Inorganic Chemistry
Article

Inorg. Chem. 2010, 49, 5611–5618 5611
DOI: 10.1021/ic100528n

Aerobic Oxidation of Lignin Models Using a Base Metal Vanadium Catalyst

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Received March 19, 2010

Dipicolinate vanadium(V) complexes oxidize lignin model complexes pinacol monomethyl ether (**A**), 2-phenoxyethanol (**B**), 1-phenyl-2-phenoxyethanol (**C**), and 1,2-diphenyl-2-methoxyethanol (**D**). With substrates having C−H bonds adjacent to the alcohol moiety (**B**−**D**), the C−H bond is broken in pyridine-d_5 solvent, yielding 2-phenoxyacetaldehyde from **B**, 2-phenoxyacetophenone from **C**, and benzoin methyl ether from **D**. In DMSO-d_6 solvent the reaction is slower, and both C−H and C−C bond cleavage products are observed for **D**. The vanadium(IV) products of these reactions have been identified and characterized. Catalytic oxidation of **C** and **D** has been demonstrated using air and (dipic)V(O)O^{i}Pr. For both substrates, the C−C bond between the alcohol and ether groups is broken in the catalytic oxidation. 1-Phenyl-2-phenoxyethanol is oxidized to a mixture of phenol, formic acid, benzoic acid, and 2-methoxyacetophenone. The products of oxidation of 1,2-diphenyl-2-methoxyethanol depend on the solvent; in DMSO benzaldehyde and methanol are the major products, while benzoic acid and methyl benzoate are the major products obtained in pyridine solvent. Phenyl substituents on the model complex facilitate the oxidation, with relative rates of oxidation **D** > **C** > **B**.

Introduction

The development of alternatives to petroleum-based fuels and chemicals is becoming increasingly urgent because of concerns over climate change, growing world energy demand, and energy security issues. Biomass is the only renewable carbon feedstock available, and thus much recent effort has focused on developing technologies that convert biomass into chemicals and fuels.[1,2] The majority of non food-derived biomass is in the form of lignocellulose, which is often not fully utilized because of difficulties associated with breaking down both lignin and cellulose.[3] Recently, a number of methods have been reported to transform cellulose directly into more valuable materials such as glucose,[4] sorbitol,[5] 5-(chloromethyl)furfural,[6] and ethylene glycol.[7] Less progress has been made with selective transformations of lignin,[8−11] which is typically treated in paper and forest industries by kraft pulping or incineration.[12,13] Currently, more than 40 million tons of lignin are produced annually worldwide, roughly 95% of which is burned for energy.[14] In coming years, as technologies which employ fermentation or other selective conversions of cellulose and hemicellulose are implemented, production of lignin is anticipated to increase dramatically. The discovery of new methods to convert lignin directly to value-added products would allow for more efficient use of this natural resource.

Lignin is a randomized polymer containing methoxylated phenoxy propanol units.[15] A number of different linkages occur naturally; one of the most prevalent is the β-O-4 linkage shown in Figure 1,[15] containing a C−C bond with 1,2-hydroxy ether substituents. We envisioned that a selective oxidative cleavage of this carbon−carbon bond could be used to break lignin into smaller, more utilizable components, for example, aromatic product streams that could feed into existing industrial markets. Air (oxygen) would be the ideal oxidant for this transformation.

While the oxidative C−C bond cleavage of 1,2-diols is well established for a variety of metals, including vanadium, iron,

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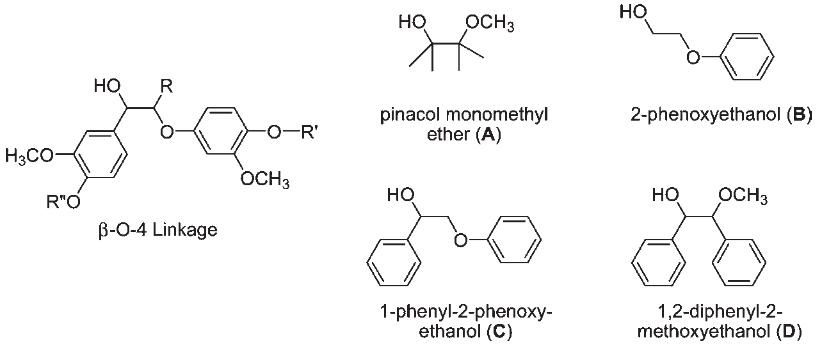

Figure 1. *β*-O-4 linkage and lignin model complexes.

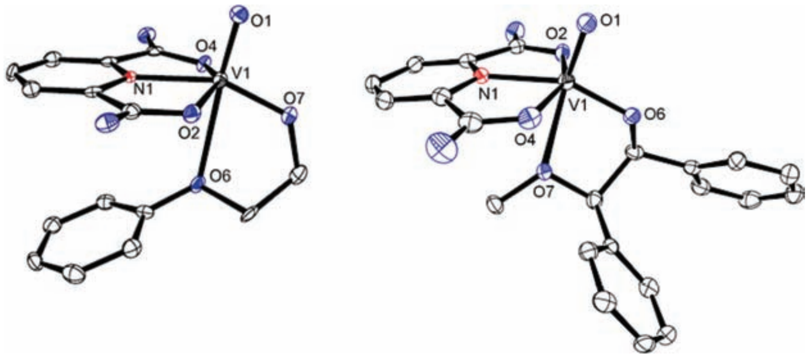

Figure 2. X-ray Structures of **3** and **5** (thermal ellipsoids at 50% probability, H atoms omitted for clarity). Selected bond lengths (Å) for **3**: V1−O1 = 1.568(2), V1−O7 = 1.775(2), V1−O6 = 2.547(2), V1−O4 = 1.929(2), V1−O2 = 1.949(2), V1−N1 = 2.060(3). For **5**: V1−O1 = 1.576(2), V1−O6 = 1.784(2), V1−O7 = 2.438(2), V1−O2 = 1.925(2), V1−O4 = 1.931(2), V1−N1 = 2.053(2).

manganese, ruthenium, and polyoxometalate complexes,[16−20] less is known about oxidative C−C bond cleavage of 1,2-hydroxyethers.[21] Permanganate and tribromide, both common reagents for C−C bond cleavage of vicinal diols, do not react with 1,2-hydroxyethers to break the carbon−carbon bond.[22−25] Instead, oxidation of only the alcohol group (yielding 1,2-carbonyl-ethers) is observed, and different mechanistic pathways have been proposed for the reactions of vicinal diols and their monoethers.[22−28] In contrast, cerium(IV) has been shown to break the C−C bond of 2-methoxycyclohexanol to give adipaldehyde (1,6-hexane-dial) and methanol.[29,30] *N*-iodosuccinimide is also an effective reagent for C−C bond cleavage of 1,2-hydroxy ethers (yielding carbonyl compounds and acetals),[31] but no catalytic version of this reaction has previously been reported.[32]

The use of an earth-abundant (non-precious) metal catalyst and air as an oxidant would represent a significant advance in our ability to break carbon−carbon bonds in 1,2-hydroxyether compounds such as lignin. We now report that dipicolinate vanadium complexes oxidize the lignin model complexes pinacol monomethyl ether, 2-phenoxyethanol, 1-phenyl-2-phenoxyethanol, and 1,2-diphenyl-2-methoxyethanol.[33] Both C−H and C−C cleavage modes have been observed in these substrates. Catalytic aerobic oxidative C−C bond cleavage has been demonstrated in 1-phenyl-2-phenoxyethanol and 1,2-diphenyl-2-methoxyethanol. To the best of our knowledge, these are the first examples of catalytic aerobic C−C bond cleavage of 1,2-hydroxyether compounds.

Results and Discussion

Initial investigations aimed to gain insight into the stoichiometric reactivity of the 1,2-hydroxyether lignin models

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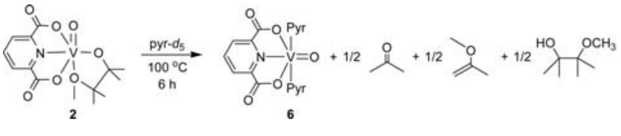
with (dipic)V^V. Reaction of (dipic)V^V(O)O^{i}Pr (**1a**) or (dipic)V^V(O)OEt (**1b**) with pinacol monomethyl ether (**A**), 2-phenoxyethanol (**B**), 1-phenyl-2-phenoxyethanol (**C**), or 1,2-diphenyl-2-methoxyethanol (**D**)[34] in acetonitrile solvent yielded new vanadium(V) complexes where the alcohol-ether ligand was bound in a chelating fashion. Complexes (dipic)V^V(O)(pinOMe) (**2**), (dipic)V^V(O)(OPE) (**3**), (dipic)V^V(O)(OPPE) (**4**) and (dipic)V^V(O)(DPME) (**5**) (pinOMe = 2,3-dimethyl-3-methoxy-2-butanoxide; OPE = 2-phenoxyethoxide; OPPE = 1-phenyl-2-phenoxyethoxide; DPME = 1,2-diphenyl-2-methoxyethoxide), were isolated in good yields (39−88%) and characterized by NMR and IR spectroscopy, elemental analysis, and X-ray crystallography (for **2**, **3**, and **5**).

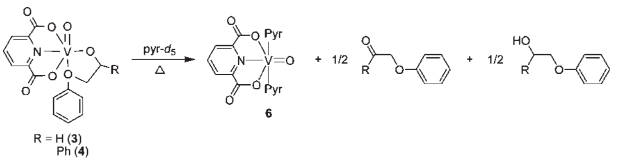
The X-ray structures of **2** (Supporting Information, Figure S1), **3** (Figure 2), and **5** (Figure 2), display similar vanadium oxo bond distances of 1.573(2), 1.568(2), and 1.576(2) Å, respectively. In each case the substrate binds in a chelating manner, similar to the previously reported vanadium(V) pinacolate complex (dipic)V(O)(pinOH).[35]

When pinacol monomethyl ether complex **2** was heated in pyr-d_5 solution (6 h at 100 °C, or 3 weeks at 25 °C), the previously reported vanadium(IV) complex (dipic)V^{IV}(O)(pyr)$_2$ (**6**),[35] acetone, 2-methoxypropene, and pinacol monomethyl ether were formed. Yields of the organic products were determined by integration of the ^{1}H NMR spectrum against an internal standard (*p*-xylene); acetone, 2-methoxypropene, and pinacol monomethyl ether were formed in 94%, 76%, and 92% of the theoretical maximum yields based on the oxidizing equivalents of vanadium consumed, suggesting the stoichiometry shown in eq 1.



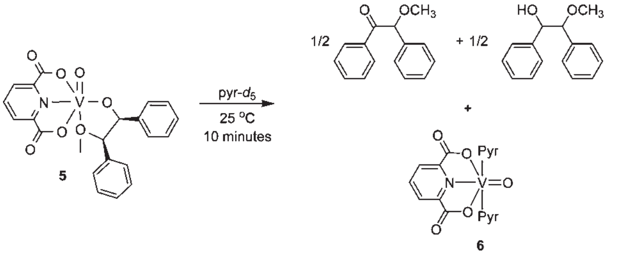
(1

In contrast to compound **2**, all the compounds having secondary C−H bonds on the coordinated alcohol moiety underwent oxidative C−H bond cleavage under stoichiometric conditions in pyridine solution. Heating 2-phenoxyethoxide complex **3** in pyr-d_5 solution (10 min at 100 °C) afforded **6**, 2-phenoxyacetaldehyde (78%), and 2-phenoxyethanol (98%), suggesting the stoichiometry shown in eq 2. The formation of 2-phenoxyacetaldehyde was confirmed by comparison with an authentic sample prepared according to a literature procedure.[36]



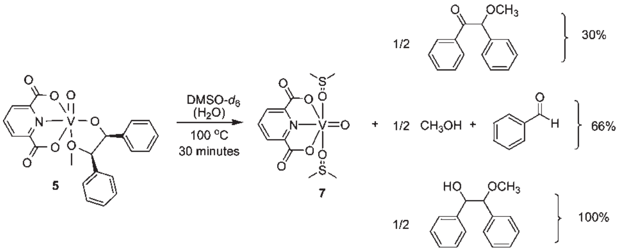
(2)

When dissolved in pyridine-d_5 solution, 1-phenyl-2-phenoxyethoxide complex **4** reacted rapidly at room temperature (10 min) to form **6** and a 1:1 ratio of 2-phenoxyacetophenone and 1-phenyl-2-phenoxyethanol (eq 2). 2-Phenoxyacetophenone was prepared independently according to a published procedure[37] and spiked into the reaction mixture, confirming the identity of this product. Complex **5** also underwent C−H bond cleavage when dissolved in pyr-d_5 at room temperature, reacting completely within 10 min to form **6** and a 1:1 ratio of benzoin methyl ether (2-methoxy-2-phenylacetophenone) and 1,2-diphenyl-2-methoxyethanol (eq 3)



(3)

However, in the absence of pyridine, conversion of **5** was significantly slower, and in addition to C−H bond cleavage, C−C bond cleavage was observed even for compounds having secondary C−H bonds on the coordinated alcohol moiety. Heating a DMSO-d_6 solution of complex **5** (30 min at 100 °C) resulted in a mixture of C−H and C−C bond cleavage products (eq 4). The organic products of this reaction consisted of benzoin methyl ether (30%), coproducts methanol and benzaldehyde (66%), and 1,2-diphenyl-2-methoxyethanol (100%). The green vanadium product of this reaction was the new vanadium(IV) complex (dipic)V^{IV}(O)(DMSO)$_2$ (**7**). Complex **7** showed a V=O stretch in the IR spectrum at 948 cm^{-1} and was characterized by X-ray crystallography (Figure 3). The V=O bond length in **7** (1.605(2) Å) is similar to that observed in **6** (1.611(2) Å).[35] Complex **7** could be independently prepared by the thermolysis of the pinacolate complex (dipic)V(O)(Hpin)[35] in DMSO solvent and was isolated in 83% yield.



(4)

The mechanism of the C−C cleavage reaction depicted in eq 4 is currently under investigation, but one possible pathway involves initial reaction of **5** to form benzaldehyde and a methoxybenzyl radical. Subsequent reaction of the methoxybenzyl radical with water and a second equivalent of **5** would form methanol, a second equivalent of benzaldehyde, and release 1,2-diphenyl-2-methoxyethanol.[38] Similar radical pathways have been proposed for the cleavage reactions of

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[34] Prepared as an 85:15 mixture of u (*R*,*S* + *S*,*R*):l (*S*,*S* + *R*,*R*) diastereomers by the acid-catalyzed ring opening of *trans*-stilbene oxide in CH$_3$OH (see Experimental Section for details).

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[38] Attempts to test this hypothesis by the addition of radical traps to the reaction were inconclusive. Complex **5** reacted directly with BHT (2,6-di-*tert*-butyl-4-methylphenol) and PPh$_3$ to give products that were not further characterized. When 9,10-dihydroanthracene was added to the reaction mixture, only trace (< 1%) anthracene was detected, with the reaction course being otherwise unaffected.

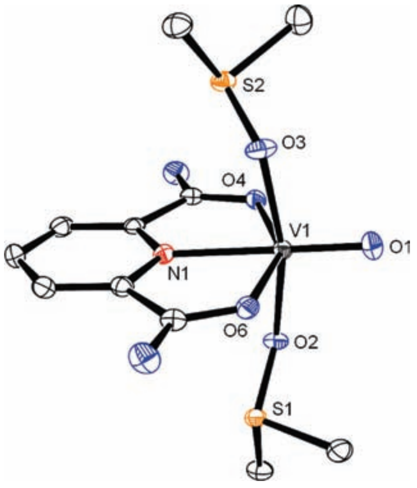

Figure 3. X-ray structure of **7** (thermal ellipsoids at 50% probability, H atoms omitted for clarity). Selected bond lengths (Å) for **7**: V1−O1 = 1.605(2), V1−O2 = 2.020(2), V1−O3 = 2.062(2), V1−O4 = 2.020(2), V1−O6 = 2.030(2), V1−N1 = 2.145(2).

monoprotected diols by Ce^{IV} and *N*-iodosuccinimide mentioned above.[29,31]

After observing stoichiometric oxidation of lignin model compounds **A**−**D**, we tested the *catalytic* oxidation of 2-phenoxyethanol, 1-phenyl-2-phenoxyethanol, and 1,2-diphenyl-2-methoxyethanol. Oxidations were carried out using 2.5−10 mol % (dipic)V^{V}(O)O^{i}Pr (**1a**) under an atmosphere of air in pyridine-d_5 or DMSO-d_6 solvents at 100 °C. In general, phenyl substituents on the carbon backbone facilitated the oxidation, with 1,2-diphenyl-2-methoxyethanol being the most reactive substrate, and 2-phenoxyethanol the least. Control reactions under air with no vanadium catalyst in DMSO-d_6 or pyr-d_5 solvents showed no reaction for 2-phenoxyethanol or 1-phenyl-2-phenoxyethanol and only trace oxidation ($<5\%$) of 1,2-diphenyl-2-methoxyethanol after 1 week at 100 °C.

A DMSO-d_6 solution of 1-phenyl-2-phenoxyethanol (substrate **C**) was heated under an atmosphere of air at 100 °C with 10 mol % **1a** (Table 1, entry 2). After 1 week, integration of the ^{1}H NMR spectrum against the internal standard (1,3,5-tri-*tert*-butylbenzene) revealed that 95% of the starting material had been consumed. The products of this reaction consisted of formic acid (46%), benzoic acid (81%), phenol (77%), and 2-phenoxyacetophenone (9%) (yields expressed as a percentage of the theoretical maximum based on the initial amount of substrate). At 50% conversion, 2-phenoxyacetophenone was detected in 35% overall yield, suggesting that the ketone is formed initially and further oxidized to benzoic acid, phenol, and formic acid. The exact reason for the low yield of formic acid is unclear at this time and may be due to deeper oxidation to CO_2, which is difficult to detect under the reaction conditions (air). However, a separate experiment demonstrated that (dipic)V(O)O^{i}Pr (10 mol %) is an inefficient catalyst for the aerobic oxidation of formic acid, with less than 5% formic acid reacting after 3 days at 100 °C under air in DMSO-d_6 solvent.

For 1,2-diphenyl-2-methoxyethanol (substrate **D**), the products of the catalytic oxidation differed in DMSO-d_6 and pyr-d_5 solvents. Heating a solution of 1,2-diphenyl-2-methoxyethanol and 5 mol % **1a** in DMSO-d_6 over 20 h at 100 °C under air gave benzaldehyde (73%), methanol (69%), and benzoin methyl ether (13%), with the remaining products consisting of benzoic acid and methyl benzoate (5% or less each) (Table 1, entry 3). Nearly complete consumption (94%) of the starting material was observed: a total of 19 turnovers (turnover = mol 1,2-diphenyl-2-methoxyethanol consumed per mol V). Using a lower catalyst loading (2.5 mol %) resulted in a greater turnover number (37), but required a longer reaction time (40 h).

A different product distribution was observed when the catalytic reaction was run in pyr-d_5 solvent. 1,2-Diphenyl-2-methoxyethanol was heated with 10 mol % **1a** under air at 100 °C (Table 1, entry 4). After 6 days, the starting material had been completely consumed, and the organic products consisted of benzoic acid (85%), methyl benzoate (84%), benzoin methyl ether (9%), benzaldehyde (9%), and methanol (6%). Benzil and benzoin were also detected as minor products (less than 5% each). Benzoin methyl ether is a likely intermediate in the formation of benzoic acid and methyl benzoate; this ketone was detected in the reaction mixture in 45% overall yield at 56% conversion.

Model compound 2-phenoxyethanol (substrate **B**), having no backbone phenyl substituents, was oxidized only very slowly by complex **1a** (Table 1, entry 1). When a DMSO-d_6 solution of 2-phenoxyethanol was heated with 10 mol % **1a** at 100 °C for 1 week under air, only approximately 20% of the starting material was consumed (integration against the internal standard). Phenol (18%), formic acid (6%), and several other minor unidentified products were detected in the reaction mixture at this time. Conducting the catalytic reaction in pyr-d_5 solvent also gave poor results; only 35% conversion had occurred after 1 week at 100 °C.

For the oxidations of **B**−**D** in DMSO-d_6, ^{51}V NMR spectra of the reaction mixtures acquired at the end of the reaction time showed one resonance at −518 ppm, consistent with the *cis*-dioxo anion [(dipic)V(O)$_2$]$^{-}$ (**8**). The identity of this species was confirmed by comparison with spectra obtained from authentic samples of known complexes [(dipic)V(O)$_2$]HPyr[35] and [(dipic)V(O)$_2$]K[39] in DMSO-d_6. The *cis*-dioxo anion could also be formed by oxidation of the vanadium(IV) complex **7**. When a solution of **7** was heated in DMSO-d_6 solution at 100 °C under air (18 h), the green color faded, and **8** was detected by ^{1}H and ^{51}V NMR spectroscopy.

Control experiments were conducted to investigate a possible role of the DMSO-d_6 solvent in the catalysis. Under anaerobic conditions, a solution of the vanadium(IV) complex (dipic)V^{IV}(O)(pyr)$_2$ in DMSO-d_6 showed no turnovers with 1,2-diphenyl-2-methoxyethanol after 1 week at 100 °C, suggesting that the DMSO solvent was not acting as the oxidant in the catalytic reaction. Reactions under anaerobic conditions with (dipic)V^{IV}(O)(DMSO)$_2$ and 2-phenoxyethanol or 1-phenyl-2-phenoxyethanol also showed no reaction after heating in DMSO-d_6 at 100 °C for 1 week. No dimethylsulfide was detected in the reaction mixtures from the catalytic oxidation of **B**−**D** by ^{13}C NMR spectroscopy or GC-MS, providing further support that the DMSO solvent is not the terminal oxidant. However, some oxidation of the DMSO solvent does take place under the catalytic conditions, as dimethylsulfone-d_6 was detected in the ^{13}C NMR spectra and GC-MS traces of the reaction mixtures from oxidation of **B**−**D**. Oxidation of DMSO solvent has been

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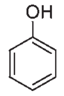
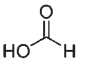
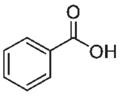
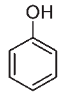
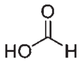
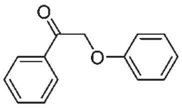
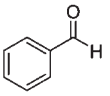
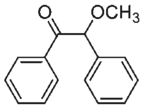
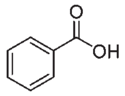
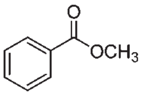
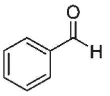
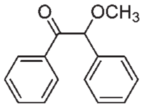
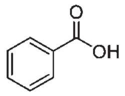
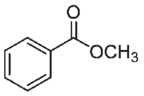
Table 1. Catalytic Oxidation of Lignin Models **B**−**D**[e]

entry	substrate	solvent	conv (%)	products
1[a]	**B**	DMSO-d_6	20	 18%  6% unidentified 2-5%
2[b]	**C**	DMSO-d_6	95	 81%  77%  46%  9%
3[c]	**D**	DMSO-d_6	94	 73% CH_3OH 69%  13%  5%  5%
4[d]	**D**	pyr-d_5	99	 9% CH_3OH 6%  9%  85%  84%

[a] 10 mol % (dipic)V(O)O^{i}Pr, 7 days. [b] 10 mol % (dipic)V(O)O^{i}Pr, 7 days. [c] 5 mol % (dipic)V(O)O^{i}Pr, 20 h. [d] 10 mol % (dipic)V(O)O^{i}Pr, 6 days. [e] Conditions: All runs were carried out at 100 °C.

reported previously in the aerobic oxidation of HMF (5-hydroxymethyl-2-furaldehyde) catalyzed by supported vanadyl-pyridine complexes.[40]

Although we previously found evidence suggesting the involvement of vanadium(III) in the catalytic oxidation of pinacol, reduction of vanadium(IV) to vanadium(III) does not occur with the 1,2-hydroxyether substrates. No reaction was observed upon heating (dipic)V^{IV}(O)(pyr)$_2$ (**6**) under anaerobic conditions with pinacol monomethyl ether, 1-phenyl-2-phenoxyethanol, or 1,2-diphenyl-2-methoxyethanol in pyr-d_5 at 100 °C for up to a week, in contrast with the reaction between **6** and pinacol in pyr-d_5 at 100 °C, which formed a vanadium(III) μ-oxo dimer within 48 h.[35] Although the mechanism for reduction to vanadium(III) is not well understood at this time, these results suggest that the reduction may be facilitated by two adjacent −OH functional groups.

Conclusions

Dipicolinate vanadium(V) complexes stoichiometrically oxidize the lignin model complexes pinacol monomethyl ether, 2-phenoxyethanol, 1-phenyl-2-phenoxyethanol, and 1,2-diphenyl-2-methoxyethanol. Both C−H and C−C bond cleavage products are observed in these reactions, which proceed by reduction of the metal center to form well-defined vanadium(IV) complexes. Successful catalytic, aerobic oxidative C−C bond cleavage of 1-phenyl-2-phenoxyethanol and 1,2-diphenyl-2-methoxyethanol has also been demonstrated. Phenyl substitution on the carbon backbone facilitates the C−C bond cleavage reaction, with unsubstituted substrate 2-phenoxyethanol reacting only very slowly under catalytic conditions. The precise mechanisms of the oxidations are the subject of ongoing detailed experimental and computational investigations.

Using the base-metal vanadium catalyst and air as the oxidant is a completely new method for breaking carbon−carbon bonds in 1,2-hydroxy ether compounds. This approach affords aromatic monomers from the lignin model complexes under mild conditions. The results described here suggest the potential utility of dipicolinate vanadium complexes in the selective oxidative disassembly of lignin. Furthermore, the homogeneous nature of the catalyst provides new opportunities for ligand design to optimize activity and selectivity in these reactions. Future work will focus on the design of more active catalysts and extension of this catalytic oxidation reaction to more complex model systems and lignins.

Experimental Section

General Considerations. Unless specified otherwise, all reactions were carried out under a dry argon atmosphere using standard glovebox and Schlenk techniques. Pyridine-d_5, DMSO-d_6, and CD_3CN were purchased from Cambridge Isotope Laboratories. Pyridine-d_5 and CD_3CN were dried over CaH_2. Anhydrous grade acetonitrile, pyridine, and diethyl ether were obtained from Acros and used as received. 1-Phenyl-2-phenoxyethanol was purchased from Princeton Biomolecular Research (Monmouth Junction, NJ). ^1H, ^{13}C, and ^{51}V NMR spectra were obtained at room temperature on a Bruker AV400 MHz spectrometer, with chemical shifts (δ) referenced to the residual solvent signal (^1H and ^{13}C) or referenced externally to $VOCl_3$ (0 ppm). UV−vis spectra were obtained on a Varian CARY 500 Scan instrument and IR spectra were obtained on a Varian 1000 FT-IR Scimitar Series instrument. GC-MS analysis was obtained using a Hewlett-Packard 6890 GC system

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(40) Navarro, O. C.; Canos, A. C.; Chornet, S. I. *Top. Catal.* **2009**, *52*, 304–314.

equipped with a Hewlett-Packard 5973 mass selective detector. Elemental analyses were performed by Midwest Microlab in Indianapolis, IN. (dipic)V^{V}(O)O^{i}Pr (**1a**),[41] (dipic)V^{V}(O)OEt (**1b**),[42] (dipic)V^{V}(O)OCH$_3$,[41] (dipic)V^{V}(O)(Hpin),[35] and [(dipic)V^{V}(O)$_2$]HPyr (**6**)[35] were prepared according to published procedures.

Pinacol monomethyl ether (**A**) was prepared by a modified version of the published procedure for 1-methoxy-2-decanol.[43] 2,3-Dimethyl-2,3-epoxybutane (tetramethyloxirane) (1.196 g, 11.96 mmol) was dissolved in CH$_3$OH (10 mL). Less than one drop of sulfuric acid was carefully added by pipet, resulting in immediate warming of the solution. After 1 h, water (10 mL) was added, and the mixture extracted with diethyl ether (2 × 50 mL). The ether extracts were combined, dried over MgSO$_4$, and decanted. The ether was removed by rotovap, and the resulting clear oil was subjected to vacuum for 20 min. The clear oil pinacol monomethyl ether (1.495 g, 85%) contained about 0.5 equiv of CH$_3$OH (as determined by ^{1}H NMR) and was used without further purification in the synthesis of (dipic)V(O)(pinOMe). ^{1}H NMR (py-d_5, 400 MHz) δ 5.58 (br, s, 1H, pin-O*H*), 3.63 (s, 3 H, CH$_3$OH), 3.27 (s, 3H, pin-OC*H*$_3$), 1.42 (s, 6H, C(C*H*$_3$)$_2$), 1.29 (s, 6H, C(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (py-d_5, 100 MHz) δ 80.38 (s, 1C, *C*(CH$_3$)$_2$), 75.55 (s, 1C, *C*(CH$_3$)$_2$), 50.36 (s, 1C, *C*H$_3$OH), 50.31 (s, 1C, pin-O*C*H$_3$), 26.01 (s, 2C, C(*C*H$_3$)$_2$), 20.08 (s, 2C, C(*C*H$_3$)$_2$).

u-1,2-Diphenyl-2-methoxyethanol (**D**). *trans*-Stilbene oxide (0.705 g, 3.60 mmol) was dissolved in CH$_3$OH (10 mL) at room temperature. Sulfuric acid (less than 1 drop) was carefully added by pipet, resulting in gradual warming of the solution. After reacting for 1 h, the solution was treated with NaHCO$_3$ (approximately 100 mg) and allowed to stand for 30 min. The solution was filtered, and the solvent removed under vacuum, yielding a white solid. Yield 0.780 g (95%). The white solid product could be recrystallized from hot methanol, but was used without further purification in the synthesis of (dipic)V(O)(DPME) (**5**). Integration of the benzylic protons in the ^{1}H NMR spectrum showed that the product was a mixture of 85:15 u (*R*,*S* + *S*,*R*): l (*R*,*R* + *S*,*S*) diastereomers.[44] Similar diastereoselectivity has been reported for the ring-opening of *trans*-stilbene oxide by Cp$_2$ZrCl$_2$ (85:15)[45] and polymer-supported Fe and Ru catalysts (84:16).[46] ^{1}H NMR (benzene-d_6, 400 MHz) δ 7.24 (d, 2H, J = 6.8 Hz, Ph), 7.14−6.87 (m, 8H, Ph), 4.81 (d, 0.85H, J = 5.6 Hz, benzylic hydrogen on u diastereomer), 4.73 (d, 0.15H, J = 8.4 Hz, benzylic hydrogen on l diastereomer), 4.16 (d, 0.85H, J = 5.6 Hz, benzylic hydrogen on u diastereomer), 3.97 (d, 0.15H, J = 8.4 Hz, benzylic hydrogen on l diastereomer), 2.94 (s, 3H, OC*H*$_3$). Anal. Calcd for C$_{15}$H$_{16}$O$_2$: C, 78.92; H, 7.06. Found: C, 79.04; H, 6.91.

(dipic)V(O)(pinOMe) (**2**). Pinacol monomethyl ether (0.320 g, 2.42 mmol) and (dipic)V(O)OEt (0.406 g, 1.26 mmol) were combined in CH$_3$CN (10 mL). The reaction mixture was stirred for 15 min and filtered through a Teflon syringe filter. Diethyl ether (5 mL) was added, and the solution cooled to −15 °C overnight, yielding yellow crystals. The supernatant was decanted, the crystals washed with diethyl ether (2 × 3 mL), and dried under vacuum (yielding 0.220 g). Addition of another 5 mL diethyl ether to the supernatant and cooling to −15 °C gave a second crop of crystals (0.060 g). Total yield: 0.280 g (61%). ^{1}H NMR (py-d_5, 400 MHz) δ 8.52 (t, 1H, J = 7.6 Hz, Py), 8.42 (d, 2H, J = 7.6 Hz, Py), 2.48 (s, 3H, pin-OC*H*$_3$), 1.58 (s, 6H, C(C*H*$_3$)$_2$), 1.04 (s, 6H, C(C*H*$_3$)$_2$). IR (thin film): $\nu_{C=O}$ = 1699 cm^{-1}, $\nu_{V=O}$ = 993 cm^{-1}. Anal. Calcd for C$_{14}$H$_{18}$NO$_7$V: C, 46.29; H, 4.99; N, 3.86. Found: C, 46.23; H, 4.82; N, 3.72.

(dipic)V(O)(OPE) (**3**). (dipic)V(O)OEt (0.298 g, 0.923 mmol) was dissolved in CH$_3$CN (5 mL), and the solution filtered through glass wool/Celite into a vial containing 2-phenoxyethanol (0.331 g, 2.40 mmol). The reaction mixture was allowed to stand at room temperature. After 1 h, diethyl ether (15 mL) was added, and the yellow solution was cooled to −15 °C overnight, yielding yellow crystals. The supernatant was decanted, the crystals washed with diethyl ether (2 × 4 mL), and dried under vacuum (yielding 0.2005 g). A second crop was isolated by addition of another 8 mL of diethyl ether to the supernatant and cooling to −15 °C (0.059 g). Total yield: 0.2596 g (76%). ^{1}H NMR (py-d_5, 400 MHz) δ 8.38 (t, 1H, J = 7.6 Hz, Py), 8.31 (d, 2H, J = 7.6 Hz, Py), 7.31 (t, 2H, J = 8.4 Hz, OPh), 7.13 (d, 2H, J = 8.4 Hz, OPh), 6.99 (t, 1H, J = 7.6 Hz, OPh), 6.52 (t (broad), 2H, J = 4.4 Hz, V-OC*H*$_2$), 4.51 (t, 2H, J = 4.4 Hz, V-OCH$_2$-C*H*$_2$-OPh). IR (thin film): $\nu_{C=O}$ = 1691 cm^{-1}, $\nu_{V=O}$ = 991 cm^{-1}. Anal. Calcd for C$_{15}$H$_{12}$NO$_7$V: C, 48.80; H, 3.28; N, 3.79. Found: C, 48.76; H, 3.21; N, 3.79.

(dipic)V(O)(OPPE) (**4**). (dipic)V(O)OCH$_3$ (0.073 g, 0.247 mmol) and 1-phenyl-2-phenoxyethanol were dissolved in CH$_3$CN (2 mL). After 1 h the solvent was removed under vacuum, leaving an orange oil. Diethyl ether (6 mL) was added, forming a yellow slurry, which was stirred at room temperature (1 h). The yellow solid was allowed to settle, and the supernatant removed by pipet. The yellow powder was washed with diethyl ether (2 × 5 mL) and dried under vacuum. Yield: 0.0962 g (88%). ^{1}H NMR (CD$_3$CN, 400 MHz) δ 8.34 (t, 1H, J = 7.6 Hz, Py), 8.12 (d, 1H, J = 7.6 Hz, Py), 7.79 (d, 1H, J = 7.6 Hz, Py), 7.55−7.44 (m, 5H, Ph), 7.00 (t, 2H, J = 7.2 Hz, Ph), 6.89 (t, 1H, J = 6.8 Hz, Ph), 6.60 (m (br), 1H, V-OC*H*), 6.50 (d, 2H, J = 8.0 Hz, Ph), 4.60 (t, 1H, J = 9.6 Hz, −C*H*H-), 4.35 (dd, 1H, J = 9.6 Hz, 4.0 Hz, −CH*H*-). ^{51}V NMR (CD$_3$CN, 105 MHz) −551.1 (s). IR (thin film): $\nu_{C=O}$ = 1702 cm^{-1}, $\nu_{V=O}$ = 995 cm^{-1}.

(dipic)V(O)(DPME) (**5**). (dipic)V(O)O^{i}Pr (0.191 g, 0.544 mmol) and 1,2-diphenyl-2-methoxyethanol (0.251 g, 1.10 mmol, an 85:15 mixture of u:l diastereomers)[44] were dissolved in CH$_3$CN (2 mL) by stirring at room temperature for 5 min. The solvent was immediately removed under vacuum, leaving a yellow-orange oil. The oil was redissolved in CH$_3$CN (2 mL), and diethyl ether (5 mL) was added, resulting in a small amount of a pale blue-green precipitate. The mixture was filtered through a Teflon syringe filter, giving an orange solution, which was immediately cooled to −15 °C. Over 2 days at −15 °C, orange crystals formed. The supernatant was decanted, the orange crystals washed with diethyl ether (3 × 2 mL), and dried under vacuum. The u isomer of complex **5** crystallized preferentially and was used in all subsequent reactions. Yield: 0.0966 g (39%). ^{1}H NMR (CD$_3$CN, 400 MHz) δ 8.66 (t, 1H, J = 7.0 Hz, Py), 8.35 (d, 1H, J = 7.0 Hz, Py), 8.33 (d, 1H, J = 7.0 Hz, Py), 7.18−7.08 (m, 10H, Ph), 6.74 (br s, 1H, V-OC*H*Ph), 5.08 (d, 1H, J = 6.0 Hz, V-OCHPh−C*H*Ph), 2.45 (s, 3H, OC*H*$_3$). ^{51}V NMR (CD$_3$CN, 105 MHz) −536.3 (s). IR (thin film): $\nu_{C=O}$ = 1705 cm^{-1}, $\nu_{V=O}$ = 1001 cm^{-1}. Anal. Calcd for C$_{22}$H$_{18}$NO$_7$V: C, 57.53; H, 3.95; N, 3.05. Found: C, 57.73; H, 3.83; N, 3.08. The orange crystals were stored at −15 °C.

Thermolysis of (dipic)V(O)(pinOMe). In a resealable Teflon-capped NMR tube, **2** (9.3 mg, 0.026 mmol) was dissolved in pyridine-d_5 (0.6 mL) containing *p*-xylene as an internal standard (3.3 mM). The solution was allowed to react at room temperature over the course of 3 weeks, resulting in a color change from yellow to green. Integration against the internal standard revealed formation of acetone (94%), 2-methoxypropene (76%), and pinacol monomethyl ether (92%). A broad signal in the ^{1}H

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NMR spectrum (pyr-d_5) at 7.39 ppm and the green color of the solution were consistent with formation of the previously reported (dipic)V(O)(pyr)$_2$ (**6**). The identity of 2-methoxypropene was confirmed by spiking the sample with the authentic compound (purchased from Aldrich). Reducing the volume of the solution to ~0.2 mL by slow evaporation yielded green needles of **6** (6.1 mg, 61%).

A similar reaction in a resealable Teflon-capped NMR tube involving thermolysis of **2** at 100 °C for 6 h showed formation of **6**, acetone, 2-methoxypropene, and pinacol monomethyl ether. After initially turning green, the solution color did not change upon heating for a total of 6 days at 100 °C, nor were any changes in the composition of the organic products observed, indicating no conversion to the previously reported V(III) μ-oxo dimer,[35] which is dark purple (λ = 518 nm ε = 5000 M^{-1} cm^{-1}, λ = 598 nm, ε = 4600 M^{-1} cm^{-1}).

Thermolysis of (dipic)V(O)(OPE). In an NMR tube, complex **3** (6.6 mg, 0.018 mmol) was dissolved in pyr-d_5 (0.6 mL) containing *p*-xylene (3.4 mM) as an internal standard. A ^{1}H NMR spectrum was immediately recorded, and then the solution heated at 100 °C for 10 min. After cooling to room temperature, examination of the ^{1}H NMR spectrum revealed complete disappearance of **3** and formation of 2-phenoxyacetaldehyde (78%) and 2-phenoxyethanol (98%). Yields were determined by the average of 4 runs of this type. The UV−vis spectrum of the reaction mixture was consistent with the vanadium product (dipic)V(O)(pyr)$_2$ (**6**). Spiking the reaction mixture with 2-phenoxyacetaldehyde prepared by a published procedure (Swern oxidation)[36] confirmed the identity of this product.

Thermolysis of 4 in pyr-d_5. Complex **4** (3.4 mg, 0.0076 mmol) was dissolved in pyr-d_5 (0.6 mL) containing *p*-xylene as an internal standard (19.6 mmol). Within 10 min, the solution changed color from yellow to green. Examination of the ^{1}H NMR spectrum showed complete consumption of the vanadium(V) and a 1:1 mixture of 2-phenoxyacetophenone and 1-phenyl-2-phenoxyethanol. The identity of the 2-phenoxyacetophenone was confirmed by spiking the reaction mixture with the authentic compound prepared according to a published procedure.[37] The UV−vis spectrum of the reaction mixture was consistent with the vanadium(IV) product **6**.

Thermolysis of 5 in pyr-d_5. Complex **5** (6.1 mg, 0.013 mmol) was dissolved in pyr-d_5 (0.6 mL) containing *p*-xylene as an internal standard (6.3 mM). Over approximately 5 min at room temperature the solution color changed from yellow to green. Examination of the ^{1}H NMR spectrum after 10 min revealed a 1:1 ratio of benzoin methyl ether/1,2-diphenyl-2-methoxyethanol (u diastereomer). The UV−vis spectrum of the solution was consistent with the vanadium product (dipic)V(O)(pyr)$_2$ (**6**).

Thermolysis of 5 in DMSO-d_6. Under argon, complex **5** (4.5 mg, 0.010 mmol) was dissolved in DMSO-d_6 (0.6 mL, used as received from Cambridge Isotope Laboratory, not dried) containing 1,3,5-tri-*tert*-butylbenzene (2.5 mM) as an internal standard. An initial ^{1}H NMR spectrum was recorded, and the solution immediately heated at 100 °C for 30 min, during which time the color changed from the initial yellow to green. Examination of the ^{1}H NMR spectrum revealed formation of coproducts methanol and benzaldehyde (66%), benzoin methyl ether (33%), and 1,2-diphenyl-2-methoxyethanol (u diastereomer) (100%). The UV−vis spectrum of the solution was consistent with formation of (dipic)V^{IV}(O)(DMSO)$_2$ (**7**).

Preparation of (dipic)V^{IV}(O)(DMSO)$_2$ (7). In a small thick-walled glass vessel equipped with a Teflon stopcock, (dipic)V^V(O)(Hpin) (0.119 g, 0.341 mmol) was suspended in DMSO (1 mL). The suspension was heated at 100 °C for 30 min, during which time all the material dissolved, forming a dark green solution. Slow diffusion of diethyl ether (2 mL) at room temperature gave large green crystals. The crystals were washed with diethyl ether (3 × 1.5 mL) and dried under vacuum. Yield: 0.110 g (83%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.31 (br, $\Delta\nu_{1/2}$ = 280 Hz). IR (DMSO-d_6 solution): $\nu_{C=O}$ = 1666 cm^{-1}, 1335 cm^{-1}, $\nu_{V=O}$ = 947 cm^{-1}. UV−vis (DMSO): λ = 384 nm, ε = 210 M^{-1} cm^{-1}.

Control Reaction of (dipic)V^{IV}(O)(pyr)$_2$ (6) with 1,2-Diphenyl-2-methoxyethanol in DMSO-d_6. Under argon in a resealable Teflon-capped NMR tube, complex **6** (4.8 mg, 0.012 mmol) and 1,2-diphenyl-2-methoxyethanol (5.9 mg, 0.026 mmol, an 85:15 mixture of u:l diastereomers) were dissolved in DMSO-d_6 (0.6 mL) containing *p*-xylene (11.8 mM) as an internal standard. The tube was heated at 100 °C and monitored by ^{1}H NMR spectroscopy. After 1 week at 100 °C, the green color of the solution had not changed, and only trace benzaldehyde (< 1%, no turnovers) had formed.

Control Reaction of (dipic)V^{IV}(O)(DMSO)$_2$ (7) with 2-Phenoxyethanol in DMSO-d_6. In a resealable Teflon-capped NMR tube under an atmosphere of Ar, 2-phenoxyethanol (11.1 mg, 0.080 mmol) and **7** (8.8 mg, 0.023 mmol) were dissolved in DMSO-d_6 containing 1,3,5-tri-*tert*-butylbenzene (2.5 mM) as an internal standard. An initial ^{1}H NMR spectrum was recorded, and then the solution was heated for 1 week at 100 °C. Examination of the ^{1}H NMR spectrum showed no reaction of 2-phenoxyethanol. No change in the green color of the solution occurred.

Control Reaction of (dipic)V^{IV}(O)(DMSO)$_2$ (7) with 1-Phenyl-2-phenoxyethanol in DMSO-d_6. Under an atmosphere of Ar in a resealable Teflon-capped NMR tube, 1-phenyl-2-phenoxyethanol (10.4 mg, 0.049 mmol) and **7** (11.1 mg, 0.029 mmol) were dissolved in DMSO-d_6 (0.6 mL) containing 1,3,5-tri-*tert*-butylbenzene (2.5 mM) as an internal standard. An initial ^{1}H NMR spectrum was recorded, then the solution was heated at 100 °C for 1 week. Integration against the internal standard revealed that no reaction of 1-phenyl-2-phenoxyethanol occurred. The solution color did not change from its initial green.

Catalytic Oxidation of 1-Phenyl-2-phenoxyethanol in DMSO-d_6. 1-Phenyl-2-phenoxyethanol (33.3 mg, 0.156 mmol) and 10 mol % (dipic)V(O)O^{i}Pr (5.4 mg, 0.015 mmol) were dissolved in DMSO-d_6 (1 mL) containing 1,3,5-tri-*tert*-butylbenzene (2.4 mM) as an internal standard. An initial ^{1}H NMR spectrum was recorded, then the solution was transferred under air to a thick-walled 100 mL Schlenk tube equipped with a Teflon stopcock. The reaction was heated at 100 °C with stirring and monitored periodically by ^{1}H NMR. After 2 days, approximately 50% of the starting material had been consumed, with the products consisting of 2-phenoxyacetophenone (35%), benzoic acid (15%), formic acid (10%), and phenol (13%). After 1 week, 95% of the starting material had been consumed, with the products consisting of formic acid (46%), benzoic acid (81%), phenol (77%), and 2-phenoxyacetophenone (9%). Yields are expressed as a percentage of the theoretical maximum based on the initial amount of substrate, and were determined by an average of two runs of this type. A ^{51}V NMR spectrum recorded at the end of the reaction revealed a single peak at −518 ppm, corresponding to the *cis*-dioxo anion [(dipic)V(O)$_2$]$^-$. The ^{13}C NMR spectrum showed a heptet at 41.35 ppm (*J* = 20 Hz) corresponding to dimethylsulfone-d_6. A GC-MS trace of the reaction mixture also showed dimethylsulfone-d_6 M/Z = 100.

A control reaction using an analogous procedure was conducted where 1-phenyl-2-phenoxyethanol (16.8 mg, 0.079 mmol) was heated in DMSO-d_6 under air at 100 °C (no vanadium). After 7 days, no oxidation products were detected by ^{1}H NMR, and integration against the internal standard (*p*-xylene) revealed that none of the substrate had reacted.

Attempted Oxidation of Formic Acid with (dipic)V(O)O^{i}Pr. In an NMR tube, formic acid (0.043 g, 0.930 mmol), and 10 mol % (dipic)V(O)O^{i}Pr (32.4 mg, 0.092 mmol) were dissolved in DMSO-d_6 containing 1,3,5-tri-*tert*-butylbenzene (2.5 mM) as an internal standard. An initial ^{1}H NMR spectrum was recorded. The reaction mixture was transferred to a thick-walled

100 mL Schlenk tube equipped with a Teflon stopcock and heated under air with stirring at 100 °C. After 3 days, examination of the ^{1}H NMR spectrum revealed that less than 5% of the formic acid had been consumed.

Catalytic Oxidation of 1,2-Diphenyl-2-methoxyethanol in DMSO-d_6. 1,2-Diphenyl-2-methoxyethanol (31.8 mg, 0.140 mmol, an 85:15 mixture of u:l diastereomers) and 5 mol % (dipic)V(O)O^{i}Pr (15.5 μL of a 0.45 M stock solution in DMSO-d_6, 0.007 mmol) were dissolved in DMSO-d_6 (1 mL) containing 1,3,5-tri-*tert*-butylbenzene (0.91 mM) as an internal standard. An initial ^{1}H NMR spectrum was recorded, and under air the reaction mixture was transferred to a 100 mL glass vessel equipped with a Teflon stopcock and stirbar. The vessel was sealed and heated with stirring at 100 °C. It was periodically opened to air and monitored by ^{1}H NMR spectroscopy (by transferring the solution to an NMR tube). After 20 h at 100 °C, integration of the ^{1}H NMR spectrum revealed that 94% of the starting material had been consumed (19 turnovers). The products consisted of benzaldehyde (73%), methanol (69%), benzoin methyl ether (13%), and methyl benzoate and benzoic acid (approximately 5% or less each) (yields expressed in terms of theoretical maximum per initial amount of substrate). A ^{51}V NMR spectrum recorded at this time showed a single peak at −518 ppm, corresponding to the *cis*-dioxo anion [(dipic)V(O)$_2$]$^-$. Both the ^{13}C NMR spectrum and the GC-MS trace of the reaction mixture indicated that dimethylsulfone-d_6 was present at the end of the catalytic run. No dimethylsulfide-d_6 was detected.

An analogous procedure was conducted using 1,2-diphenyl-2-methoxyethanol (34.6 mg, 0.152 mmol, an 85:15 mixture of u:l diastereomers) and 2.5 mol % (dipic)V(O)O^{i}Pr (8.4 μL of a 0.45 M stock solution in DMSO-d_6, 0.004 mmol) in DMSO-d_6 (1 mL) containing 1,3,5-tri-*tert*-butylbenzene (3.7 mM) as an internal standard. After 40 h at 100 °C, integration of the ^{1}H NMR spectrum revealed that 93% of the starting material had been consumed (37 turnovers). The products consisted of benzaldehyde (72%), methanol (73%), benzoin methyl ether (11%), and methyl benzoate and benzoic acid (5% or less each).

A control reaction with 1,2-diphenyl-2-methoxyethanol only (no vanadium) in DMSO-d_6 under air showed no reaction when heated at 100 °C for 1 week.

Catalytic Oxidation of 1,2-Diphenyl-2-methoxyethanol in pyr-d_5. 1,2-Diphenyl-2-methoxyethanol (29.8 mg, 0.131 mmol, an 85:15 mixture of u:l diastereomers) and (dipic)V(O)O^{i}Pr (4.8 mg, 0.013 mmol) were dissolved in pyr-d_5 (0.8 mL) containing *p*-xylene (5 μL, 0.041 mmol) as an internal standard. An initial ^{1}H NMR spectrum was recorded, and under air the reaction mixture was transferred to a 100 mL glass vessel equipped with a Teflon stopcock and stirbar. The mixture was heated at 100 °C with stirring and monitored periodically by ^{1}H NMR spectroscopy. After 3 days, 56% of the starting material had been consumed. The products consisted of benzoin methyl ether (45%), benzaldehyde (5%), methanol (3%), benzoic acid (4%), and methyl benzoate (5%) (yields expressed in terms of theoretical maximum based on the initial amount of substrate). Benzil and benzoin could also be detected (less than 2% each) in the ^{1}H NMR spectrum. After 6 days at 100 °C, the starting material had been completely consumed. The products consisted of benzoic acid (85%), methyl benzoate (84%), benzoin methyl ether (9%), benzaldehyde (9%), methanol (6%), benzil (less than 5%), and benzoin (less than 5%).

A control reaction with 1,2-diphenyl-2-methoxyethanol only (no vanadium) in pyr-d_5 under air showed no reaction when heated at 100 °C for 1 week.

Attempted Catalytic Oxidation of 2-Phenoxyethanol. 2-Phenoxyethanol (30.8 mg, 0.223 mmol) and 10 mol % (dipic)V(O)O^{i}Pr (7.8 mg, 0.022 mmol) were dissolved in DMSO-d_6 (1 mL) containing 1,3,5-tri-*tert*-butylbenzene (3.3 mM) as an internal standard. An initial ^{1}H NMR spectrum was recorded. The solution was transferred to a 100 mL Schlenk tube equipped with a Teflon stopcock and heated at 100 °C under air. After 1 week at 100 °C, integration of the ^{1}H NMR spectrum against the internal standard revealed that only approximately 20% of the starting material had been consumed. The organic products consisted of phenol (18%), formic acid (6%), as well as several other unidentified products. The ^{51}V NMR spectrum showed a single peak at −518 ppm, corresponding to the *cis*-dioxo anion [(dipic)V(O)$_2$]$^-$. Dimethylsulfone-d_6 was detected in both the ^{13}C NMR spectrum and the GC-MS trace of the reaction mixture. A control reaction with 2-phenoxyethanol only (no vanadium) in DMSO-d_6 showed no reaction after 1 week under air at 100 °C.

Reaction of 6 with 1-Phenyl-2-phenoxyethanol. Complex **6** (4.4 mg, 0.011 mmol) and 1-phenyl-2-phenoxyethanol (3.8 mg, 0.018 mmol) were dissolved in pyr-d_5 containing *p*-xylene (4.7 mM) as an internal standard. An initial ^{1}H NMR spectrum was recorded, then the solution heated at 100 °C for 1 week. No color change was observed, nor any reaction of the 1-phenyl-2-phenoxyethanol detected by ^{1}H NMR.

Reaction of 7 with Air. In an NMR tube, DMSO vanadium(IV) complex **7** (10.2 mg, 0.026 mmol) was dissolved in DMSO-d_6 (0.4 mL). The solution was opened to air, and then the NMR tube was capped and heated at 100 °C for 18 h. During this time, the solution changed color from green to a very pale blue. After cooling to room temperature, the *cis*-dioxo anion [(dipic)V(O)$_2$]$^-$ was detected by both ^{1}H and ^{51}V NMR.

Acknowledgment. This work was supported by Los Alamos National Laboratory LDRD (Director's PD Fellowship to S.K. H.) and NSF via the Center for Enabling New Technologies through Catalysis (CENTC). We thank L. A. (Pete) Silks (LANL), R. Wu (LANL), and Professors W. T. Borden (UNT), S. L. Scott (UCSB), and P. C. Ford (UCSB) for helpful discussions.

Supporting Information Available: CIF files for **2**, **3**, **5**, and **7**, and X-ray crystallographic data for **2**, **3**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.