$, Ar = 3,5-C_6H_2-*t*-Bu_2; ($O_2NO^{BuBuFurf}$) = $C_4H_3OCH_2N(CH_2ArOH)_2$, Ar = 3,5-C_6H_2-*t*-Bu_2) were synthesized and characterized by NMR spectroscopy, MALDI-TOF mass spectrometry and UV-vis data. The catalytic activity of **1**-**4** as homogeneous catalysts in the aerobic oxidation of 4-methoxybenzyl alcohol and 1,2-diphenyl-2-methoxyethanol was explored. **1** and **2** showed moderately superior activity compared with **3** and **4**, which might be due to increased stability of these complexes. **1**-**4** showed limited reactivity in H_2O_2-mediated oxidation of diphenylether and benzylphenylether.

Introduction

Nowadays, chemistry related to biomass (in particular, lignocellulose) is of significant interest because of the desire for renewable chemical and fuel production.[1] This has been brought about for a number of reasons including political conflicts, and the negative effects of petroleum on the environment and the advantages of renewable resources, such as their abundance, sustainability and often low cost. Among the three components of lignocellulose (cellulose, hemicellulose, and lignin), a large amount of research has been directed towards biofuel production (e.g. ethanol) from cellulose.[2] In contrast, the utilization of lignin as a feedstock has been hampered due to lignin's structural complexity, which leads to challenges in its use as a feedstock.[3] However, the development of new homogeneous catalysts to depolymerize lignin in a selective fashion may lead to efficient conversion technologies, which could provide lignin-derived aromatic feedstocks for chemical production.[4] Many of these catalysts perform aerobic oxidation or H_2O_2-mediated C-O bond cleavage reactions.

Recently, the field of aerobic oxidation catalysis has grown significantly as the search for new green oxidation processes continues. Many 3*d* transition metals (V, Mo, Fe, Cu) are attractive in terms of their abundance and low cost as the active centres for aerobic oxidation processes.[3d] [5] In particular, vanadium complexes are well known as an attractive class of catalysts,[6] [7] mediating the aerobic oxidation of organic substrates including benzylic, allylic, and propargylic alcohols.[8] Hanson and co-workers have shown that the complex $(HQ)_2VO(OiPr)$ (HQ = 8-quinolinate), (Figure 1), **I**, efficiently catalyzed the oxidation of benzylic, allylic, and propargylic alcohols with air in the presence of NEt_3.[9] It should be noted that using air instead of pure oxygen is advantageous, as it reduces the safety hazard associated with heating organic solvents under elevated O_2 pressure.[10]

A growing number of vanadium(IV) and (V) complexes of multidentate N-O donor ligands have been reported as very active catalysts for C−O and C−C bond cleavage reactions in model compounds of lignin, which show a significant diversity of reactivity.[3a, 9, 11] In 2010, Son and Toste reported that a series of vanadium (V) complexes bearing Schiff base ligands (**II**-**IV**) (Figure 1), which could be used as catalysts for C−O bond cleavage in dimeric lignin model compounds containing a β-O-4 linkage.[3a] More recently, Toste's group used the same vanadium catalysts to treat lignin samples isolated from *Miscanthus giganteus* at 80 °C for 24 h with air as the oxidant.[11e] The results showed that the catalytic system was effective in depolymerizing

actual lignin at β-O-4′ linkages, also, it was selectively cleaved in the degradation process, just as in the case of lignin models. Furthermore, they investigated the effect of the 8-quinolinate vanadium complex (Figure 1, **VII)** which was previously reported by Hanson et al.,[11c] on organosolv lignins, and showed that catalyst **VII** lowers the molecular weights of organosolv lignins to a similar degree as catalyst **V**.

In a study by Hanson *et al.* dipicolinate vanadium (V) complexes (Figure 1 **VII a, b**) were used as catalysts to oxidize lignin model compounds.[11a, b] The results showed that both C−H and C−C were cleaved in these reactions. They also reported in another study that vanadium catalysts **VII, I** [11c],[3a] showed a significant difference in selectivity for the aerobic oxidation of phenolic and non-phenolic lignin model compounds compared with earlier work by Toste. The vanadium catalysts allowed the cleavage of the C-C bond between the aryl ring and the adjacent alcohol group, and C-O bond cleavage products were also afforded.[11c],[12]

Our group, and others, have been studying the chemistry and catalytic behaviour of aminophenolate metal complexes over the past decade. As the ligands contain a mixed set of N- and O-donor atoms, they have shown a great ability to coordinate to a range of metal centres and their steric and electronic properties are easily varied by changing their backbone and phenol substituents.[13] Recently vanadium (V) complexes of bis(phenolate) pyridine and amino-bis(phenolate) ligands have been reported by Hanson's group to be excellent catalysts (Figure 1, **IX** and **X**) for aerobic oxidative C−O bond cleavage reactions in several different non-phenolic lignin model compounds,[11f] with similar reactivity to their earlier dipicolinate catalysts **VII a** and **b**.

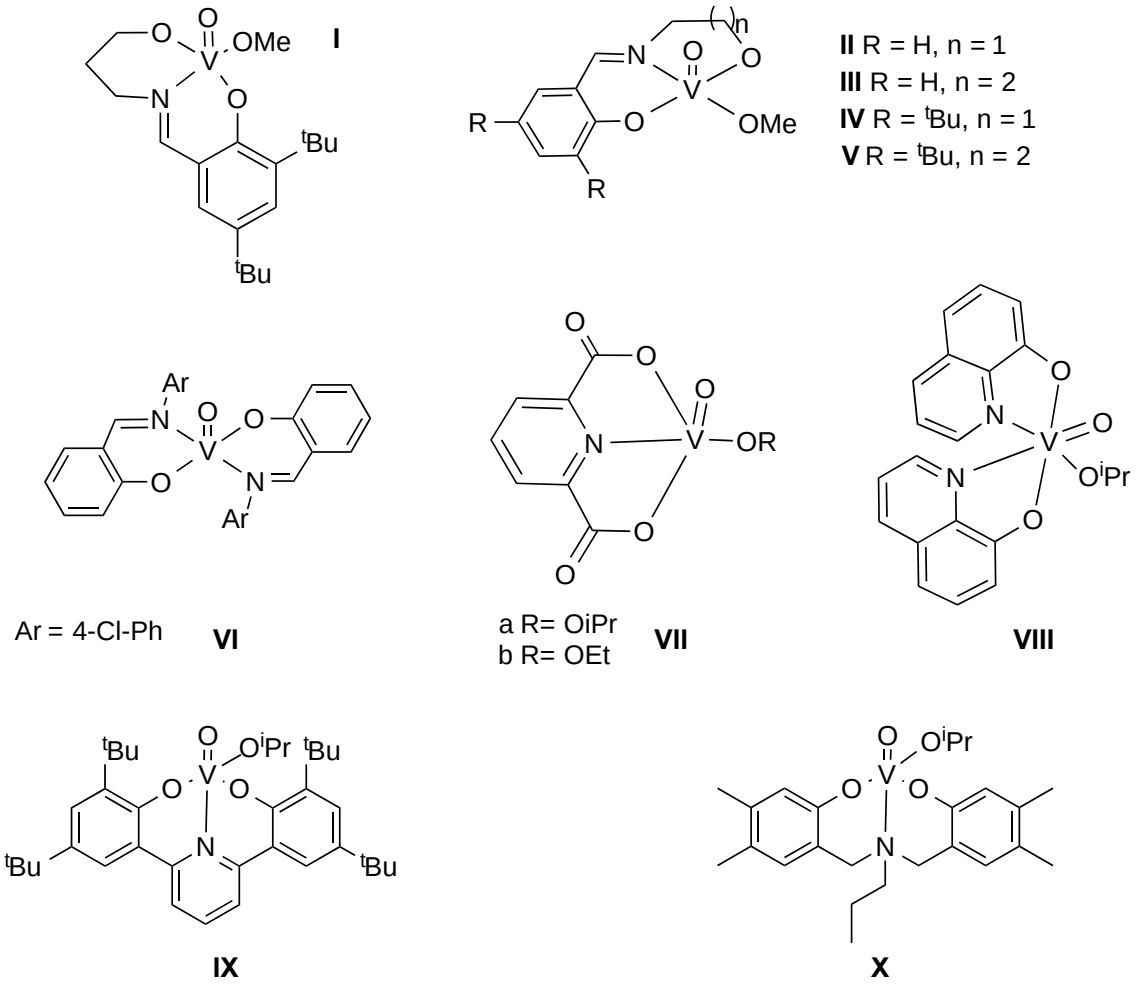


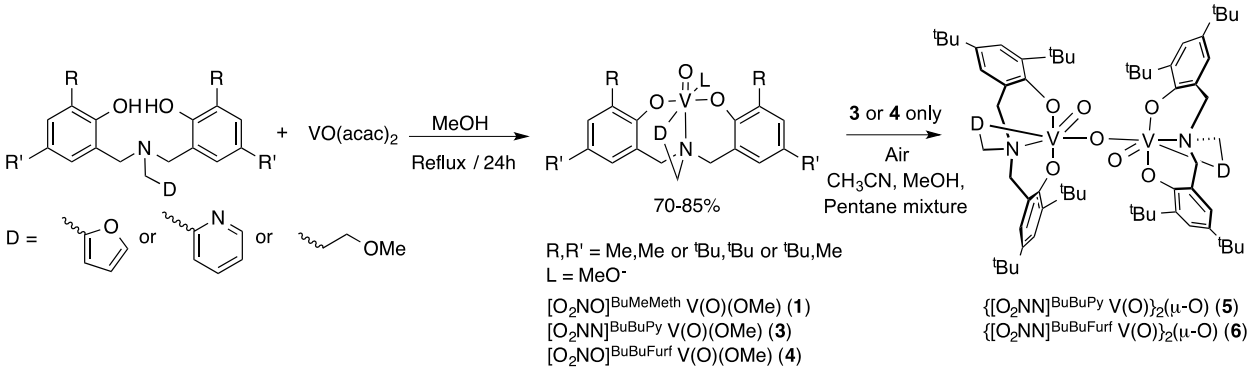
Figure 1. Structures of vanadyl-derived catalysts for transformations of model lignin compounds

Herein, we describe the syntheses and structures of amino-bis(phenolate) vanadyl complexes containing tetradentate tripodal ligands $[ONOL]^{RR'}$ where L is a neutral N or O-containing donor group and R/R' are alkyl groups found in the *ortho* and *para* positions of the phenolate donor. We also report their use as catalysts for the aerobic oxidation of alcohols and C–O bond cleavage reactions in simple lignin model compounds.

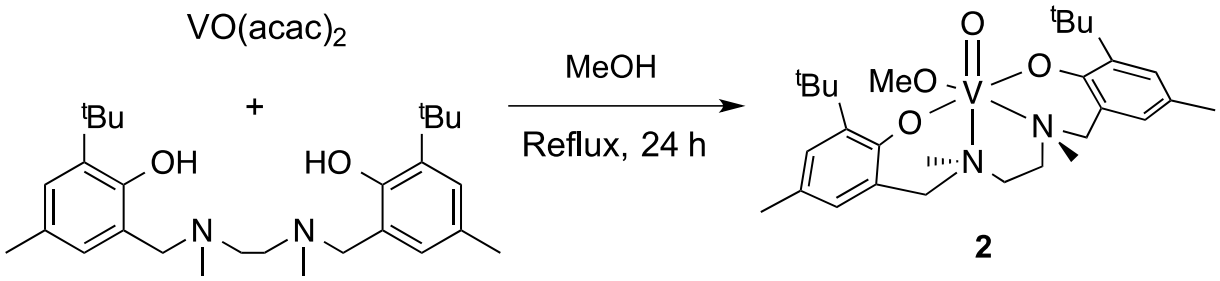
Results and discussion

Synthesis and characterization of V complexes

The amine-bis(phenol) protio ligands $H_2[O_2NO]^{BuMeMeth}$, $H_2[ON_2O]^{BuMe}$, $H_2[O_2NN]^{BuBuPy}$, and $H_2[O_2NO]^{BuBuFurf}$ were prepared according to previously reported procedures.[14] All ligands contain 2,4-alkyl-substituted phenols but contain different pendant donor groups (methoxy, pyridyl and furfuryl), or two tertiary amines situated in the backbone of the ligand. V(V) complexes **1**-**4** were synthesized *via* reaction of the protonated ligands in methanol with $VO(acac)_2$ for 24 h, affording dark black, purple or blue solids complex in 70-85% yield (Schemes 1 and 2). The methoxide ligand is apparent in the NMR and MALDI-TOF mass spectra of the crude and purified products. In some cases, the compounds decompose upon recrystallization to form oxo-bridged complexes (Scheme 1). Related oxo-bridged complexes have been prepared by others.[15] **1**-**4** were characterized using ^{1}H NMR spectroscopy, MALDI-TOF mass spectrometry, X-ray crystallography, UV-vis spectroscopy and elemental analysis (see Supporting Information for spectra). The absence of acetylacetonate ligands was confirmed by FT-IR spectroscopy. The ^{1}H NMR spectra of **1**-**4** contain the expected signals typical of diamagnetic transition metal aminophenolate complexes. They also all contain a diagnostic signal close to δ 5.00, which was assigned to the methoxide ligand (δ 5.30, 5.05, 4.89, 5.33 for complexes **1**-**4** respectively).



Scheme 1. Synthesis of vanadium complexes (**1**, **3**, and **4**) and oxo-bridged complexes (**5** and **6**).



Scheme 2 . Synthesis of vanadium complex **2**.

The MALDI-TOF mass spectra were obtained via charge transfer ionization in the presence of the neutral UV-absorbent matrix, anthracene.[16], [17] The mass spectra generated for the V(V) complexes described herein showed characteristic fragment ions. In particular they exhibited $\{[O_2NO]^{BuMeMeth}V{=}O\}^{+\bullet}$ (**1**), $\{[ON_2O]^{BuMe}V{=}O\}^{+\bullet}$ (**2**), $\{[O_2NN]^{BuBuPy}V{=}O\}^{+\bullet}$ (**3**), $\{[O_2NO]^{BuBuFurf}V{=}O\}^{+\bullet}$ (**4**) fragments at *m/z* 492.16, 505.20, 609.24 and 602.25 respectively. The experimental isotopic distribution pattern for each of these ions shows good agreement with the theoretical patterns (Figures S5–S8). Additional peaks in the lower mass region of the spectra correspond to ligand fragments. For the oxo-bridged complexes **5** and **6**, there are small peaks at *m/z* 1234.6 and 1212.6, which correspond to their respective molecular ions.

Electronic absorption spectra of complexes **1**-**4** in CH_2Cl_2 show multiple bands in the UV and visible regions (Table 1 and Figures S9-S13). The highest energy bands (<300 nm) result from ligand $\pi \rightarrow \pi^*$ transitions. Other intense bands also present in the UV region (300–350 nm), were assigned to charge-transfer from the out-of-plane pπ orbital (HOMO) of the phenolate oxygen to the empty d_{x2-y2}/d_{z2} orbitals of the V centre. The lowest energy bands (visible region) arise from charge-transfer transitions from the in-plane π orbital of the phenolate to the empty d orbitals on V.

Table 1. UV−Vis spectral data of the vanadium complexes in CH_2Cl_2.

Complex	$\pi \rightarrow \pi^*$	out-of-plane $p\pi \rightarrow d$	in-plane $p\pi \rightarrow d$
	λ /nm (ε /$M^{-1}cm^{-1}$)	λ /nm (ε /$M^{-1}cm^{-1}$)	λ /nm (ε /$M^{-1}cm^{-1}$)
$[O_2NO]^{BuMeMeth}$ V(O)(OMe) (**1**)	248(10900)	276 (115000)	684 (34000)
$[ON_2O]^{BuMe}$ V(O)(OMe) (**2**)	243 (99000)	252 (92000)	601 (56000)
$[O_2NN]^{BuBuPy}$ V(O)(OMe) (**3**)	240 (98570)	275 (105000)	594 (10250)
$[O_2NO]^{BuBuFurf}$ V(O)(OMe) (**4**)	240 (105000)	278(115000)	603 (47500)

Single crystals suitable for X-ray analysis were obtained after several weeks from a saturated methanol solution cooled to −20 °C (**1**, **2**) or a mixture of methanol, pentane and acetonitrile stored at 6 °C (**3**, **4**). ORTEP drawings are shown in Figures 2-5 with selected bond distances and angles given in Table 2.

The solid-state structures of **1** and **2** (VNO_5) and (VN_2O_4) confirm that the V^V centres reside in distorted octahedral environments. For **1** O(1)−V(1)−O(2), O(3)−V(1)−O(4) and N(1)−V(1)−O(5) angles are 159.78(7)°, 172.13(8)°, and 156.59(7)° respectively; for **2**, O(1)−V(1)−O(2), O(4)−V(1)−N(1), and O(3)−V(1)−N(2), angles are 164.06(15)°, 161.33(17)° and 167.28(16)° respectively. The phenolate oxygen atoms are *trans* orientated for **1** and **2** with V(1)–O(1) distances, 1.899(20) and 1.858(3) Å and V(1)–O(2), distances, 1.886(18) and 1.878(3) Å respectively. The N1 atom in **1** is *trans* to the methoxide oxygen O(5) and *cis* to the oxo atom O(4). In **2**, the methoxide bond (V−O4) is slightly shorter than the corresponding bond in **1** (V−O5). This might be due to steric considerations when the orientation of the *tert*-butyl groups are taken into account. The longer V(1)−O(3) distance in **1** (2.2567(16) Å) implies weak binding of the ether group in the sidearm to the vanadium, and also reflects the *trans* effect of the oxo group, as has been observed in other complexes.[18] The $V-O_{phenolate}$ distances are within the values that have been observed for these types of complexes previously.[18-19]

Upon recrystallization in air, **3** and **4** formed oxo-bridged complexes. The solid-state structures of the resulting compounds **5** and **6** confirm that the V^V centres reside in distorted octahedral environments. Although only small amounts of **5** and **6** were obtained, mass spectrometric and elemental analytical data confirmed their formulation. In **5**, O(1)−V(1)−O(2), O(3)−V(1)−N(1) and N(2)−V(1)−O(4) angles are 165.16(12)°, 166.04(13)°, and 160.09(10)° respectively; in **6**, O(1)−V(1)−O(2), O(4)−V(1)−O(3), and O(5)−V(1)−N(1), angles are

164.71(8)°, 162.40(5)° and 164.27(8)° respectively. For **5** atoms O(1), O(2), N(2), and O(4) lie in the plane and *cis* to the terminal oxo O(3) group and the nitrogen atom N(1), and for **6** atoms O(1), O(2), O(3), and O(4) lie in the plane and are *cis* to the terminal oxo O(5) group and the nitrogen atom N(1). The two vanadium centres are linked by a linear V−O−V bridge; both complexes **5** and **6** have nearly identical vanadium-oxo bond distances, which are longer than in a similar complex.[19] The terminal V=O bond distance for both complexes are also consistent, but moderately shorter than the values that were reported for similar complexes.[19] The $V-O_{phenolate}$ distances are in agreement with those of **1**, **2** and with those observed in related complexes.[18-19] Unfortunately, we were not able to isolate sufficient quantities of **5** and **6** to study in detail their behaviour in subsequent catalytic reactions.

Table 2. Selected Bond Lengths (Å) and Angles (°) for **1**, **2**, **5**, **6**

	1	**2**	**5**	**6**
V(1)−N(1)	2.244(2)	2.272(4)	2.377(3)	2.344(2)
V(1)−N(2)		2.355(4)	2.243(3)	
V(1)−O(1)	1.8994(20)	1.858(3)	1.865(3)	1.8576(18)
V(1)−O(2)	1.8860(18)	1.878(3)	1.896(3)	1.8525(18)
V(1)−O(3)	2.2567(16)	1.579(4)	1.620(3)	2.1655(19)
V(1)−O(4)	1.5851(16)	1.766(3)	1.8071(7)	1.7737(4)
V(1)−O(5)	1.7923(20)			1.6052(17)
O(1)−V(1)−O(2)	159.78(7)	164.06(15)	165.16(12)	164.71(8)
O(1)−V(1)−O(3)	83.68(7)	97.32(16)	94.86(14)	84.75(8)
O(2)−V(1)−O(3)	83.95(6)	94.00(15)	95.22(13)	83.75(8)
O(4)−V(1)−O(1)	95.16(9)	93.88(13)	94.79(9)	93.66(6)
O(4)−V(1)−O(2)	94.91(7)	93.62(14)	92.71(9)	94.26(6)
O(3)−V(1)−O(4)	172.13(8)	106.49(18	106.69(10)	162.40(5)
O(1)−V(1)−N(1)	83.35(7)	80.61(12)	83.25(12)	83.89(7)
O(2)−V(1)−N(1)	77.86(8)	87.85(12)	84.35(11)	83.08(7)
O(3)−V(1)−N(1)	73.65(7)	91.94(17)	166.04(13)	72.56(7)
O(4)−V(1)−N(1)	98.49(9)	161.33(17)	87.27(8)	89.83(5)
O(1)−V(1)−O(5)	97.79(7)			94.78(9)
O(2)−V(1)−O(5)	96.54(9)			95.59(9)
O(3)−V(1)−O(5)	83.20(7)			91.71(8)
O(4)−V(1)−O(5)	104.67(9)			105.90(7)
N(1)−V(1)−O(5)	156.59(7)			164.27(8)
O(1)−V(1)−N(2)		80.61(12)	87.44(12)	
O(2)−V(1)−N(2)		82.63(14)	81.22(12)	
O(3)−V(1)−N(2)		167.28(16)	92.80(13)	
O(4)−V(1)−N(2)		86.00(15)	160.09(10)	
N(2)−V(1)−N(1)		75.73(14)	73.33(12)	

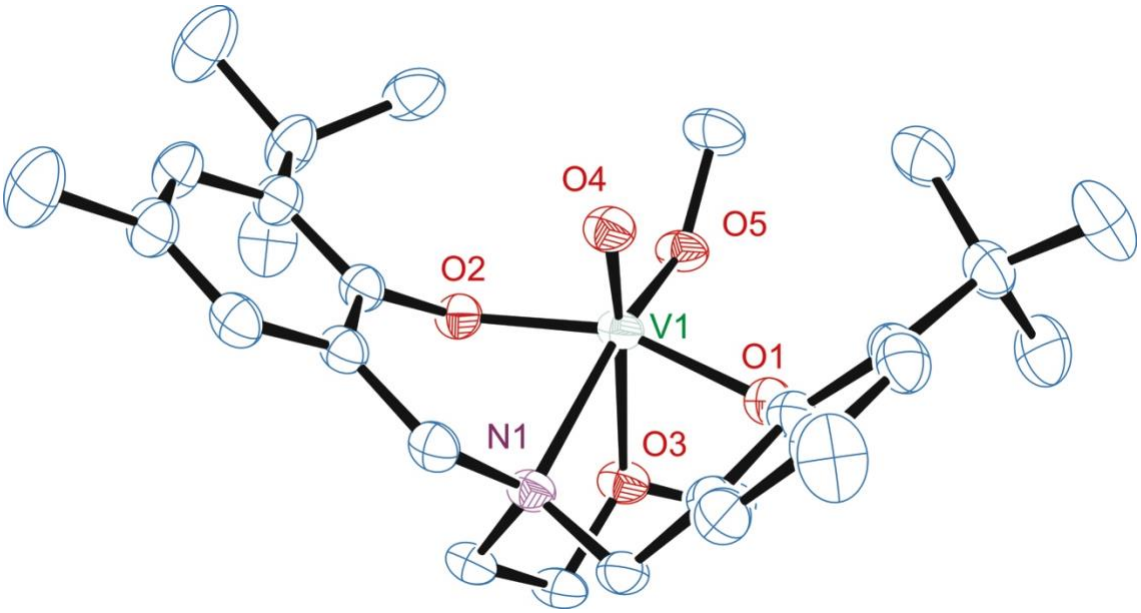


Figure 2. X-ray structure of **1** (thermal ellipsoids at 50% probability, H atoms omitted for clarity).

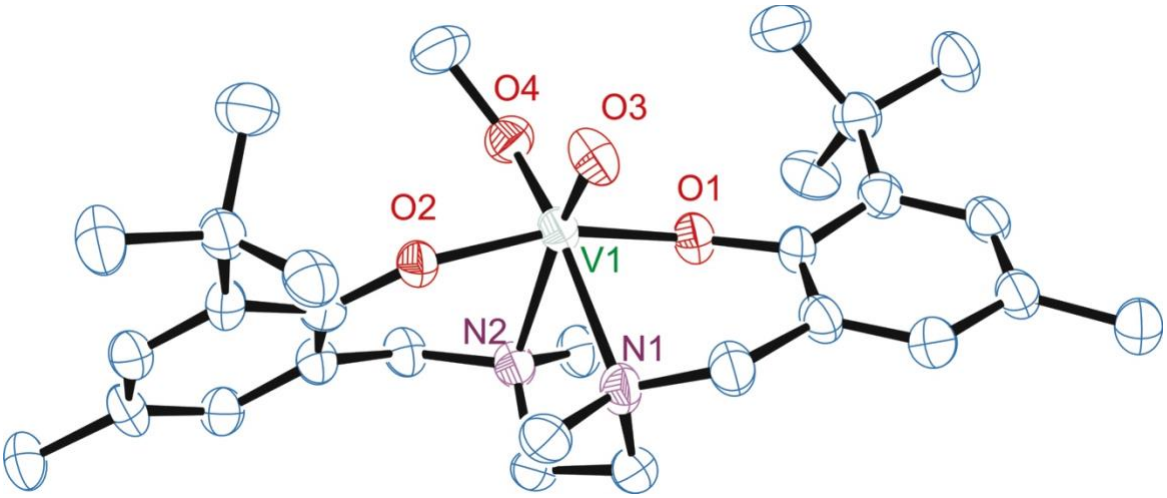


Figure 3. X-ray structure of **2** (thermal ellipsoids at 50% probability, H atoms omitted for clarity).

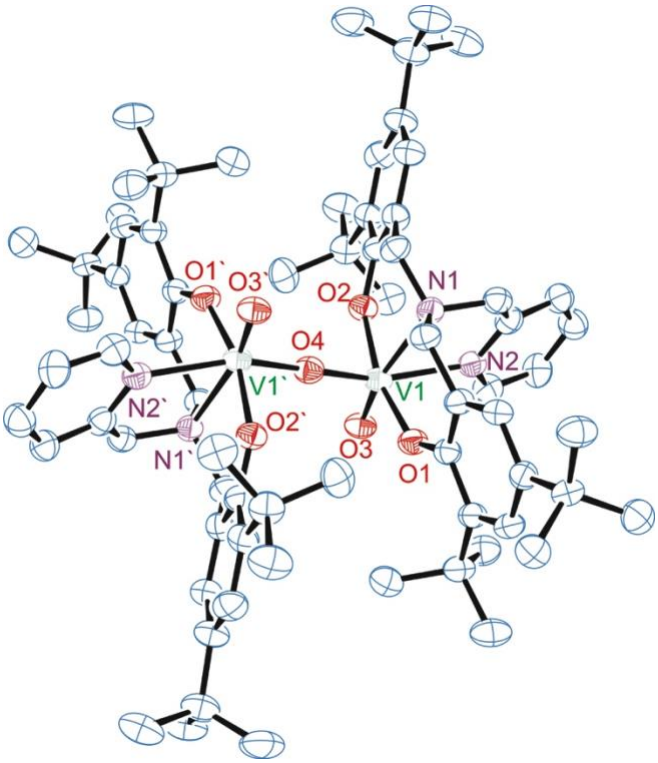


Figure 4. X-ray structure of **5** (thermal ellipsoids at 50% probability, H atoms omitted for clarity).

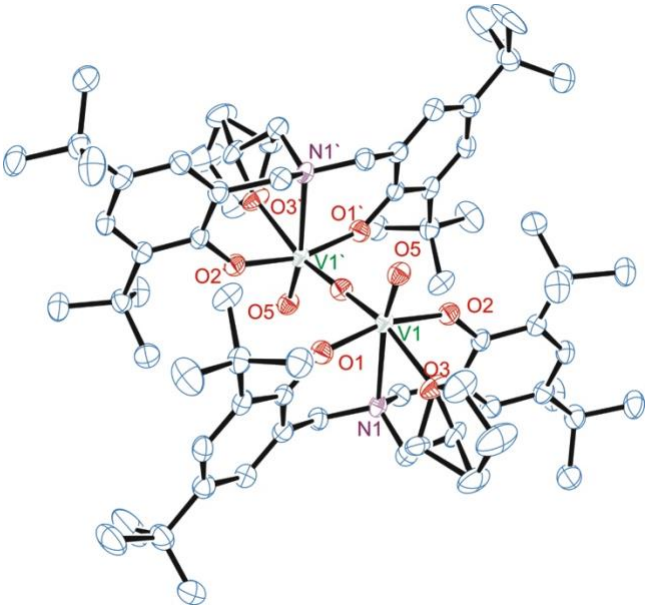
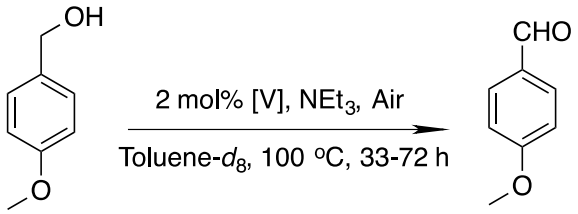


Figure 5. X-ray structure of **6** (thermal ellipsoids at 50% probability, H atoms omitted for clarity).

Catalytic oxidation reactions

Inspired by the recent results obtained by the group of Hanson,[11f] complexes **1**-**4** were screened

for their activity in the aerobic oxidation of 4-methoxybenzyl alcohol at several different temperatures 80-140 °C using toluene as the solvent in the absence of a base additive. We postulated, that in the case of **3**, the pendant pyridyl might act as an internal base. No significant oxidation of the substrate was observed under the following conditions: 0.5 mmol of alcohol, 2 mol% of V (**1**-**4**), in toluene-*d8* 100 °C (Table 3, entry 1). However, addition of a base (NEt_3) facilitated the oxidation of 4-methoxybenzyl alcohol with conversions of up to 90% (Table 3, entry 2). It should be noted that at shorter reaction times there was little difference in activities between the four complexes studied. They all achieved approximately 30% conversion in 12 h. This suggests that complexes **3** and **4**, which give lower conversions after 72 h compared with **1** and **2**, are less stable catalysts. Based on the structures described above, we propose that they decompose to form catalytically inactive oxo-bridged compounds such as **5** and **6.** Mechanisms proposed to date indicate that metal-alkoxide bonds are crucial in these reactions,[20] and these bonds do not exist in oxo-complexes **5** and **6**. Increasing the reaction temperature from 80 to 100 °C led to moderate improvements in conversion (100%, 93% for **1** and **2**, respectively, after 60 h under air in toluene, Table 3, entry 3). Data for the reactions at 140 °C is also reported (Table 3, entry 4) and similar conversions can be achieved after 36 h. A control reaction with 4-methoxybenzyl alcohol and base only (no vanadium) in toluene-*d8* under air showed no reaction when heated at 140 °C for 3 days. Reactions were also performed in acetonitrile-*d3*, as it is a widely used solvent in oxidation chemistry. Conversion levels in this, even at longer reaction times, were significantly lower than in toluene (Table 3, entry 5). **1** and **2** are slightly less reactive than related compounds (Figure 1, **IX**, **VIII**) previously studied by Hanson and co-workers (up to 99%, 60-80 °C, 24-48 h) respectively.[11c, f] These differences in activities are likely associated with the donor ability of the pendant group.



Scheme 3. Catalytic aerobic oxidation of using V complexes

Table 3. Aerobic Oxidation of 4-Methoxybenzylalcohol Using Vanadium Complexes (**1**-**4**) [a]

Entry	Additive	T (°C)	Time (h)	Conversion (%) [b]
1	none	80	72	trace (**1**-**4**)
2	NEt_3	80	72	(**1**) 90 (**2**) 85 (**3**) 70 (**4**) 75 (**X**) 93
3	NEt_3	100	60	(**1**) 100 (**2**) 93 (**3**) 77 (**4**) 85
4	NEt_3	140	36	(**1**) 100 (**2**) 100 (**3**) 84 (**4**) 95
5 [c]	NEt_3	120	106	(**1**) 52
6	NEt_3	80	65	(**IX**) 99 (**X**) 80 [8f]
7	NEt_3	60	24	(**VIII**) 99 [8c]

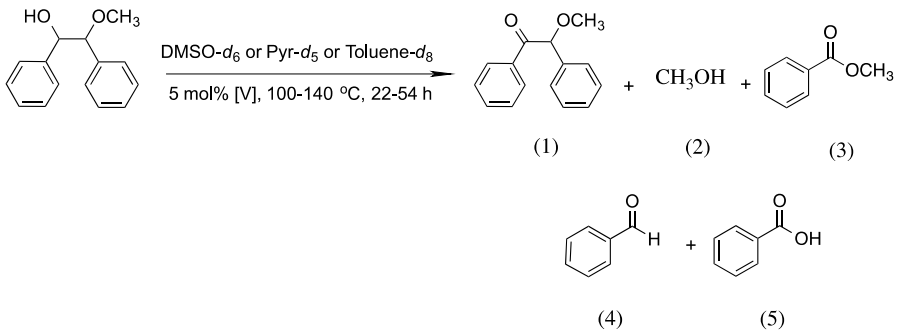
[a] Conditions: 2 mol% of **1**, **2**, **3** or **4**, 10 mol% additive, in toluene-*d8*. Vanadium complex identified in parentheses. [b] Conversion determined by ^{1}H NMR spectroscopy. [c] In acetonitrile-*d3*.

We propose that our homogeneous vanadium (V) catalysts perform these oxidations *via* a mechanism similar to that proposed by Hanson and co-workers, *i.e.* a two-electron base-assisted redox dehydrogenation mechanism.[21] [22] The alkoxide ligand on the vanadium complex exchanges readily with free benzyl alcohol in the first step. The base then deprotonates the benzyl alkoxide at the methylene, which leads to the formal dehydrogenation of the benzyl alcohol and two-electron reduction of the metal centre (V^{5+} to V^{3+}).

Studying model compounds of lignin instead of lignin itself is a good way to get a better understanding of the reactivity of corresponding lignin substructures because of the difficulty associated with the characterization of structural changes of lignin. In this study, 1,2-diphenyl-2-methoxyethanol, diphenylether, and benzylphenylether were chosen to represent the lignin model compounds, air and hydrogen peroxide were using as oxidizing agents under the catalytic influence of the vanadium complexes.

After the promising results concerning the aerobic oxidation of 4-methoxybenzylalcohol,

the vanadium complexes were evaluated as catalysts for the aerobic oxidation of the lignin model compound 1,2-diphenyl-2-methoxyethanol (Scheme 4). The substrate was heated with 5 mol% of vanadium complex (**1**-**4**) at 100 °C for 54 h. The product distribution for the catalytic oxidation differed in DMSO-*d6*, pyr-*d5* and toluene-*d8* solvents but similar conversions were achieved (Table 4, data provided for **4**, although **1**-**3** also gave similar yields of each product). Product identities were confirmed via GC-MS analyses. Control reactions with 1,2-diphenyl-2-methoxyethanol only (no vanadium) in DMSO-*d6*, pyr-*d5* and toluene-*d8* solvents under air showed no reaction when heated at 140 °C for 3 days. Table 5 provides a direct comparison of compounds **1**-**4** for the conversion of 1,2-diphenyl-2-methoxyethanol over time. These data suggest that there is very little ligand effect in these catalytic reactions within this family of complexes. The nature of the amine used in preparing ligand (leading to the presence or absence of a pendant arm, or the type of pendant donor) does not significantly influence the conversion levels achieved, which were in all cases 90-100%. As the substrate can yield multiple molecules upon oxidation via bond cleavage reactions, it should be noted that the sum of the product yields can be in excess of 100%. In DMSO-*d6*, **4** gave benzaldehyde (90%), methanol (46%), methyl benzoate (36%) and benzoin methyl ether (18%) as the major products and a small amount of benzoic acid (Table 4, entry 1). A different product distribution was observed when the catalytic reaction was run under the same reaction conditions in pyr-*d5* solvent. After 54 h, the starting material had been completely consumed, and the organic products consisted of, methyl benzoate (67%), benzoin methyl ether (15%), and methanol (2%). Benzaldehyde was detected as a minor product (1%) and no benzoic acid was detected (Table 4, entry 2). Whereas, when the catalytic reaction was run under the same reaction conditions in toluene-*d8* solvent, a third product distribution was observed (Table 4, entry 3). The major products were methyl benzoate (57%) and benzaldehyde (51%), and a small amount of benzoic acid (2%) was also detected. No benzoin methyl ether and methanol were not observed. For comparison, Hanson and co-workers under similar reaction conditions in DMSO-*d6* or pyr-*d5* as the solvent observed a different product distribution at conversion levels of 95%; benzaldehyde 73% (DMSO), 9% (pyr), methyl benzoate 69% (DMSO), 6% (pyr), benzoic acid 5% (DMSO), 85% (pyr), and methyl benzoate 5% (DMSO), 84% (pyr).



Scheme 4. Reaction of vanadium complexes with 1,2-diphenyl-2-methoxyethanol

Table 4. Aerobic oxidation of 1,2-diphenyl-2 methoxyethanol using **4** in a range of solvents[a]

Entry	Conv (%)	Solvent	Yield of products[b]				
			1 [%]	2 [%]	3 [%]	4 [%]	5 [%]
1	90	DMSO-d_6	18	46	36	90	0.2
2	99	Pyr-d_5	15	2	67	1	--
3	99	Toluene-d_8	--	--	57	51	2

[a] 0.5 mmol of lignin model, 5 mol% of **4**, 54 h. All runs were carried out at 100 °C, using pyridine-d_5, DMSO-d_6, or toluene-d_8 as solvents, conversions and yields determined by integration against an internal standard (*p*-xylene). [b] Up to 5 products were identified as shown in Scheme 4.

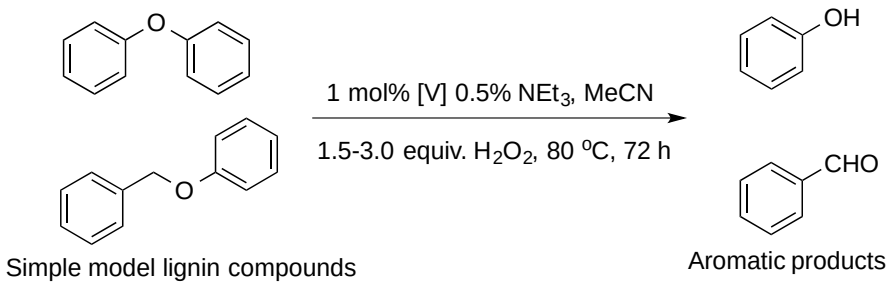
Table 5. Comparison of conversion levels for aerobic oxidation of 1,2-diphenyl-2 methoxyethanol using **1**-**4** [a]

Entry	Time	**1**	**2**	**3**	**4**
1	12 h	62	75	72	75
2	24 h	90	86	84	78
3	36 h	94	100	100	100

[a] 5 mol% **1**-**4**, 0.5 mmol of lignin model, 140 °C, toluene-d_8. Conversion determined by integration against an internal standard (*p*-xylene).

Diphenylether and benzylphenylether were then studied as simple substrates for catalytic oxidation reactions using H_2O_2 as the oxidant to determine if benzylic ether cleavage was selective compared with aromatic, Ph-O-Ph, cleavage. A solution of H_2O_2 was added over a period of 1 h at 1 mL h^{-1} using a syringe pump to a solution of the substrate and catalyst, **1**-**4** (2 mol%) at 80 °C. However, no significant oxidation of the substrate was observed under these conditions. Addition of a base (NEt_3) and use of a different solvent (acetone or toluene) did not

prompt the oxidation of either compound. However, when acetonitrile was used as a solvent diphenylether, and benzylphenylether, gave 10% and 9% yield of phenol, and 15% yield of benzaldehyde for benzylphenylether, after stirring the reaction mixture at 80 °C for 72 h (Table 5). This shows that no selectivity in terms of C-O-C cleavage was observed and reactivity towards such bonds is poor especially when compared with reactions of 1,2-diphenyl-2 methoxyethanol using **1**-**4** in air. Control reactions showed no reaction when base, solution of H_2O_2 and diphenylether or benzylphenylether (no vanadium) were heated and stirred in acetonitrile under air at 80 °C for 3 days.



Scheme 5. Reaction of vanadium complexes in H_2O_2-mediated oxidation of aromatic ethers.

Table 6. Catalytic oxidation of diphenylether and benzylphenylether using **1**-**4** with H_2O_2 [a]

Entry	Substrate	Additive	Conv[%]	Yield of products	
				Phenol	Benzaldehyde
1	Diphenyl ether	--	< 1	--	--
2	Benzylphenyl ether	--	< 1	--	--
3[a]	Diphenyl ether	Et_3N	10	10	--
4[a]	Benzylphenyl ether	Et_3N	15	9	15

[a] 0.5 mmol of ether, 2 mol% **4**, 10 mol% additive,1.5 mmol H_2O_2 in MeCN, 72 h, conversions determined by GC using dodecane as an internal standard. Note: similar reactivity was observed for compounds **1**-**3**.

Conclusions

Four new vanadium (V) complexes of amino-bis(phenolate) ligands have been synthesized and four structures determined by single crystal X-ray diffraction. Crystallography showed that some of the alkoxide derivatives decompose to yield oxo-bridged dimers upon storage in air. Their parent complexes were also less active in oxidation reactions of 4-methoxybenzylalcohol, which suggests that the bridged complexes might be catalytically inactive species formed during oxidation processes. All complexes were also tested for catalytic

aerobic oxidative C-C bond cleavage of 1,2-diphenyl-2-methoxyethanol, which afforded benzaldehyde and methyl benzoate as the major products. Catalytic, oxidative C-O bond cleavage of diphenylether, and benzylphenylether was also demonstrated, however, the conversions were quite low. Future work will focus on designing more active and stable catalysts for aerobic oxidation reactions as well as examining the reactivity of these species in other catalytic processes.

Experimental

General methods and materials: Starting materials for all syntheses were purchased from Strem, Aldrich or Alfa Aesar and were used as received. Ligands were prepared via literature procedures.[14c] $CDCl_3$, toluene-d_8, DMSO-d_6 were purchased from Cambridge Isotope Laboratories and pyridine-d_5 from Aldrich. HPLC grade solvents were used as purchased. All syntheses were performed under ambient laboratory atmosphere unless otherwise specified. NMR spectra were recorded on Bruker Avance-500 or Avance III-300 spectrometers and referenced internally to TMS. MALDI-TOF mass spectra were recorded in reflectron mode on an Applied Biosystems Voyager DE-PRO equipped delayed ion extraction and high performance nitrogen laser (337 nm). Samples were prepared at a concentration of 0.02 mg L^{-1} in toluene. Anthracene was used as the matrix, which was mixed at a concentration of 0.02 mg L^{-1}. UV-vis spectra were recorded on an Ocean Optics USB4000+ spectrophotometer. GC-MS data were obtained on an Agilent Technologies 7890 GC with 5975 MSD. Elemental analyses were carried out by Canadian Micro-analytical Service Ltd, Delta, BC, Canada. X-ray data were collected for single crystals of **1**, **2**, **5**, and **6** (details provided below).

Synthesis of vanadium complexes

$[O_2NO]^{BuMeMeth}$ V(O)(OMe) (**1**): $H_2[O_2NO]^{BuMeMeth}$ (1.00 g, 2.25 mmol) and $[VO(acac)_2]$ (0.5970 g, 2.25 mmol) were placed in a flash, methanol (50 mL) was added and the mixture was heated to reflux overnight to yield a dark blue solution. The solvent was removed under vacuum and a dark blue solid (0.88 g) was obtained, 73% yield. Compounds **2-4** were prepared in a similar fashion. $[ON_2O]^{BuMe}$ V(O)(OMe) (**2**) was isolated as a dark blue solid 0.95 g, 80% yield. $[O_2NN]^{BuBuPy}$ V(O)(OMe) (**3**) was isolated as a black solid 0.92 g, 78 % yield. $[O_2NO]^{BuBuFurf}$ V(O)(OMe) (**4**) was isolated as a dark blue solid with yield 0.95 g, 80 % yield. Using a Johnson-Matthey magnetic susceptibility balance, all compounds were confirmed to be diamagnetic and did not give rise to any signals in EPR experiments. Upon recrystallization in air, crystals of **1** and **2** suitable for X-ray structure determination were obtained. Upon storing in a refrigerator, solutions of **3** and **4** afforded oxo-bridged compounds **5** and **6**.

(1) $C_{28}H_{45}NO_5V$: calcd. C 66.26, H, 8.34, N 2.76; found: C 65.88, H 8.12, N 2.99. IR: $\nu_{V=O}$, 951 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ =7.11 (d, J = 1.8 Hz, 2H, ArH), 6.82 (d, J = 1.6 Hz, 2H, ArH), 5.30 (s, 3H, V-OCH_3), 4.57 (d, J = 13.7 Hz, 2H, OCH_2-C), 3.75 (d, *J* = 13.8 Hz, 2H, NCH_2-CH_2), 3.38 (s, 3H, C-OCH_3), 3.23 (s, 2H, ArC-CH_2-N), 2.82 (s, 2H, ArC-CH_2-N), 2.35 – 2.29 (m, 6H, $ArCH_3$), 1.47 (s, 18H, $ArC(CH_3)_3$.

(**2**) $C_{29}H_{45}N_2O_4V$: calcd. C 66.52, H 8.37, N 5.54; found: C 66.75, H 8.20, N 5.68. IR: $\nu_{V=O}$, 951cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.12 – 7.03 (m, 2H, ArH), 6.73 (d, *J* = 1.6 Hz, 1H, Ar), 6.66 (d, *J* = 1.8 Hz, 1H, ArH), 5.05 (s, 3H, OCH_3), 4.67 (d, *J* = 14.6 Hz, 1H, N-CH_2-C), 4.43 (d, *J* = 13.6 Hz, 1H, N-CH_2-C), 3.75 – 3.62 (m, 1H, N-CH_2-C), 3.63 – 3.34 (m, 1H, N-CH_2-C), 3.11 (d, *J* = 13.6 Hz, 2H, ArC-CH_2-N), 3.08 – 2.97 (m, 2H, ArC-CH_2-N), 2.57 (s, 3H, NCH_3), 2.53 (s, 3H, NCH_3), 2.28 (s, 3H, $ArCH_3$), 2.27 (s, 3H, $ArCH_3$), 1.55 (s, 9H, $ArC(CH_3)_3$), 1.45 (s,9H, $ArC(CH_3)_3$).

(**3**) $C_{37}H_{53}N_2O_4V$: calcd. C 70.91, H 8.27, N 4.59; found: C 71.15, H 8.03, N 4.83. IR: $\nu_{V=O}$, 951 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.04 (d, *J* = 4.7 Hz, 1H, ArH), 7.35 (td, *J* = 7.7, 1.6 Hz, 1H, ArH), 7.08 (d, *J* = 2.4 Hz, 2H, ArH), 7.02 – 6.96 (m, 1H, ArH), 6.91 (d, *J* = 2.4 Hz, 2H, ArH), 6.49 (d, *J* = 7.8 Hz, 1H, ArH), 4.89 (s, 3H, OCH_3), 4.52 (d, *J* = 12.4 Hz, 2H, N-CH_2-C), 3.75 (d, *J* = 14.9 Hz, 2H, N-CH_2-C), 3.36 (d, *J* = 12.5 Hz, 2H, N-CH_2-C), 2.28 – 2.17 (m, 2H, N-CH_2-C), 1.38 (s, 18H, $ArC(CH_3)_3$), 1.24 (s, 18H, $ArC(CH_3)_3$).

(**4**) $C_{36}H_{52}NO_5V$: calcd. C 68.66, H 8.32, N 2.22; found: C 69.15; H 8.03; N 2.19. IR: $\nu_{V=O}$, 951 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.25 (m, 2H, ArH), 6.96 (dd, *J* = 20.3, 2.1 Hz, 2H, ArH), 5.33 (s, 3H, OCH_3), 4.97 (d, *J* = 15.0 Hz, 1H, $CH(CH_2)_2$), 4.50 – 4.21 (m,1H, ArH), 3.84 (d, *J* = 15.1 Hz, 1H, ArH), 3.56 (ddd, *J* = 30.2, 20.5, 8.4 Hz,4H, CH_2-N-CH_2), 3.02 – 2.18 (m, 2H, N-CH_2-C), 1.59 – 1.41 (m, 18H, $ArC(CH_3)_3$), 1.35 – 1.26 (m, 18H, $ArC(CH_3)_3$).
(**5**) $C_{72}H_{100}N_4O_7V_2$: calcd. C 70.00, H 8.16, N 4.53; found C 69.97, H 8.17, N 4.66.
(**6**) $C_{70}H_{98}N_2O_9V_2$: calcd. C 69.29, H 8.14, N 2.31; found C 69.46, H 8.21, N 2.52.

Experimental for single crystal X-ray determinations

Crystals of **1**, **2**, **5** and **6** were mounted on a low temperature diffraction loops. All measurements were made on a Rigaku Saturn70 CCD diffractometer using graphite monochromated Mo-Kα radiation. For all four structures, all non-hydrogen atoms were located in difference map positions and were refined anisotropically, while all hydrogen atoms were introduced in calculated positions and refined on a riding model. In the structure of **1**, no H-atoms were found on O5, which suggests that this is a methoxide ion (H_3CO^-), therefore, for charge balance, vanadium must be in the +5 oxidation state. Bond valence sum calculations were attempted with VaList in order to confirm this assignment, [23] however, V(V) cannot be unambiguously assigned using this method. Calculations for V(III) and V(IV) gave results that were high (~4.8), which does suggest that the species is most consistent with V(V) and this is supported by other experimental evidence (e.g. NMR spectroscopy). Crystals of **2** were irregular and appeared cracked. Multiple domains with the same unit cell were identified, but refinement using all components did not yield satisfactory results. A single domain was used for the reported results. Connectivity is similar to **1** around the vanadium centre. Crystals of **5** were small and diffracted weakly. A solvent accessible void is present in the unit cell, however, application of a solvent mask did not improve the refinement statistics, and therefore this was left untreated. Finally, **6** exhibited three areas of disorder; one of the lattice solvent acetonitrile molecules was refined as two parts ([C38,N3]:[C38A,N3A] 0.136(11):0.864(11)). Distance and angle restraints were used to model this solvent molecule. H-atoms associated with this solvent were omitted form the model, but included in the formula for the calculation of intensive properties. Distance and angle restraints were applied to this molecule. Next, one of the ligand carbon atoms, and corresponding H-atoms, in the pendant THF was refined as two parts (C16:C16A, 0.553(9):0.447(9)). Finally,

one of the ligand t-butyl groups, and corresponding H-atoms, was also refined as two parts ([C25,C26,C27]:[C25A,C26A,C27A], 0.423(11):0.577(11)]). Similar disorder has been seen in other metal complexes of this ligand.

Crystal Data for **1**: $C_{28}H_{42}NO_5V$ (*M* =523.59 g/mol), monoclinic, space group C2/c (no. 15), *a* = 32.094(11) Å, *b* = 11.055(3) Å, *c* = 19.787(7) Å, *β* = 127.184(3)°, *V* = 5593(3) Å^3, *Z* = 8, *T* = 163(2) K, μ(MoKα) = 0.391 mm^{-1}, *Dcalc* = 1.244 g/cm^3, 22592 reflections measured (5.24° ≤ 2Θ ≤ 53°), 5706 unique (and 5242 with I>2σ(I); R_{int} = 0.0610) which were used in all calculations. The final R_1 was 0.0569 (>2σ(I)) and wR_2 was 0.1623 (all data). CCDC no. 1419296

Crystal Data for **2**: $C_{29}H_{45}N_2O_4V$ (*M* =536.61 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.3406(8) Å, *b* = 24.0686(19) Å, *c* = 9.3036(7) Å, *β* = 92.780(6)°, *V* = 2760.1(4) Å^3, *Z* = 4, *T* = 123.15 K, μ(MoKα) = 0.396 mm^{-1}, *Dcalc* = 1.291 g/cm^3, 25008 reflections measured (3.304° ≤ 2Θ ≤ 59.586°), 6832 unique (and 3831 with I>2σ(I); R_{int} = 0.3546, R_{sigma}= 0.2006) which were used in all calculations. The final R_1 was 0.1163 (I > 2σ(I)) and wR_2 was 0.3179 (all data). CCDC no. 1410297

Crystal Data for **5**: $C_{72}H_{100}N_4O_7V_2$ (*M* =1235.43 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 14.6760(11) Å, *b* = 17.4805(9) Å, *c* = 15.9994(11) Å, *β* = 113.184(9)°, *V* = 3773.1(5) Å^3, *Z* = 2, *T* = 123.15 K, μ(MoKα) = 0.297 mm^{-1}, *Dcalc* = 1.087 g/cm^3, 18149 reflections measured (5.16° ≤ 2Θ ≤ 50.054°), 6630 unique (and 4573 with I>2σ(I); R_{int} = 0.0688, R_{sigma} = 0.1240) which were used in all calculations. The final R_1 was 0.0895 (I > 2σ(I)) and wR_2 was 0.2301 (all data). CCDC no. 1410298

Crystal Data for **6**: $C_{78}H_{118}N_6O_9V_2$ (*M* =1385.66 g/mol): monoclinic, space group I2/a (no. 15), *a* = 14.1027(3) Å, *b* = 17.1339(5) Å, *c* = 32.0775(7) Å, *β* = 90.371(2)°, *V* = 7750.9(3) Å^3, *Z* = 4, *T* = 123.15 K, μ(MoKα) = 0.298 mm^{-1}, *Dcalc* = 1.187 g/cm^3, 34379 reflections measured (5.08° ≤ 2Θ ≤ 53°), 8029 unique (and 6581 with I>2σ(I); R_{int} = 0.0596, R_{sigma} = 0.0459) which were used in all calculations. The final R_1 was 0.0747 (I > 2σ(I)) and wR_2 was 0.2223 (all data). CCDC no. 1410299

General procedure for the catalytic aerobic oxidation of 4-methoxybenzyl alcohol.

In a 25 mL round-bottom flask, or in a 20 mL microwave vial, 4-methoxybenzyl alcohol (69 mg, 0.50 mmol) was combined with vanadium complex (**1-4**) (0.01 mmol, 2 mol%), NEt_3 (7 μL, 0.05 mmol, 10 mol%), and *p*-xylene (5 μL, 0.041 mmol) as an internal standard. The mixture was dissolved in toluene-d_8 (1 mL) under air, and the flask equipped with a stir bar and an air

condenser. If the reaction was performed in a microwave vial, it was sealed. The reaction mixture was heated with stirring in an oil bath at 80-140 °C for 36-60 h under air. The reaction mixture was cooled to room temperature, and the yield of oxidized product 4-methoxybenzaldehyde determined by integration of the ^{1}H NMR spectra against the internal standard.

General procedure for the catalytic aerobic oxidation of 1,2-diphenyl-2-methoxyethanol

In a 25 mL round-bottom flask, or in 20 mL microwave vial, 1,2-diphenyl-2-methoxyethanol (29.8 mg, 0.131 mmol) was combined with a vanadium complex (**1**-**4**) (0.0066 mmol, 5 mol%), and *p*-xylene (5 µL, 0.041 mmol) as an internal standard. The mixture was dissolved in toluene-d_8 (1 mL) under air, and the flask equipped with a stir bar and an air condenser. If the reaction was performed in a microwave vial, it was sealed. The reaction mixture was heated with stirring in an oil bath at 100-140 °C for 12-36 h under air. The reaction mixture was cooled to room temperature, and the yields of oxidized products were determined by integration of the ^{1}H NMR spectra against the internal standard. Product identities were further confirmed via GC-MS analyses.

General Procedure for H_2O_2-mediated oxidation of diphenylether and benzylphenylether

Acetonitrile (9 mL) was added to a vanadium complex (**1**-**4**) (0.005 mmol, 1 mol%), NEt_3 (7 µL, 0.05 mmol, 10 mol%), in a 50 mL of round bottom flask. The ether substrate (0.5 mmol) was added to the solution at room temperature in air. 30% aqueous H_2O_2 (170 µL, 1.5 mmol or 340 µL, 3.0 mmol) was dissolved in acetonitrile (870 µL or 1660 µL, respectively) and was added to the reaction mixture over a period of 1 or 2 h by a syringe pump. The flask was then equipped with a stir bar and an air condenser. The flask was heated with stirring in an oil bath at 80 °C for 48 h. The reaction was cooled to room temperature and the solvent was removed under vacuum. The residue of the reaction mixture was dissolved in diethyl ether and dodecane (100 or 50 µL as internal standard) was added, the mixture was analyzed by GC-MS and quantified using a calibration curve.

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