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Aerobic Oxidation Reactions Catalyzed by Vanadium Complexes of Bis(Phenolate) Ligands

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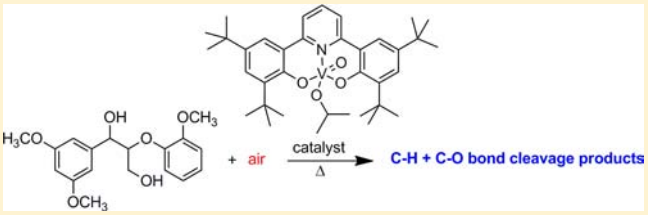
Supporting Information

ABSTRACT: Vanadium(V) complexes of the tridentate bis(phenolate)pyridine ligand **H_2BPP** (**H_2BPP** = 2,6-$(HOC_6H_2$-2,4-$^tBu_2)_2NC_5H_3$) and the bis(phenolate)amine ligand **H_2BPA** (**H_2BPA** = *N*,*N*-bis(2-hydroxy-4,5-dimethylbenzyl)propylamine) have been synthesized and characterized. The ability of the complexes to mediate the oxidative C−C bond cleavage of pinacol was tested. Reaction of the complex (BPP)V^V(O)(O^iPr) (**4**) with pinacol afforded the monomeric vanadium(IV) product (BPP)V^{IV}(O)(HO^iPr) (**6**) and acetone. Vanadium(IV) complex **6** was oxidized rapidly by air at room temperature in the presence of NEt_3, yielding the vanadium(V) *cis*-dioxo complex $[(BPP)V^V(O)_2]HNEt_3$. Complex (BPA)V^V(O)(O^iPr) (**5**) reacted with pinacol at room temperature, to afford acetone and the vanadium(IV) dimer $[(BPA)V^{IV}(O)(HO^iPr)]_2$. Complexes **4** and **5** were evaluated as catalysts for the aerobic oxidation of 4-methoxybenzyl alcohol and arylglycerol β-aryl ether lignin model compounds. Although both **4** and **5** catalyzed the aerobic oxidation of 4-methoxybenzyl alcohol, complex **4** was found to be a more active and robust catalyst for oxidation of the lignin model compounds. The catalytic activities and selectivities of the bis(phenolate) complexes are compared to previously reported catalysts.



INTRODUCTION

Recent years have seen tremendous growth in the field of aerobic oxidation catalysis.[1−3] In 2007, the American Chemical Society Green Chemistry Institute Pharmaceutical Roundtable identified the search for new green oxidation processes as a key future synthetic research and development challenge.[4] As catalysts for aerobic oxidation, earth-abundant metals offer practical advantages in terms of abundance and cost.[5] In particular, vanadium complexes have emerged as an attractive class of catalysts,[6] mediating the aerobic oxidative kinetic resolution of α-hydroxy esters,[7] acids,[8] amides,[9] and ketones,[10] and the aerobic oxidation of benzylic, allylic, and propargylic alcohols.[11−13] Vanadium exhibits a remarkable diversity of reactivity, also catalyzing oxidative processes that are proposed to involve radical intermediates, such as the oxidative dimerization of phenols[14,15] and the C−C bond cleavage of α-hydroxyketones.[3]

Beyond synthetic applications, vanadium complexes have been investigated as catalysts for C−O and C−C bond cleavage reactions in lignin model compounds.[16,17] Lignin, an irregular polymer composed of methoxy-substituted phenolic subunits, is an integral constituent of nonfood biomass and potential source of valuable aromatic compounds.[18] The development of new methods to break lignin down in a selective fashion could provide access to renewable building blocks for chemicals or fuels.[19−21] Recently, Son and Toste reported a vanadium(V) complex **1** (Figure 1) that cleaves the C−O bond in a nonphenolic lignin model compound.[16] We have demonstrated that the vanadium complexes (dipic)V^V(O)(O^iPr) (**2**, dipic = dipicolinate) and (HQ)V^V(O)(O^iPr) (**3**, HQ = 8-quinolinate) (Figure 1) catalyze aerobic oxidative C−C bond cleavage reactions in several different lignin model compounds.[17] Although these reports illustrate the promise of vanadium to catalyze aerobic oxidation processes and break C−C and C−O bonds in lignin, the impact of varying the ligand backbone on the activity and selectivity of vanadium catalysts is not well understood.

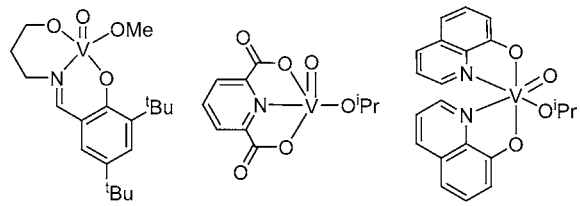


Figure 1. Vanadium catalysts for the aerobic oxidation of lignin model compounds.

Having previously studied catalysts **2** and **3** with dipicolinate and 8-quinolinate ligands, we were interested in how a more electron-donating ligand set might influence the catalysis. Specifically, it was envisioned that a tridentate scaffold with phenolate donor groups could provide a more electron-rich environment and an additional open site at the metal center that might facilitate the reaction of V^{III} or V^{IV} with oxygen. As

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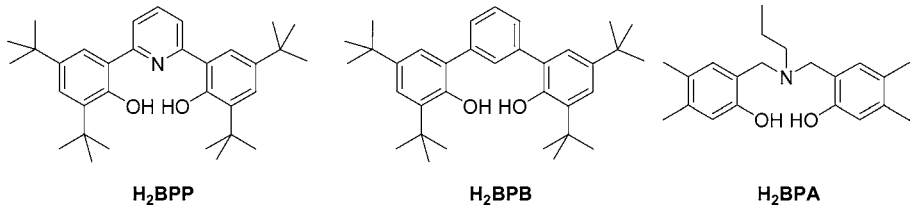

Figure 2. Ligands H_2**BPA**, H_2**BPP**, and H_2**BPB**.

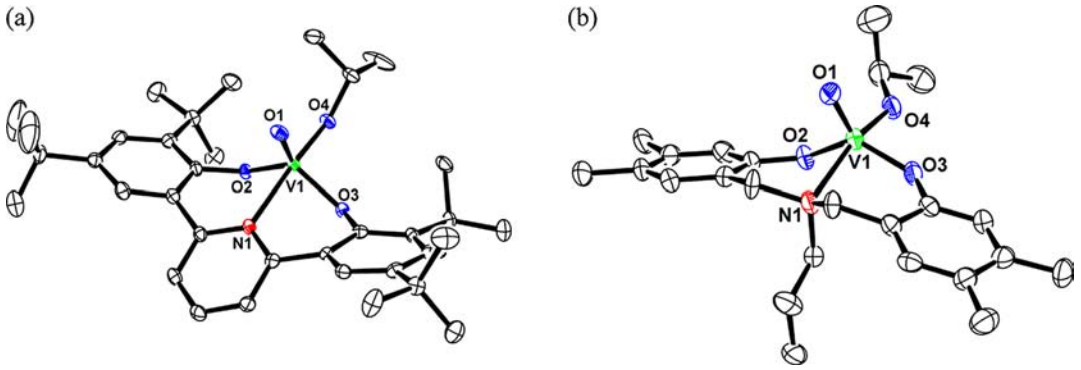

Figure 3. (a) X-ray structure of vanadium(V) complex **4** (thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths (Å): V1−O1 = 1.589(2), V1−O4 = 1.772(2), V1−O2 = 1.823(2), V1−O3 = 1.830(2), V1−N1 = 2.277(3). (b) X-ray structure of vanadium(V) complex **5** (one of two crystallographically independent molecules, thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths (Å): V1−O1 = 1.589(3), V1−O4 = 1.762(3), V1−O3 = 1.814(3), V1−O2 = 1.848(3), V1−N1 = 2.272(4).

possible ligand candidates, we identified the bis(phenolate)-pyridine ligand **H_2BPP** (**H_2BPP** = 2,6-$(HOC_6H_2$-2,4-$^tBu_2)_2NC_5H_3$), the bis(phenolate)benzene ligand **H_2BPB** (**H_2BPB** = 2,6-$(HOC_6H_2$-2,4-$^tBu_2)_2C_6H_4$), and the bis-(phenolate)amine ligand **H_2BPA** (**H_2BPA** = *N*,*N*-bis(2-hydroxy-4,5-dimethylbenzyl)propylamine), (Figure 2).[22,23] None of the bis(phenolate) ligands have previously been explored in the context of vanadium-mediated aerobic oxidation catalysis.

This work describes the synthesis of vanadium complexes bearing bis(phenolate) ligands **H_2BPP** and **H_2BPA**. The reactivity of the complexes has been explored, and their ability to catalyze aerobic oxidation reactions has been evaluated for several substrates. While both complexes (BPP)V^V(O)(O^iPr) (**4**) and (BPA)V^V(O)(O^iPr) (**5**) catalyzed aerobic oxidation reactions, complex **4** was found to be a more stable and active catalyst.

RESULTS AND DISCUSSION

Synthesis of Vanadium Complexes. The bis(phenolate)-pyridine ligand (**H_2BPP**) and bis(phenolate)benzene ligand (**H_2BPB**) were prepared via Negishi cross-coupling reactions, as previously described by Agapie and Bercaw.[23] Using a previously published procedure,[22] **H_2BPA** was prepared by a Mannich condensation of 3,4-dimethylphenol, propylamine, and formaldehyde in CH_3OH. The bis(phenolate)pyridine ligand **H_2BPP** reacted with V^V(O)(O^iPr)$_3$ at room temperature in isopropanol solution, affording dark red-brown solid complex (BPP)V^V(O)(O^iPr) (**4**). A similar reaction between **H_2BPA** and V^V(O)(O^iPr)$_3$ in isopropanol yielded complex (BPA)-V^V(O)(O^iPr) (**5**). Surprisingly, no reaction was observed between **H_2BPB** and V^V(O)(O^iPr)$_3$ in isopropanol-d_8 solvent; ^{1}H and ^{51}V NMR spectra of the reaction mixture showed only signals corresponding to the starting material, even after heating at 50 °C for 2 h.

Complexes **4** and **5** were characterized by NMR and IR spectroscopy, X-ray crystallography, and elemental analysis. Distinctive features in the ^{1}H NMR spectra of complexes **4** and **5** include the signals for the vanadium-isopropoxide ligand, which are shifted significantly downfield from free isopropanol. The V-isopropoxide methine signal (V-OC*H*) appears as a septet at 5.61 ppm for complex **4** and 5.54 ppm for complex **5**, as compared to 6.35 ppm (CD_3CN) for (dipic)V^V(O)(O^iPr) (**2**) and 6.25 ppm for $(HQ)_2V^V$(O)(O^iPr) (**3**). Previously, for a series of substituted dipicolinate ligands, it was found that the chemical shift of the isopropoxide methine V-OC*H* signal correlated with the electronic nature of the ligand, shifting downfield as the electron-withdrawing character of the ligand increased. This suggests that the bis(phenolate) ligand frameworks are more electron donating than the dipicolinate or bis(8-quinolinate) ligand scaffolds.

The X-ray structures of **4** and **5** are shown in Figure 3. For complex **5**, single crystal X-ray diffraction analysis revealed two crystallographically independent molecules in the unit cell. The two molecules display very similar bond lengths (see Supporting Information for details of the other crystallographically independent molecule). Both complexes **4** and **5** have trigonal bipyramidal geometries where the V^V centers are raised out of the ONO plane. Selected bond lengths for **4** and **5** are listed in Figure 3; complexes **4** and **5** have nearly identical vanadium-oxo bond distances, and the V−O^{i}Pr distances are also quite similar (1.772(2) vs 1.762(3) Å).

Several V^V complexes of bis(phenolate)-[24] and tris-(phenolate)-amine[25,26] ligands have previously been reported. Ali and co-workers prepared vanadium alkoxide complexes of bis(phenolate)amine ligands similar to **H_2BPA**;[27,28] these complexes were evaluated for the catalytic oxidation of toluene and xylene using H_2O_2. In these proposed radical reactions, high yields of benzoic acid products were obtained at elevated temperatures.[27] Several multidentate phenolate-amine type

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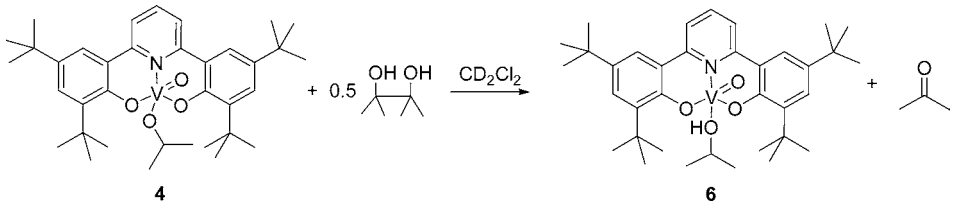
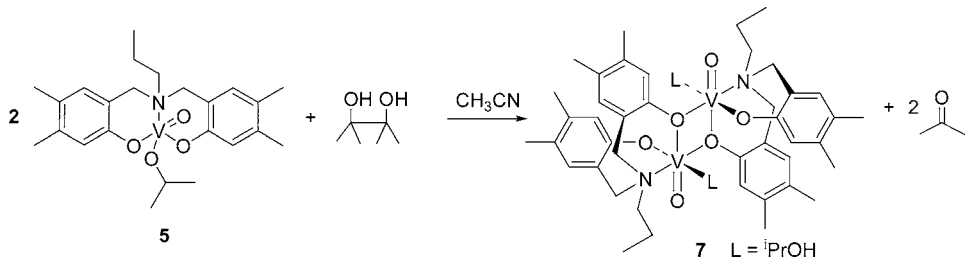
Scheme 1. Oxidation of Pinacol by Vanadium(V) Complex 4



Scheme 2. Reaction of Complex 5 with Pinacol



ligands have also been investigated for the assembly of mixed valent V^V–V^{IV} species.[29,30]

Stoichiometric Oxidation of Pinacol. To initially assess the potential of the vanadium complexes to mediate oxidative C–C bond cleavage reactions, the reactions of **4** and **5** were tested with pinacol. Complex **4** reacted readily with pinacol (5 equiv) at room temperature, affording dark green crystals of the vanadium(IV) complex **6** in 95% yield (Scheme 1). When the reaction was conducted in CD_2Cl_2 and monitored by ^{1}H NMR spectroscopy, the C–C bond cleavage product acetone was detected (1 equivalent based on V), consistent with the overall stoichiometry shown in Scheme 1. Complex **6** was characterized by IR and UV–vis spectroscopy, elemental analysis, and X-ray crystallography. The X-ray structure of complex **6** (see Supporting Information, Figure S2) indicates that it is a mononuclear V^{IV} complex. In the X-ray structure of **6**, the coordinated solvent molecule is disordered (see Supporting Information for details). Most likely, the bulky *tert*-butyl substituents on the phenolate donors contribute to the monomeric nature of complex **6**, preventing dimerization via bridging phenolate groups.

When excess pinacol was added to a suspension of **5** in CH_3CN, the vanadium complex reacted over the course of 20 h at room temperature, affording light purple crystals of vanadium(IV) dimer **7** in nearly quantitative yield (97%). When the reaction was conducted in CD_3CN and monitored by ^{1}H NMR spectroscopy, acetone was detected as a reaction product, suggesting the overall stoichiometry shown in Scheme 2.

As depicted in Figure 4, in the solid state complex **7** is a centrosymmetric V^{IV} dimer, in which each ligand binds to a V^{IV} center in a chelating mode and one of the phenolate groups bridges to another V^{IV} center by a μ-oxo bridging mode. In complex **7** the phenolate oxygen atoms and amine nitrogen atom are in a facial arrangement, with one of the phenolate donor groups positioned trans to the vanadium-oxo ligand. Isopropanol molecules are also present in the structure of the V^{IV} product, saturating the coordination sphere of each V^{IV} center.[31] Selected bond lengths for **7** are given in Figure 4; the vanadium oxo bond distance of 1.601(4) Å is longer than those of V^V complexes **4** and **5**. The distance between the vanadium center and the phenolate oxygen located trans to the oxo ligand

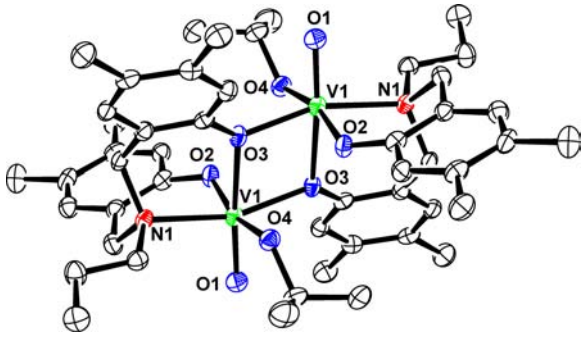


Figure 4. X-ray structure of vanadium(IV) dimer **7** (thermal ellipsoids at 50% probability, hydrogen atoms and co-crystallized acetonitrile omitted for clarity). Selected bond lengths (Å): V1–O1 = 1.601(2), V1–O2 = 1.928(2), V1–O3 = 2.131(2), V1–O3′ = 2.004(2), V1–O4 = 2.152(2), V1–N1 = 2.164(2).

(2.131(2) Å) is significantly longer than the distance between the vanadium center and the phenolate oxygen trans to the isopropanol ligand (1.928(2) Å).

A vanadium(IV) dimer of a tetradentate bis(phenolate)-amine-glycine ligand with bridging phenolate moieties has previously been described by Ceccato and co-workers.[32] Unlike complex **7**, in this previously reported example the phenolate oxygen atoms and amine nitrogen atom are in a meridonal arrangement. A nonoxo V^{IV} complex bearing two bis-(phenolate)amine ligands has also previously been reported.[33]

Having demonstrated that both complexes **4** and **5** mediated the stoichiometric C–C bond cleavage of pinacol, we then tested the reaction of the vanadium(IV) complex **6** with air, which would be required to complete a catalytic cycle. When a solution of paramagnetic complex **6** in CD_2Cl_2 was exposed to air at room temperature in the presence of NEt_3 (2 equiv), an instantaneous color change from green to brown was observed. ^{1}H and ^{51}V NMR spectra of the resulting solution were consistent with the formation of a new V^V species [(BPP)-$V^V(O)_2$]$HNEt_3$ (**8**). Complex **8** could also be synthesized independently from the reaction of **4** with water and NEt_3. The X-ray structure of **8** is shown in Figure 5. The vanadium oxo distance (V1–O1 = 1.621(2) Å) is longer than that of complex **4**. The distance between the O2 oxo ligand and the nitrogen on

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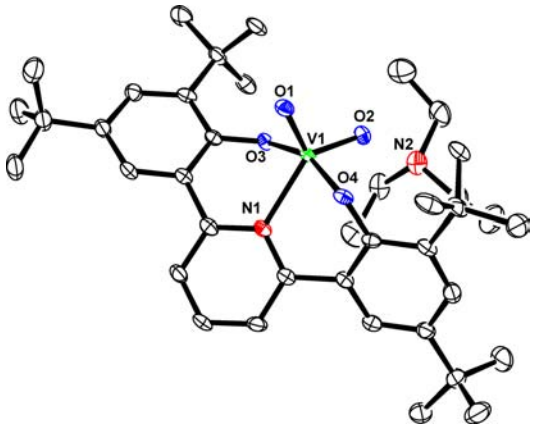


Figure 5. X-ray structure of vanadium(V) *cis*-dioxo complex **8** (thermal ellipsoids at 50% probability, hydrogen atoms and co-crystallized CH_3OH omitted for clarity). Selected bond lengths (Å): V1−O1 = 1.621(2), V1−O2 = 1.644(2), V1−O3 = 1.919(2), V1−O4 = 1.920(2), V1−N1 = 2.172(2).

the $HNEt_3$ counterion is about 2.657 Å, consistent with a hydrogen bonding interaction.

The rapid reactivity of the vanadium(IV) complex **6** with air stands in contrast to that previously observed for the complex $(dipic)V^{IV}(O)(pyr)_2$, which reacted with air only upon heating for several days at 100 °C.[17c] This indicates that the ligand framework has a significant influence on the rate of the reaction of V^{IV} with air, with the more electron-donating **BPP** ligand framework promoting the reaction relative to dipicolinate.

■ CATALYTIC OXIDATIONS

We recently reported that the 8-quinolinate vanadium complex **3** catalyzed the aerobic oxidation of activated alcohols, and evaluated several different vanadium complexes as catalysts for the aerobic oxidation of 4-methoxybenzyl alcohol using a base additive (NEt_3).[13] To compare with the previously reported results and optimize reaction conditions, V^V complexes **4** and **5** were tested for the catalytic aerobic oxidation of 4-methoxybenzyl alcohol. Initially, the aerobic oxidation of 4-methoxybenzyl alcohol was attempted using bis(phenolate)-pyridine complex **4** (2 mol %) as a catalyst at 60 °C in 1,2-dichloroethane. However, no significant oxidation of the substrate was observed under these conditions (Table 1, entry 1). Addition of a base (NEt_3) and use of a different solvent (THF or toluene) did not prompt the oxidation of 4-methoxybenzyl alcohol. However, increasing the reaction temperature to 80 °C afforded 4-methoxybenzaldehyde in ~99% NMR yield after 65 h under air in toluene solvent (Table 1, entry 5).

Compared to previously reported 8-quinolinate catalyst **3**, complex **4** was a slower catalyst for the aerobic oxidation of 4-methoxybenzyl alcohol, requiring both a longer reaction time and a higher temperature (Table 1, entry 6).[13] However, as was the case for catalyst **3**, a base promoter was found to be crucial for the catalytic reaction (Table 1, entry 8). We tested several different bases as promoters for the oxidation of 4-methoxybenzyl alcohol using **4** in toluene at 80 °C (Table 1, entries 10−15). In addition to triethylamine, diisopropylethyl-amine, piperidine, and DBU (DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene) were effective promoters of the vanadium complex, affording 4-methoxybenzaldehyde in high yields after 65 h. Dimethylaminopyridine (DMAP), potassium carbonate, and sodium acetate proved to be less effective for promoting the reaction. Bis(phenolate)amine V^V complex **5** was also found to catalyze the aerobic oxidation of 4-methoxybenzyl alcohol under the optimized reaction conditions, but afforded 4-methoxybenzaldehyde in somewhat lower yield (80%) (Table 1, entry 16).

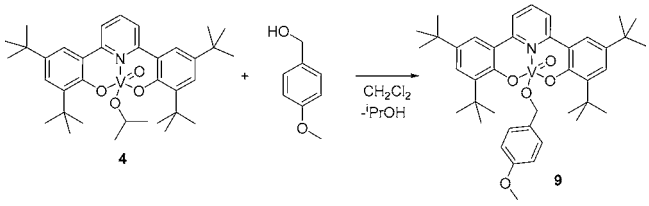
Table 1. Aerobic Oxidation of 4-Methoxybenzylalcohol Using Bis(phenolate)pyridine Complex 4[a]

entry	additive (10 mol %)	solvent	*T* (°C)	time (h)	% yield (NMR)
1	none	1,2-dichloroethane	60	24	0
2	NEt_3	1,2-dichloroethane	60	24	trace
3	NEt_3	THF	60	24	trace
4	NEt_3	toluene	60	24	trace
5	NEt_3	toluene	80	65	99
6	NEt_3	toluene	80	24	45
7	NEt_3	toluene	80	48	81
8	none	toluene	80	24	0
9	NEt_3	toluene	70	24	2
10	$N(^iPr)_2Et$	toluene	80	65	91
11	piperidine	toluene	80	65	99
12	DBU	toluene	80	65	89
13	DMAP	toluene	80	65	14
14	K_2CO_3	toluene	80	65	1
15	CH_3COONa	toluene	80	65	9
16[b]	NEt_3	toluene	80	65	80

[a]Conditions: 2 mol % of **4**, 10 mol % additive. [b]2 mol % of **5** was used as a catalyst. Yields determined by integration against an internal standard (hexamethylbenzene).

To further investigate the interaction of V^V catalyst **4** with the substrate, the reaction of **4** with 4-methoxybenzyl alcohol was monitored by NMR spectroscopy. When 1 equiv of 4-methoxybenzyl alcohol was added to a toluene-d_8 solution of **4**, new signals corresponding to the vanadium(V) species $(BPP)V^V(O)(OCH_2C_6H_4\text{-}p\text{-}OCH_3)$ (**9**) appeared in the ^1H and ^{51}V NMR spectra within 5 min at room temperature. Addition of an excess (3 equiv) of 4-methoxybenzyl alcohol to complex **4** allowed for the isolation of complex **9** (Scheme 3),

Scheme 3. Reaction of Complex 4 with 4-Methoxybenzyl Alcohol



which was characterized by NMR and IR spectroscopy, elemental analysis, and X-ray crystallography. Complex **9** shows a singlet at 6.39 ppm in the ^1H NMR spectrum (CD_2Cl_2) for the V-OCH_2 protons, consistent with an environment of C_s symmetry. For the previously reported complex $(HQ)_2V^V(O)(OCH_2C_6H_4\text{-}p\text{-}OCH_3)$, the V-$OCH_2$ protons appear at downfield chemical shifts of 6.72 and 6.57 ppm, suggesting that the bis(8-quinolinate) ligand framework is somewhat more electron-withdrawing.[13] The X-ray structure of **9** is shown in Figure 6. The vanadium-oxo bond and vanadium benzyloxy bond distances in **9** are 1.577(2) and 1.783(2) Å, respectively, which differ only slightly from those in **4**.

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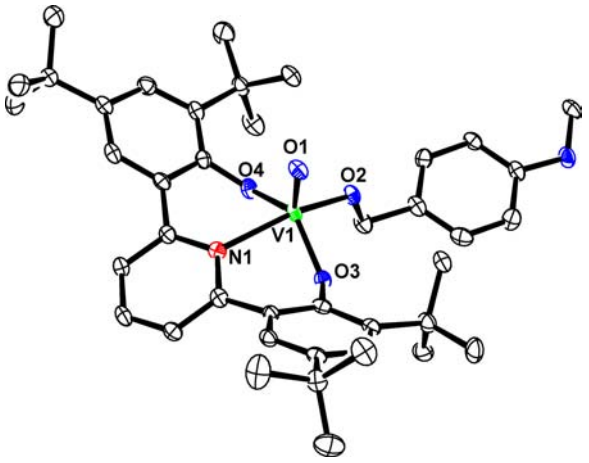
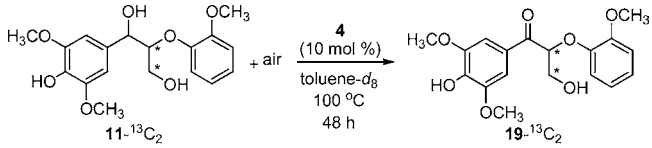


Figure 6. X-ray structure of complex **9** (thermal ellipsoids at 50% probability, hydrogen atoms omitted for clarity). Selected bond lengths (Å): V1−O1 = 1.583(2), V1−O2 = 1.785(2), V1−O4 = 1.833(2), V1−O3 = 1.841(2), V1−N1 = 2.236(2).

Lignin Model Compounds. Having found that both complexes **4** and **5** catalyzed the aerobic oxidation of 4-methoxybenzylalcohol, we evaluated **4** and **5** as catalysts for the aerobic oxidation of the previously reported arylglycerol *β*-aryl ether lignin model compounds **10**-$^{13}C_2$ and **11**-$^{13}C_2$ (Schemes 4 and 5).[17b,34] When nonphenolic lignin model **10**-$^{13}C_2$ was heated in toluene-d_8 solution with bis(phenolate)pyridine complex **4** (10 mol %), approximately 84% conversion occurred after 48 h at 100 °C. ^{1}H and ^{13}C NMR analysis of the resulting reaction mixture revealed the formation of a mixture of products, including ketone **12**-$^{13}C_2$, alkene **13**-$^{13}C_2$, **14**-$^{13}C_2$, 2-methoxyphenol (**15**), 3,5-dimethoxybenzaldehyde (**16**), formic acid-$^{13}C_1$ (**17**-$^{13}C_1$), and 3,5-dimethoxybenzoic acid (**18**) (yields given in Scheme 4). Products **12**-$^{13}C_2$ and **13**-$^{13}C_2$ have been reported previously,[17b] and the identity of 3,5-dimethoxybenzaldehyde and 3,5-dimethoxybenzoic acid was confirmed by comparison with commercial samples. Product

Scheme 5. Aerobic Oxidation of Lignin Model Compound 11-$^{13}C_2$ Using Vanadium Catalyst 4 (10 mol %)

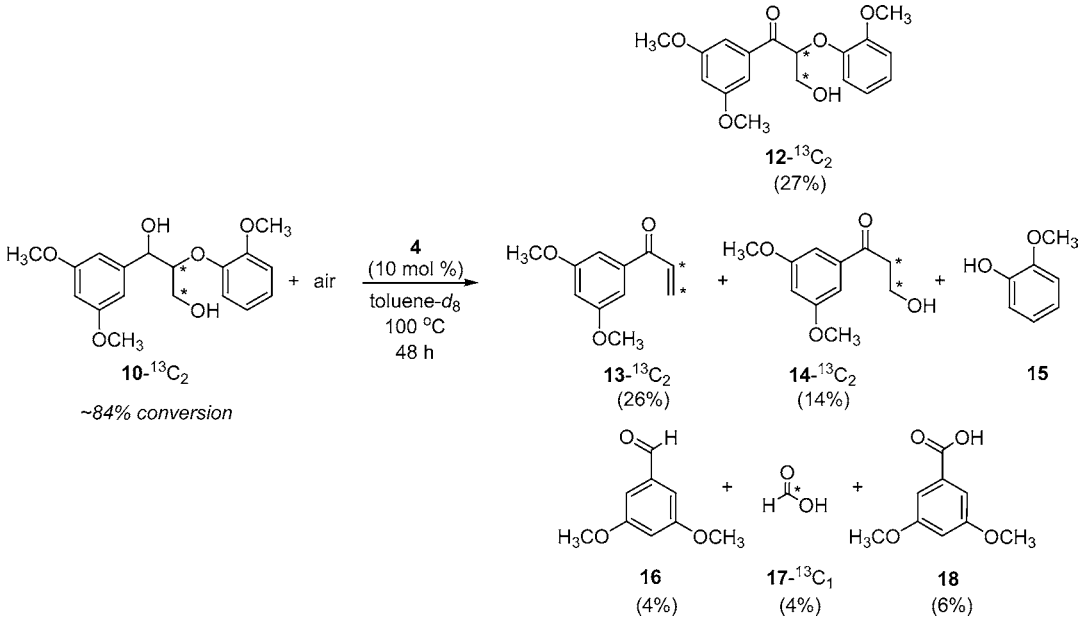


~20% conversion

14-$^{13}C_2$ has not been observed previously, and is tentatively assigned as the alcohol 1-(3,5-dimethoxyphenyl)-3-hydroxy-propan-1-one (Scheme 4), on the basis of NMR spectroscopy. The $^{13}C\{^1H\}$ NMR spectrum of **14**-$^{13}C_2$ shows two signals arising from the labeled carbons in **14** at 58.2 and 40.8 ppm ($^1J_{C-C}$ = 38 Hz). In the proton-coupled carbon NMR spectrum, the signal at 58.2 appears as a multiplet, displaying coupling to the two protons on the labeled carbon ($^1J_{C-H}$ = 105 Hz), the adjacent labeled carbon ($^1J_{C-C}$ = 38 Hz), and the two protons on the adjacent carbon ($^2J_{C-H}$ = 4 Hz) (See Supporting Information for details). A similar pattern is observed for the labeled carbon at 40.8 ppm, which shows one-bond coupling to two protons ($^1J_{C-H}$ = 124 Hz), coupling to the adjacent labeled carbon ($^1J_{C-C}$ = 38 Hz), and coupling to the two protons on the adjacent labeled carbon ($^2J_{C-H}$ = 2 Hz).

For the oxidation of nonphenolic lignin model compound **10**-$^{13}C_2$, the selectivity of catalyst **4** bears similarity to previously reported dipicolinate catalyst **2** (Figure 1),[17b] giving predominantly a mixture of C−O and C−H bond cleavage products. This stands in contrast to catalyst **1**, which was previously reported by Son and Toste to give a high selectivity (94%) for C−O bond cleavage in a closely related nonphenolic lignin model.[16] This is also distinct from 8-quinolinate catalyst **3**, which gave only C−H bond cleavage products (ketone **12**-$^{13}C_2$) upon aerobic oxidation of **10**-$^{13}C_2$ (Table 2, entry 1).[34] Previously, Son and Toste have suggested that the selectivity for C−O bond cleavage vs C−H bond cleavage products is influenced by the ligand bite angle.[16] Although the origin of selectivity remains under investigation, the C−O and

Scheme 4. Aerobic Oxidation of Lignin Model Compound 10-$^{13}C_2$ Using Vanadium Catalyst 4 (10 mol %)



~84% conversion

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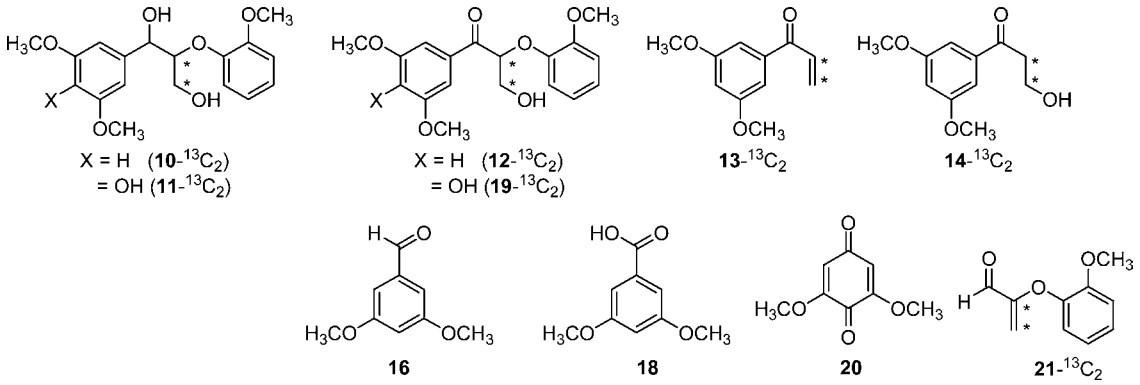
Table 2. Comparison of Products Obtained from Vanadium Catalysts 3 and 4

substrates: *products:*



				percent yield							
entry	substrate	catalyst	% conv.	**12**	**13**	**14**	**16**	**18**	**19**	**20**	**21**
1	**10**-$^{13}C_2$	**3**[a]	65	55	0	0	0	0			
2	**10**-$^{13}C_2$	**4**[b]	84	27	26	14	4	6			
3	**11**-$^{13}C_2$	**3**[a]	100						27	30	34
4	**11**-$^{13}C_2$	**4**[b]	20						19	trace	trace

[a]Conditions: 10 mol % catalyst, pyridine-d_5, 80 °C, 48 h. [b]Conditions: 10 mol % catalyst, toluene-d_8, 100 °C, 48 h.

C−H bond cleavage reactions likely proceed through different mechanisms, as suggested by the varied selectivities observed for vanadium catalysts **1**−**4**.

Bis(phenolate)amine catalyst **5** was also tested as a catalyst for the aerobic oxidation of **10**-$^{13}C_2$. However, when **10**-$^{13}C_2$ was heated in toluene-d_8 (100 °C, 48 h) with **5** (10 mol %), a low conversion was observed and signals corresponding to 4,5-dimethylsalicylaldehyde were detected in the ^{1}H NMR spectrum, suggesting the decomposition of the vanadium catalyst. The identity of the 4,5-dimethylsalicylaldehyde was confirmed by GC-MS analysis, which showed a peak arising from this product with the expected mass (m/z = 150). The 4,5-dimethylsalicylaldehyde likely results from oxidation of the benzylic position of the **BPA** ligand and subsequent C−N bond cleavage. Previously, Kol and co-workers have reported reactivity at the benzylic position of a closely related bis(phenolate)amine ligand, which underwent β-hydrogen abstraction upon thermolysis of a tantalum tribenzyl complex.[35] Decomposition of vanadium catalyst **5** was also observed during the attempted catalytic oxidation of phenolic lignin model **11**-$^{13}C_2$.

Complex **4** catalyzed the oxidation of the phenolic lignin model compound **11**-$^{13}C_2$. When **4** (10 mol %) was heated with phenolic lignin model **11**-$^{13}C_2$ in toluene-d_8 solvent under air (100 °C, 48 h), only partial conversion of **11**-$^{13}C_2$ was observed (ca. 20%), and the reaction afforded ketone **19**-$^{13}C_2$ (19%) (Scheme 5). Surprisingly, although catalyst **4** generates C−O bond cleavage products upon oxidation of the non-phenolic lignin model compound **10**-$^{13}C_2$, no C−O bond cleavage products were observed in the oxidation of phenolic lignin model compound **11**-$^{13}C_2$ using catalyst **4**. Previously, alkyl-phenyl bond cleavage products (**20** and **21**-$^{13}C_2$, Table 2) were observed as the major products when the oxidation of **11** was carried out with 8-quinolinate catalyst **3**;[34] using catalyst **4** only trace alkyl-phenyl bond cleavage products were detected by ^{1}H and ^{13}C NMR spectroscopy (Table 2, entries 3 and 4).

CONCLUSIONS

New vanadium(V) complexes of bis(phenolate) pyridine and bis(phenolate)amine ligands have been synthesized and characterized. Both complexes **4** and **5** react with pinacol at room temperature, affording acetone and vanadium(IV) products **6** and **7**, respectively. Complexes **4** and **5** were evaluated as catalysts for the aerobic oxidation of 4-methoxybenzylalcohol. Complex **4** (2 mol %) was an active catalyst, affording 4-methoxybenzaldehyde in nearly quantitative yield, while a lower conversion was observed with complex **5**. The vanadium complexes were also tested for the aerobic oxidation of lignin model compounds **10**-$^{13}C_2$ and **11**-$^{13}C_2$. Decomposition of vanadium catalyst **5** resulting from oxidation of the bis(phenol)amine ligand was observed during the attempted aerobic oxidation of both lignin model compounds. However, complex **4** did catalyze the aerobic oxidation of lignin model compounds **10**-$^{13}C_2$ and **11**-$^{13}C_2$. In general, complex **4** is a somewhat slower catalyst for the aerobic oxidation reactions than previously reported 8-quinolinate catalyst **3**. The NMR features of complexes **4** and **9** are consistent with the bis(phenolate)pyridine ligand scaffold being more electron rich than the bis(8-quinolinate) ligand set. Overall, in considering a complete catalytic cycle, the evidence suggests that while the more electron rich bis(phenolate) ligand set may accelerate the reaction of vanadium(IV) with air, the opposite trend is expected for the alcohol oxidation step, which would be promoted by more electron deficient ligands. Designing more active vanadium catalysts for aerobic oxidation reactions will require balancing the electronic requirements of both steps.

EXPERIMENTAL SECTION

General Considerations. Unless specified otherwise, all reactions were carried out under a dry argon or nitrogen atmosphere using standard glovebox and Schlenk techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories. CD_2Cl_2 and CD_3CN were dried over CaH_2. Anhydrous grade solvents were obtained from Acros and used as received. ^{1}H, ^{13}C, and ^{51}V NMR spectra were obtained at room temperature on a Bruker AV400 MHz spectrometer,

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with chemical shifts (δ) referenced to the residual solvent signal (^{1}H and ^{13}C) or referenced externally to $VOCl_3$ (0 ppm). IR spectra were obtained on a Perkin-Elmer Spectrum One instrument. GC-MS analysis was obtained using a Hewlett-Packard 6890 GC system equipped with a Hewlett-Packard 5973 mass selective detector. Elemental analyses were performed by Atlantic Microlab in Norcross, GA. Ligands **H_2BPA**,[22] **H_2BPP**,[23] and **H_2BPB**[23] were synthesized according to previously published procedures.

Preparation of (BPP)V^V(O)(O^{i}Pr) (4). The ligand **H_2BPP** (243 mg, 0.500 mmol) was suspended in isopropanol (5.0 mL) and $V(O)(O^iPr)_3$ (122 mg, 0.500 mmol) was added. The mixture was stirred overnight at room temperature, and then the brown solid was collected by filtration, washed with isopropanol (2 × 2 mL), and dried under vacuum. Yield: 0.260 g (85%). Brown blocks suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2-^{i}PrOH solution of the complex. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (t, J = 7.9 Hz, 1H, Py), 7.80 (d, J = 7.9 Hz, 2H, Py), 7.56 (m, 4H, aryl), 5.61 (m, 1H, V-OCH(CH$_3$)$_2$), 1.51 (s, 18H, C(CH_3)$_3$), 1.45 (d, J = 6.2 Hz, 6H, V-OCH(CH_3)$_2$), 1.39 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 160.7, 155.6, 143.6, 139.7, 136.4, 127.2, 124.9, 123.9, 123.6, 105.6, 35.7, 35.0, 31.9, 30.4, 25.3. ^{51}V NMR (105 MHz, CD_2Cl_2) δ −512.7 (s). IR (thin film): $\nu_{V=O}$ = 970 cm^{-1}. Anal. Calcd. for $C_{36}H_{50}NO_4V$: C, 70.68; H, 8.24; N, 2.29. Found: C, 70.82; H, 8.23; N, 2.35.

Preparation of (BPA)V^V(O)(O^{i}Pr) (5). In a glass vial, **H_2BPA** (305 mg, 0.932 mmol) and $V(O)(O^iPr)_3$ (228 mg, 0.934 mmol) were suspended in isopropanol (5 mL). The mixture was stirred at room temperature for 20 h, during which time a brown solid formed. The brown solid was collected on a frit, washed with isopropanol (2 × 1 mL), and dried under vacuum. Yield: 289 mg (68%). ^{1}H NMR (400 MHz, CD_3CN) δ 6.92 (s, 2H, aryl), 6.48 (s, 2H, aryl), 5.54 (h, 1H, J = 6.0 Hz, V-OCH(CH$_3$)$_2$), 4.76 (d, 2H, J = 15.2 Hz, CH_2), 3.93 (d, 2H, J = 15.2 Hz, CH_2), 2.46 (br s, 2H, N−CH_2CH$_2$CH$_3$), 2.20 (s, 6H, aryl-CH_3), 2.19 (s, 6H, aryl-CH_3), 1.41 (d, 6H, J = 6.4 Hz, V-OCH(CH_3)$_2$), 1.35 (br s, 2H, N−CH$_2$CH_2CH$_3$), 0.45 (br t, 3H, J = 6.0 Hz, N−CH$_2$CH$_2$CH_3). ^{51}V NMR (105 MHz, CD_3CN) δ −518.0 (s). IR (thin film): $\nu_{V=O}$ = 961 cm^{-1}. Anal. Calcd. for $C_{24}H_{34}NO_4V$: C, 63.85; H, 7.59; N, 3.10. Found: C, 63.88; H, 7.53; N, 3.27.

Preparation of (BPP)V^{IV}(O)(HO^{i}Pr) (6). In a glass vial, complex **4** (30.6 mg, 0.050 mmol) was dissolved in CH_2Cl_2 (3 mL) and pinacol (17.7 mg, 0.150 mmol) was added. n-Hexane (1 mL) was then added into the solution, and the resulting reaction mixture was slowly evaporated at room temperature over a period of 3 days, during which time dark-green crystals formed. The supernatant was decanted, and the crystals washed with n-hexane (2 × 1 mL) and dried under vacuum. Yield: 0.029 g (95%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.21 (br), 4.26 (br), 1.96 (br s), 1.57 (br), 1.43 (br s), 1.28 (br s). IR (thin film): $\nu_{V=O}$ = 953 cm^{-1}. Anal. Calcd. for $C_{36}H_{49}NO_4V$·^{i}PrOH: C, 69.83; H, 8.56; N, 2.09. Found: C, 69.14; H, 8.12; N, 2.18.

Preparation of [(BPA)V^{IV}(O)(HO^{i}Pr)]$_2$ (7). In a glass vial, complex **5** (0.1534 g, 0.3401 mmol) and pinacol (0.113 g, 0.958 mmol) were suspended in CH_3CN (2 mL). The mixture was allowed to stand at room temperature overnight (20 h), during which time all of the dark red solid dissolved and pale purple crystals formed. The reaction mixture was cooled to −20 °C for a further 48 h. At this time, the supernatant was decanted, and the crystals washed with diethyl ether (3 × 2 mL) and dried under vacuum. Yield: 0.148 g (96%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.34 (br s), 2.33 (br), 1.90 (br), 1.62 (br), −0.14 (br). IR (thin film): $\nu_{V=O}$ = 946 cm^{-1}. Anal. Calcd for $C_{42}H_{54}N_2O_6V_2$: C, 63.71; H, 7.80; N, 3.10. Found: C, 63.93; H, 7.93; N, 3.15.

Preparation of [(BPP)V^V(O)$_2$]HNEt$_3$ (8). Complex **4** (12.2 mg, 0.02 mmol) was dissolved in CH_2Cl_2/MeOH (4.0 mL, 3:1, v/v) in a small vial, and then water (0.1 mL) was added. To the resulting pale-brown solution was added triethylamine (10.1 mg, 0.1 mmol), and the reaction mixture was slowly evaporated at room temperature over a period of 3 days, brown blocks suitable X-ray diffraction analysis formed, which were collected by decanting the supernatant and washing with Et_2O, and then dried under vacuum. Yield: 11.5 mg (86%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.97 (t, J = 8.0 Hz, 1H, Py), 7.72 (d, J = 8.0 Hz, 1H, Py), 7.56 (d, J = 2.4 Hz, 2H, aryl), 7.46 (d, J = 2.4 Hz, 2H, aryl), 2.68 (q, J = 7.2 Hz, 6H, HNEt$_3$), 1.49 (s, 18H, C(CH_3)$_3$), 1.38 (s, 18H, C(CH_3)$_3$), 1.07 (t, J = 7.2 Hz, 9H, HNEt$_3$). ^{51}V NMR (105 MHz, CD_2Cl_2) δ −552 (s). IR (thin film): $\nu_{V=O}$ = 934 cm^{-1}, 905 cm^{-1}.

Preparation of (BPP)V^V(O)(OCH$_2$C$_6$H$_4$-*p*-OCH$_3$) (9). In a glass vial, complex **4** (30.6 mg, 0.050 mmol) was dissolved in CH_2Cl_2 (3 mL) and 4-methoxybenzyl alcohol (20.7 mg, 0.150 mmol) was added. n-Hexane (1 mL) was then added, and the resulting reaction mixture was slowly evaporated at room temperature over 5 days, during which time dark crystals formed. The supernatant was decanted, and the crystals washed with n-hexane (2 × 1 mL) and dried under vacuum. Yield: 0.030 g (86%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (t, J = 8.0 Hz, 1H, Py), 7.79 (d, J = 8.0 Hz, 2H, Py), 7.57−7.53 (m, 4H, aryl), 7.34 (d, J = 8.4 Hz, 2H, aryl), 6.90 (d, J = 8.4 Hz, 2H, aryl), 6.39 (s, 2H, V-OCH_2), 3.82 (s, 3H, -OCH_3), 1.48 (s, 18H, C(CH_3)$_3$), 1.40 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 163.1, 160.3, 159.7, 159.3, 144.6, 139.8, 136.9, 134.0, 133.2, 129.6, 129.1, 127.2, 125.3, 124.4, 123.9, 114.3, 114.1, 105.7, 66.2, 65.3, 55.8, 35.7, 35.1, 31.9, 30.4, 15.7. ^{51}V NMR (105 MHz, CD_2Cl_2) δ −481.3 (s). IR (thin film): $\nu_{V=O}$ = 972 cm^{-1}. Anal. Calcd.for $C_{41}H_{52}NO_5V$: C, 71.39; H, 7.60; N, 2.03. Found: C, 71.11; H, 7.53; N, 1.94.

General Procedure for the Catalytic Aerobic Oxidation of 4-Methoxybenzyl Alcohol. In a 25 mL round-bottom flask, 4-methoxybenzyl alcohol (69 mg, 0.50 mmol) was combined with vanadium complex **4** or **5** (0.01 mmol, 2 mol %), NEt_3 (7 μL, 0.05 mmol, 10 mol %), and a hexamethylbenzene internal standard (5.5 mg, 0.034 mmol). The mixture was dissolved in toluene (1 mL) under air, and the flask equipped with a stir bar and an air condenser. The flask was heated with stirring in an oilbath at 80 °C for 65 h under air. The reaction mixture was cooled to room temperature, the solvent removed under vacuum, and the yield of oxidized product 4-methoxybenzaldehyde determined by integration of the ^{1}H NMR spectra against the internal standard.

Aerobic Oxidation of 10-$^{13}C_2$ Using Vanadium Complex 4. In an NMR tube, lignin model **10**-$^{13}C_2$ (0.032 g, 0.095 mmol) was dissolved in toluene-d_8 (1 mL) containing dimethylsulfone (ca. 2 mg) as an internal standard. An initial spectrum was recorded, and then the solution was transferred to a 50 mL round-bottom flask containing **4** (5.8 mg, 0.0095 mmol, 10 mol %) under air. The reaction mixture was heated under air with stirring at 100 °C for 48 h, and then cooled to room temperature. The solution was transferred to an NMR tube, and additional spectra were recorded. Product yields were determined by integration against the internal standard.

Aerobic Oxidation of 11-$^{13}C_2$ Using Vanadium Complex 4. In an NMR tube, phenolic lignin model **11**-$^{13}C_2$ (0.020 mg, 0.057 mmol) was dissolved in toluene-d_8 (1 mL) containing dimethylsulfone (0.025 M) as an internal standard. An initial spectrum was recorded, and then the solution was transferred to a 50 mL round-bottom flask containing **4** (3.5 mg, 0.0057 mmol, 10 mol %) under air. The reaction mixture was heated under air with stirring at 100 °C for 48 h, and then cooled to room temperature. The solution was transferred to an NMR tube and additional spectra were recorded. Yields were determined by integration against the internal standard.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files, X-ray crystallographic data, and NMR spectra from the catalytic oxidation reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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