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# Carbon-Carbon Bond Cleavage of 1,2-Hydroxy Ethers by Vanadium(V) Dipicolinate Complexes

Susan K. Hanson, R. Tom Baker\*, John C. Gordon, Brian L. Scott, and David L. Thorn\*

The development of alternatives to current petroleum-based fuels and chemicals is becoming increasingly important due to concerns over climate change, growing world energy demand, and energy security issues. Using non-food derived biomass to produce renewable feedstocks for chemicals and fuels is a particularly attractive possibility.<sup>[1]</sup> However, the majority of biomass is in the form of lignocellulose, which is often not fully utilized due to difficulties associated with breaking down both lignin and cellulose.<sup>[2]</sup>

Recently, a number of methods have been reported to transform cellulose directly into more valuable materials such as glucose,<sup>[3]</sup> sorbitol,<sup>[4]</sup> 5-(chloromethyl)furfural,<sup>[5]</sup> and ethylene glycol.<sup>[6]</sup> Less progress has been made with selective transformations of lignin,<sup>[7,8,9]</sup> which is typically treated in paper and forest industries by kraft pulping (sodium hydroxide/sodium sulfide)<sup>[8d]</sup> or incineration.<sup>[8]</sup>

Our group has begun investigating aerobic oxidative C-C bond cleavage catalyzed by dipicolinate vanadium complexes, with the idea that a selective C-C cleavage reaction of this type could be used to produce valuable chemicals or intermediates from cellulose or lignin. Lignin is a randomized polymer containing methoxylated phenoxy propanol units.<sup>[9a]</sup> A number of different linkages occur naturally; one of the most prevalent is the  $\beta$ -O-4 linkage shown in Figure 1,<sup>[9a]</sup> containing a C-C bond with 1,2-hydroxy ether substituents. While the oxidative C-C bond cleavage of 1,2-diols has been reported for a number of metals, including vanadium, iron, manganese, ruthenium, and polyoxometalate complexes,<sup>[10]</sup> C-C bond cleavage of 1,2-hydroxy ethers is much less common.<sup>[11]</sup> We report herein vanadium-mediated cleavage of C-C bonds between alcohol and ether functionalities in several lignin model complexes.

In order to explore the scope and potential of vanadium complexes to effect oxidative C-C bond cleavage in 1,2-hydroxy ethers, we examined the reactivity of the lignin model complexes pinacol monomethyl ether (A),<sup>[12]</sup> 2-phenoxyethanol (B), and 1,2-diphenyl-2-methoxyethanol (C)<sup>[13]</sup> (Figure 1).

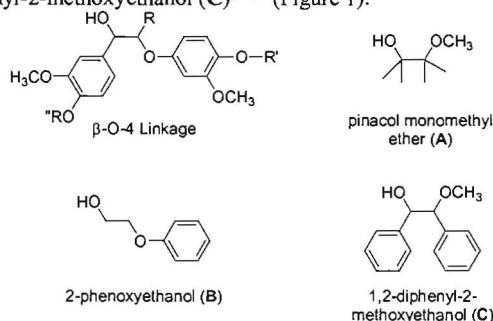


Figure 1.  $\beta$ -O-4 linkage and lignin model complexes.

Reaction of (dipic)V<sup>V</sup>(O)O<sup>i</sup>Pr (1a) or (dipic)V<sup>V</sup>(O)OEt (1b) with A, B, or C in acetonitrile yielded new vanadium(V) complexes where the alcohol-ether ligand was bound in a chelating fashion. From the reaction of 1b with pinacol monomethyl ether (A) in

acetonitrile solution, (dipic)V<sup>V</sup>(O)(pinOMe) (2) (pinOMe = 2,3-dimethyl-3-methoxy-2-butanoxide) was isolated in 61% yield. Reaction of 1b with 2-phenoxyethanol (B) in acetonitrile gave the new complex (dipic)V<sup>V</sup>(O)(OPE) (3) (OPE = 2-phenoxyethoxide), which was isolated in 76% yield. In a similar fashion, 1a reacted with 1,2-diphenyl-2-methoxyethanol (C) to give (dipic)V<sup>V</sup>(O)(DPME) (4) (DPME = 1,2-diphenyl-2-methoxyethoxide), which was isolated in 39% yield. Complexes 2, 3, and 4 were characterized by <sup>1</sup>H NMR and IR spectroscopy, elemental analysis, and X-ray crystallography.

Compared to the previously reported vanadium(V) pinacolate complex (dipic)V<sup>V</sup>(O)(pinOH)<sup>[14]</sup> the X-ray structure of complex 2 reveals a slightly shorter V=O bond, 1.573(2) Å vs 1.588(2) Å for the pinOH structure.<sup>[14]</sup> Complexes 3 and 4 display similar vanadium oxo bond distances of 1.568(2) Å and 1.576(2) Å, respectively. All three complexes show longer bonds to the ether-oxygen trans to the oxo (2.388(2) Å for 2, 2.547(2) Å for 3, and 2.438(2) Å for 4) than to the hydroxy-oxygen in the pinOH structure (2.252(2) Å).<sup>[14]</sup>

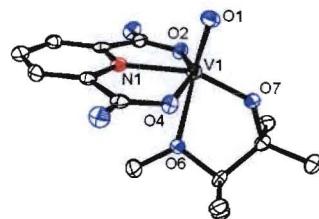


Figure 2. X-Ray Structure of 2 (thermal ellipsoids at 50% probability, H atoms omitted for clarity). Selected bond lengths (Å): V1-O1 = 1.573(2), V1-O7 = 1.761(2), V1-O6 = 2.388(2), V1-O4 = 1.945(2), V1-O2 = 1.948(2), V1-N1 = 2.057(3).

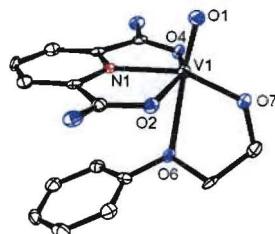
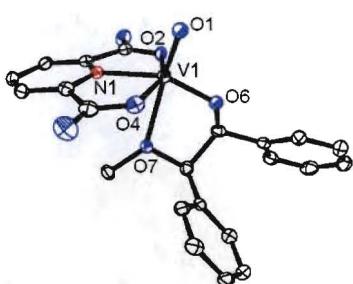
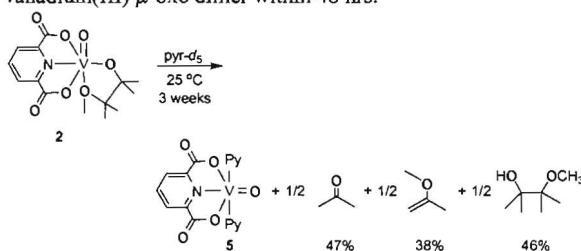


Figure 3. X-Ray Structure of 3 (thermal ellipsoids at 50% probability, H atoms omitted for clarity). Selected bond lengths (Å): V1-O1 = 1.568(2), V1-O7 = 1.775(2), V1-O6 = 2.547(2), V1-O4 = 1.929(2), V1-O2 = 1.949(2), V1-N1 = 2.060(3).



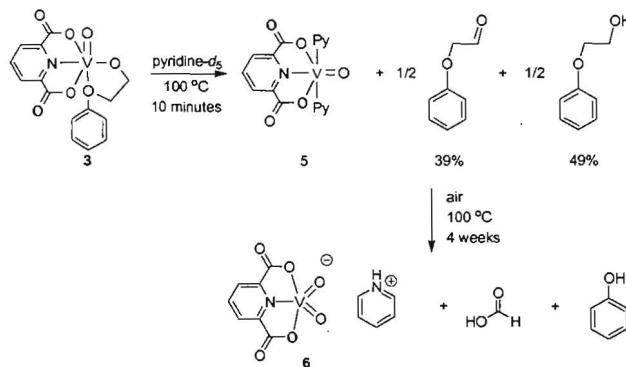
**Figure 4.** X-Ray Structure of **4** (thermal ellipsoids at 50% probability, H atoms omitted for clarity). Selected bond lengths (Å): V1-O1 = 1.576(2), V1-O6 = 1.784(2), V1-O7 = 2.438(2), V1-O2 = 1.925(2), V1-O4 = 1.931(2), V1-N1 = 2.053(2).

The reactivity of complexes **2**, **3**, and **4** was examined to investigate potential vanadium-mediated C-C bond cleavage. When complex **2** was dissolved in pyr-*d*<sub>5</sub> and the solution monitored by <sup>1</sup>H NMR spectroscopy, reaction occurred at room temperature over the course of 3 weeks to yield the previously reported vanadium(IV) complex (dipic)V<sup>IV</sup>(O)(pyr)<sub>2</sub> (**5**).<sup>[14]</sup> acetone (47%), 2-methoxypropene (38%), and pinacol monomethyl ether (46%) (yields per mol V<sup>V</sup> reacted) (Scheme 1). The same C-C bond cleavage products were observed when the thermolysis of **2** was carried out in pyr-*d*<sub>5</sub> at 100 °C for 6 h. No further reaction occurred upon heating the mixture of **5** and pinacol monomethyl ether anaerobically at 100 °C for 6 days, which is in contrast with the reaction between **5** and pinacol in pyridine at 100 °C, which formed a vanadium(III)  $\mu$ -oxo dimer within 48 hrs.<sup>[14]</sup>



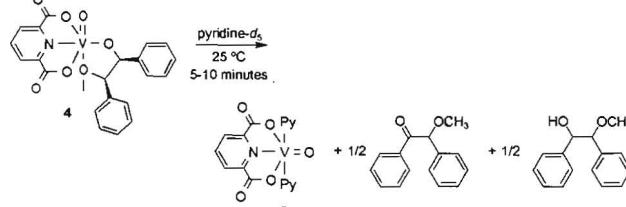
**Scheme 1.** Reaction of **2** in pyridine-*d*<sub>5</sub>.

Instead of C-C bond cleavage, 2-phenoxyethoxide complex **3** underwent a stoichiometric C-H bond cleavage reaction in pyr-*d*<sub>5</sub> solvent. When heated for 10 minutes at 100 °C, a pyr-*d*<sub>5</sub> solution of complex **3** reacted to form **5**, 2-phenoxyacetaldehyde (39%) and 2-phenoxyethanol (49%) (Scheme 2). The formation of 2-phenoxyacetaldehyde was confirmed by comparison with an authentic sample prepared according to a literature procedure.<sup>[15]</sup> Previously, we found that reaction of the vanadium(IV) complex **5** with air in pyr-*d*<sub>5</sub> solution over the course of days at 100 °C formed the *cis*-dioxo vanadium(V) complex [(dipic)V<sup>V</sup>(O)<sub>2</sub>]HPyr (**6**).<sup>[14]</sup> Consequently, the products from the reaction of **3** were heated at 100 °C under air to explore whether further oxidation of 2-phenoxyacetaldehyde would result in C-C bond cleavage. Indeed, prolonged thermolysis (4 weeks) of such a reaction mixture (**5**, 2-phenoxyacetaldehyde, and 2-phenoxyethanol) in pyr-*d*<sub>5</sub> under air at 100 °C resulted in complete consumption of both 2-phenoxyethanol and 2-phenoxyacetaldehyde, with formation of formic acid (approximately 0.7 equiv),<sup>[16]</sup> phenol (1 equiv), and **6**.



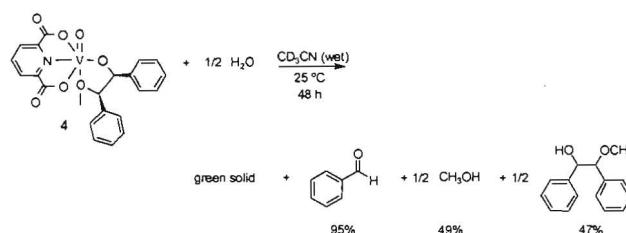
**Scheme 2.** Reaction of **3** in pyridine-*d*<sub>5</sub>.

Like complex **3**, complex **4** also underwent C-H bond cleavage when dissolved in pyr-*d*<sub>5</sub> at room temperature. A rapid color change from yellow to green was observed and the reaction was complete within 10 minutes, at which point examination of the <sup>1</sup>H NMR spectrum revealed a 1:1 ratio of benzoin methyl ether (2-methoxy-2-phenylacetophenone) and 1,2-diphenyl-2-methoxyethanol (Scheme 3). The UV-vis spectrum of this reaction mixture was consistent with the vanadium(IV) product (dipic)V<sup>IV</sup>(O)(pyr)<sub>2</sub> (**5**).<sup>[14]</sup> No evidence for reduction to V(III) was seen with this substrate; anaerobic thermolysis of the reaction mixture containing **5**, benzoin methyl ether and 1,2-diphenyl-2-methoxyethanol for 1 week at 100 °C showed no further color change or reaction of the organic products.



**Scheme 3.** Reaction of **4** in pyridine-*d*<sub>5</sub>.

In contrast to its reaction in pyridine, in wet CD<sub>3</sub>CN complex **4** underwent C-C bond cleavage to form benzaldehyde (95%), 1,2-diphenyl-2-methoxyethanol (47%), and CH<sub>3</sub>OH (49%) (Scheme 4).<sup>[17]</sup> The vanadium product of this reaction was a powdery green precipitate which displayed a vanadium-oxo stretch in the IR spectrum at 983 cm<sup>-1</sup>. This material is tentatively formulated as (dipic)V<sup>IV</sup>(O)(CH<sub>3</sub>CN)<sub>x</sub>.<sup>[18]</sup>



**Scheme 4.** Reaction of **4** in CD<sub>3</sub>CN.

The catalytic oxidation of 1,2-diphenyl-2-methoxyethanol with air was also investigated. Over 24 h at 100 °C under air, a solution of 1,2-diphenyl-2-methoxyethanol in DMSO-*d*<sub>6</sub> reacted with 2.5 mol% **1a** to form benzaldehyde (1.67 equiv), methanol (0.80 equiv), and benzoin methyl ether (0.14 equiv), with the remaining products consisting of benzoic acid and methyl benzoate (approximately 0.04 equiv or less each) (yields expressed in equiv product formed per mol 1,2-diphenyl-2-methoxyethanol reacted). Nearly complete consumption (98%) of the starting material was observed, with a total of 39 turnovers (turnover = mol 1,2-diphenyl-2-methoxyethanol consumed per mol **V**). A control experiment involving 1,2-diphenyl-2-methoxyethanol only (no vanadium) in DMSO-*d*<sub>6</sub> under air showed no reaction after 1 week at 100 °C. Furthermore, under anaerobic conditions, a solution of the vanadium(IV) complex (dipic)V(O)pyr<sub>2</sub> in DMSO-*d*<sub>6</sub> showed no turnovers with this substrate after 1 week at 100 °C, suggesting that the DMSO solvent was not acting as the oxidant in the catalytic reaction.

A different product distribution was observed when the catalytic reaction was run in pyr-*d*<sub>5</sub> solvent. 1,2-Diphenyl-2-methoxyethanol was heated with 10 mol% **1a** under air at 100 °C. After 3 days, 56% of the starting material had reacted, with the products consisting of benzoin methyl ether (0.80 equiv), benzaldehyde (0.27 equiv), methanol (0.13 equiv), benzoic acid (0.16 equiv), and methyl benzoate (0.18 equiv). Benzil and benzoin were also detected as minor products in the <sup>1</sup>H NMR spectrum (less than 0.02 equiv each). After 6 days, the starting material had been completely consumed, and the organic products further oxidized to form benzoic acid (0.86 equiv), methyl benzoate (0.85 equiv), benzoin methyl ether (0.09 equiv), benzaldehyde (0.19 equiv), and methanol (0.13 equiv). Benzil and benzoin were again present as minor products (less than 0.05 equiv each). A control experiment with no vanadium showed no reaction when 1,2-diphenyl-2-methoxyethanol was heated in pyr-*d*<sub>5</sub> under air at 100 °C for 1 week.

Thus, dipic vanadium(V) complexes effectively oxidize 1,2-hydroxy ethers. Both C-H and C-C bond cleavage modes have been observed, with the solvent significantly affecting the product distribution. In stoichiometric reactions in pyr-*d*<sub>5</sub> solvent, C-H bond cleavage dominates for substrates having C-H bonds alpha to the hydroxyl group, yielding 2-phenoxyacetaldehyde from 2-phenoxyethanol and benzoin methyl ether from 1,2-diphenyl-2-methoxyethanol. In wet CD<sub>3</sub>CN, 1,2-diphenyl-2-methoxyethanol undergoes exclusively C-C bond cleavage to form benzaldehyde and methanol. These reactivity trends are also reflected in the product distribution in the catalytic oxidation of 1,2-diphenyl-2-methoxyethanol. In DMSO-*d*<sub>6</sub>, benzaldehyde and methanol are the major products. In pyr-*d*<sub>5</sub>, benzoin methyl ether is the major product at early reaction times, while at longer times it undergoes further oxidation to form benzoic acid and methyl benzoate.

In conclusion, dipic vanadium complexes cleave C-C bonds between alcohol and ether functionalities in the lignin model complexes 2-phenoxyethanol, pinacol monomethyl ether, and 1,2-diphenyl-2-methoxyethanol. Catalytic aerobic oxidation of 1,2-diphenyl-2-methoxyethanol has been demonstrated, suggesting the potential utility of dipicolinate vanadium complexes in the oxidative degradation of lignin. Future work will explore the mechanisms of these reactions both experimentally and computationally, as well as oxidation of more complex model systems and lignin itself.

**Keywords:** vanadium, biomass, oxidation, cleavage reactions, catalysis

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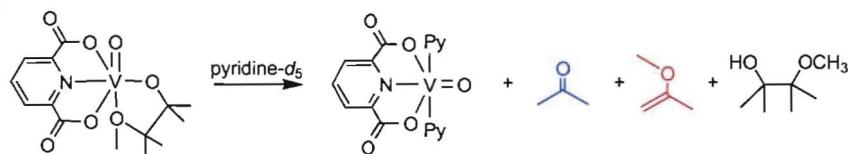
[\*\*] This work was supported by the NSF via the Center for Enabling New Technologies through Catalysis (CENTC). We thank Professors W. T. Borden (UNT), S. L. Scott (UCSB), and P. C. Ford (UCSB) for helpful discussions.

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- [13] 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<sub>3</sub>OH (see Supporting Information for details).
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- [16] The low yield of formic acid (0.7 equiv observed vs. 2.0 expected) may be due to further oxidation to CO<sub>2</sub>. In a separate experiment, formation of CO<sub>2</sub> was detected when a pyr-*d*<sub>5</sub> solution of complex **6** and formic acid was heated at 100 °C under air (See Supporting Information for details).
- [17] Reaction in dry CD<sub>3</sub>CN yielded benzaldehyde (61%), 1,2-diphenyl-2-methoxyethanol (24%) and multiple additional products (at least 5 distinct methoxy signals were evident in the <sup>1</sup>H NMR spectrum). The identity of these products is under investigation.
- [18] A material exhibiting an identical IR spectrum could be prepared by reaction of H<sub>2</sub>dipic with V<sup>IV</sup>(O)(acac)<sub>2</sub> in dry CH<sub>3</sub>CN. Integration of the <sup>1</sup>H NMR spectrum of this material (DMSO-*d*<sub>6</sub>) showed 1.2 equiv CH<sub>3</sub>CN per dipic ligand. In support of this assignment, when the green solid was dissolved in pyr-*d*<sub>5</sub>, formation of (dipic)V<sup>IV</sup>(O)pyr<sub>2</sub> was observed.

Entry for the Table of Contents

**Biorenewable chemicals and fuels**

Susan K. Hanson, R. Tom Baker\*, John C. Gordon, Brian L. Scott, and David L. Thorn\*



**Carbon-Carbon Bond Cleavage of 1,2-Hydroxy Ethers by Vanadium(V) Dipicolinate Complexes**

A selective method to break C-C bonds of 1,2-hydroxy ethers could be used to produce valuable chemicals from lignin. Dipicolinate vanadium complexes cleave C-C bonds between alcohol and ether functionalities in the lignin model complexes 2-phenoxyethanol, pinacol monomethyl ether, and 1,2-diphenyl-2-methoxyethanol. Catalytic aerobic oxidation of 1,2-diphenyl-2-methoxyethanol has been demonstrated, suggesting the potential utility of dipicolinate vanadium complexes in the oxidative degradation of lignin.

Supporting Information for:

## Carbon-Carbon Bond Cleavage of 1,2-Hydroxy Ethers by Vanadium(V) Dipicolinate Complexes

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### Experimental

**General Considerations.** Unless specified otherwise, all reactions were carried out under a dry argon atmosphere using standard glove-box and Schlenk techniques. Pyridine-*d*<sub>5</sub>, DMSO-*d*<sub>6</sub>, and CD<sub>3</sub>CN were purchased from Cambridge Isotope Laboratories. Pyridine-*d*<sub>5</sub> was dried over CaH<sub>2</sub>. Anhydrous grade acetonitrile, pyridine, and diethyl ether were obtained from Fisher Scientific and used as received. NMR spectra were obtained at room temperature on a Bruker AV400 MHz spectrometer, with chemical shifts ( $\delta$ ) reported in ppm downfield of tetramethylsilane. 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. Elemental analyses were performed by Midwest Microlab in Indianapolis, IN. (dipic)V<sup>V</sup>(O)O*i*Pr (**1a**),<sup>xix</sup> (dipic)V<sup>V</sup>(O)OEt (**1b**),<sup>xx</sup> and [(dipic)V<sup>V</sup>(O)<sub>2</sub>]H<sup>+</sup>Py (**6**)<sup>2b</sup> were prepared according to published procedures.

**u-1,2-diphenyl-2-methoxyethanol (B).** *trans*-Stilbene oxide (0.705 g, 3.60 mmol) was dissolved in CH<sub>3</sub>OH (10 mL) at room temperature. Sulfuric acid (less than 1 drop) was carefully added by pipette, resulting in gradual warming of the solution. After reacting for 1 hour, the solution was treated with NaHCO<sub>3</sub> (approximately 100 mg) and allowed to stand for 30 minutes. 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) (**4**). Integration of the benzylic protons in the <sup>1</sup>H NMR spectrum showed that the product was a mixture of 85:15 u (R,S + S,R): l (R,R + S,S) diastereomers. Similar diastereoselectivity has been reported for the ring opening of *trans*-stilbene oxide by Cp<sub>2</sub>ZrCl<sub>2</sub> (85:15)<sup>xxi</sup> and polymer-supported Fe and Ru catalysts (84:16).<sup>xxii</sup> <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 400 MHz)  $\delta$  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, OCH<sub>3</sub>). Anal. Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>: C, 78.92; H, 7.06. Found: C, 79.04; H, 6.91.

**Pinacol monomethyl ether (C)** was prepared by a modified version of the published procedure for 1-methoxy-2-decanol.<sup>xxiii</sup> 2,3-Dimethyl-2,3-epoxybutane (tetramethyloxirane) (1.196 g, 11.96 mmol) was dissolved in CH<sub>3</sub>OH (10 mL). Less than one drop of sulfuric acid was carefully added by pipette, resulting in immediate warming of the solution. After 1 hour, water (10 mL) was added and the mixture extracted with diethyl ether (2 x 50 mL). The ether extracts were combined, dried over MgSO<sub>4</sub>, and decanted. The ether was removed by rotovap, and the resulting clear oil was subjected to vacuum for 20 minutes. The clear oil pinacol monomethyl ether (1.495 g, 85%) contained about 0.5 eq CH<sub>3</sub>OH (as determined by <sup>1</sup>H NMR) and was used without further purification in the synthesis of (dipic)V(O)(pinOMe). <sup>1</sup>H NMR (py-*d*<sub>5</sub>, 400 MHz)  $\delta$  5.58 (br, s, 1H, pin-OH), 3.63 (s, 3H, CH<sub>3</sub>OH), 3.27 (s, 3H, pin-OCH<sub>3</sub>), 1.42 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 1.29 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (py-*d*<sub>5</sub>, 100 MHz)  $\delta$  80.38 (s, 1C, C(CH<sub>3</sub>)<sub>2</sub>), 75.55 (s, 1C, C(CH<sub>3</sub>)<sub>2</sub>), 50.36 (s, 1C, CH<sub>3</sub>OH), 50.31 (s, 1C, pin-OCH<sub>3</sub>), 26.01 (s, 2C, C(CH<sub>3</sub>)<sub>2</sub>), 20.08 (s, 2C, C(CH<sub>3</sub>)<sub>2</sub>).

**(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<sub>3</sub>CN (10 mL). The reaction mixture was stirred for 15 minutes 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 x 3 mL), and dried under vacuum (yielding 0.2203 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%). <sup>1</sup>H NMR (py-*d*<sub>5</sub>, 400 MHz)  $\delta$  8.52 (t, 1H, *J* = 7.6 Hz, Py), 8.42 (d, 2H, *J* = 7.6 Hz, Py), 2.48 (s, 3H, pin-OCH<sub>3</sub>), 1.58 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>), 1.04 (s, 6H, C(CH<sub>3</sub>)<sub>2</sub>). IR (thin film):  $\nu_{C=O}$  = 1699 cm<sup>-1</sup>,  $\nu_{V=O}$  = 993 cm<sup>-1</sup>. Anal. Calcd for C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub>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<sub>3</sub>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 hour, 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 x 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%). <sup>1</sup>H NMR (pyr-d<sub>5</sub>, 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-OCH<sub>2</sub>), 4.51 (t, 2H, *J* = 4.4 Hz, V-OCH<sub>2</sub>CH<sub>2</sub>-OPh). IR (thin film):  $\nu_{C=O}$  = 1691 cm<sup>-1</sup>,  $\nu_{V=O}$  = 991 cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>12</sub>NO<sub>2</sub>V: C, 48.80; H, 3.28; N, 3.79. Found: C, 48.76; H, 3.21; N, 3.79.

**(dipic)V(O)(DPME) (4).** (dipic)V(O)O<sup>i</sup>Pr (0.191 g, 0.544 mmol) and u-1,2-diphenyl-2-methoxyethanol (0.2505 g, 1.099 mmol) were dissolved in CH<sub>3</sub>CN (2 mL) by stirring at room temperature 5 minutes. The solvent was immediately removed under vacuum, leaving a yellow-orange oil. The oil was redissolved in CH<sub>3</sub>CN (2 mL), and diethyl ether (5 mL) was added, resulting 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 x 2 mL), and dried under vacuum. Yield: 0.0966 g (39%). <sup>1</sup>H NMR (CD<sub>3</sub>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-OCHPh), 5.08 (d, 1H, *J* = 6.0 Hz, V-OCHPh-CHPh), 2.45 (s, 3H, OCH<sub>3</sub>). IR (thin film):  $\nu_{C=O}$  = 1705 cm<sup>-1</sup>,  $\nu_{V=O}$  = 1001 cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>2</sub>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.

**Reaction of (dipic)V(O)(pinOMe).** In a resealable Teflon-capped NMR tube, **2** (9.3 mg, 0.0256 mmol) was dissolved in pyridine-d<sub>5</sub> (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 (47%), 2-methoxypropene (38%), and pinacol monomethyl ether (46%). A broad signal in the <sup>1</sup>H NMR spectrum (pyr-d<sub>5</sub>) at 7.39 ppm and the green color of the solution were consistent with formation of the previously reported (dipic)V(O)(pyr)<sub>2</sub> (**5**). 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 **5** (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 **5**, 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)  $\mu$ -oxo dimer,<sup>xxb</sup> which is dark purple ( $\lambda$  = 518 nm  $\epsilon$  = 5000 M<sup>-1</sup> cm<sup>-1</sup>,  $\lambda$  = 598 nm  $\epsilon$  = 4600 M<sup>-1</sup> cm<sup>-1</sup>).

**Reaction of (dipic)V(O)(OPE).** In an NMR tube, complex **3** was dissolved in pyr-d<sub>5</sub> (0.6 mL) containing *p*-xylene (3.4 mM) as an internal standard. A <sup>1</sup>H NMR spectrum was immediately recorded, and then the solution heated at 100 °C for 10 minutes. After cooling to room temperature, examination of the <sup>1</sup>H NMR spectrum revealed complete disappearance of **3** and formation of 2-phenoxyacetaldehyde (39%) and 2-phenoxyethanol (49%). 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)<sub>2</sub> (**5**). Spiking the reaction mixture with 2-phenoxyacetaldehyde prepared by a published procedure (Swern oxidation)<sup>xxiv</sup> confirmed the identity of this product.

**Reaction of (dipic)V(O)(OPE) under air.** In an NMR tube under argon, complex **3** (5.4 mg, 0.0146 mmol) was dissolved in pyr-d<sub>5</sub> (0.6 mL) containing *p*-xylene as an internal standard (8.2 mM). The solution was allowed to react at room temperature for 2 days to form **5**, 2-phenoxyacetaldehyde, and 2-phenoxyethanol. At this time the tube was opened to air, shaken, and then heated at 100 °C. After 4 weeks at 100 °C under air, the 2-phenoxyethanol was completely consumed, and the <sup>1</sup>H NMR spectrum showed phenol (1 eq), formic acid (0.7 eq), and *cis*-dioxo complex **6**.

**Reaction of **6** with formic acid.** In an NMR tube under air, **6** (4.0 mg, 0.012 mmol) and formic acid (2  $\mu$ L, 0.053 mmol) were dissolved in pyr-d<sub>5</sub> (0.6 mL). The tube was capped and heated at 100 °C for 26 h. After cooling to room temperature, examination of the <sup>13</sup>C NMR spectrum showed both formic acid (164.4 ppm) and a smaller peak corresponding to CO<sub>2</sub> (126.0 ppm).

**Reaction of **4** in pyr-d<sub>5</sub>.** Complex **4** (6.1 mg, 0.0133 mmol) was dissolved in pyr-d<sub>5</sub> (0.6 mL) containing *p*-xylene as an internal standard (6.3 mM). Over approximately 5 minutes at room temperature the solution color changed from yellow to green. Examination of the <sup>1</sup>H NMR spectrum after 10 minutes revealed a 1:1 ratio of benzoin methyl ether: 1,2-diphenyl-2-methoxyethanol. The UV-vis spectrum of the solution was consistent with the vanadium product (dipic)V(O)(pyr)<sub>2</sub> (**5**).

**Reaction of **4** in wet CD<sub>3</sub>CN.** Under argon, complex **4** (2.5 mg, 0.0054 mmol) was dissolved in CD<sub>3</sub>CN (0.6 mL, used as received from Cambridge Isotope Laboratory, not dried) containing THF (15.5 mM) as an internal standard. The solution was allowed to stand at room temperature for 2 days, during which time the color changed from the initial yellow to murky blue-green, and finally to a colorless supernatant with a green solid precipitate. Examination of the <sup>1</sup>H NMR spectrum revealed

clean formation of benzaldehyde (95%), 1,2-diphenyl-2-methoxyethanol (47%), and methanol (49%). The IR spectrum of the green solid (Nujol mull) matched that of material prepared by the reaction of H<sub>2</sub>dipic with V<sup>IV</sup>(O)(acac)<sub>2</sub> in CH<sub>3</sub>CN (see below). Dissolving this green solid in pyr-*d*<sub>5</sub> resulted in formation of (dipic)V<sup>IV</sup>(O)(pyr)<sub>2</sub>.

**Preparation of (dipic)V<sup>IV</sup>(O)(CH<sub>3</sub>CN)<sub>x</sub>.** In a 20 mL glass vial, V<sup>IV</sup>(O)(acac)<sub>2</sub> (0.306 g, 1.16 mmol) and H<sub>2</sub>dipic (0.193 g, 1.16 mmol) were suspended in CH<sub>3</sub>CN (10 mL). The reaction mixture was stirred at room temperature for 2 days, at which point it consisted of a dark gray supernatant and a pale green solid. The green solid was collected on a frit, washed with CH<sub>3</sub>CN (4 x 3 mL) and pentane (2 x 5 mL), and dried under vacuum. Yield: 0.207 g. Integration of <sup>1</sup>H NMR spectrum showed a ratio of 1.25 equivalents CH<sub>3</sub>CN per 1 dipic ligand. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz)  $\delta$  8.23 (br, 2H, Py), 8.19 (br, 1H, Py), 2.07 (s, 3H, CH<sub>3</sub>CN). IR (Nujol mull):  $\nu$ <sub>C=O</sub> = 1569 cm<sup>-1</sup>,  $\nu$ <sub>V=O</sub> = 983 cm<sup>-1</sup>.

**Catalytic oxidation of 1,2-diphenyl-2-methoxyethanol in DMSO-*d*<sub>6</sub>.** 1,2-Diphenyl-2-methoxyethanol (31.1 mg, 0.136 mmol) and (dipic)V(O)O<sup>i</sup>Pr (1.2 mg, 0.0034 mmol) were dissolved in DMSO-*d*<sub>6</sub> (0.8 mL) containing *p*-xylene (1  $\mu$ L, 0.008 mmol) as an internal standard. An initial <sup>1</sup>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 <sup>1</sup>H NMR spectroscopy (by transferring the solution to an NMR tube). After 24 h at 100 °C, integration of the <sup>1</sup>H NMR spectrum revealed that 98% of the starting material had been consumed (39 turnovers). The products consisted of benzaldehyde (1.67 equiv), methanol (0.80 equiv), benzoin methyl ether (0.14 equiv), and methyl benzoate and benzoic acid (approximately 0.04 equiv or less each) (yields expressed in equivalents formed per 1 equivalent 1,2-diphenyl-2-methoxyethanol reacted). A control reaction with 1,2-diphenyl-2-methoxyethanol only (no vanadium) in DMSO-*d*<sub>6</sub> under air showed no reaction when heated at 100 °C for 1 week.

**Control reaction of (dipic)V<sup>IV</sup>(O)(pyr)<sub>2</sub> (5) with 1,2-diphenyl-2-methoxyethanol in DMSO-*d*<sub>6</sub>.** Under argon in a resealable Teflon-capped NMR tube, complex 5 (4.8 mg, 0.0123 mmol) and 1,2-diphenyl-2-methoxyethanol (5.9 mg, 0.0259 mmol) were dissolved in DMSO-*d*<sub>6</sub> (0.6 mL) containing *p*-xylene (11.8 mM) as an internal standard. The tube was heated at 100 °C and monitored by <sup>1</sup>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.

**Catalytic oxidation of 1,2-diphenyl-2-methoxyethanol in pyr-*d*<sub>5</sub>.** 1,2-Diphenyl-2-methoxyethanol (29.8 mg, 0.131 mmol) and (dipic)V(O)O<sup>i</sup>Pr (4.8 mg, 0.013 mmol) were dissolved in pyr-*d*<sub>5</sub> (0.8 mL) containing *p*-xylene (5  $\mu$ L, 0.0406 mmol) as an internal standard. An initial <sup>1</sup>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 <sup>1</sup>H NMR spectroscopy. After 3 days, 56% of the starting material had been consumed. The products consisted of benzoin methyl ether (0.8 equiv), benzaldehyde (0.27 equiv), methanol (0.13 equiv), benzoic acid (0.16 equiv), and methyl benzoate (0.18 equiv) (yields expressed in equivalents formed per 1 equivalent 1,2-diphenyl-2-methoxyethanol reacted). Benzil and benzoin could also be detected (less than 0.02 equiv each) in the <sup>1</sup>H NMR spectrum. After 6 days at 100 °C, the starting material had been completely consumed. The products consisted of benzoic acid (0.86 equiv), methyl benzoate (0.85 equiv), benzoin methyl ether (0.09 equiv), benzaldehyde (0.19 equiv), methanol (0.13 equiv), benzil (less than 0.05 equiv), and benzoin (less than 0.05 equiv). A control reaction with 1,2-diphenyl-2-methoxyethanol only (no vanadium) in pyr-*d*<sub>5</sub> under air showed no reaction when heated at 100 °C for 1 week.

**Table S1.** Crystallographic Data Collection Parameters for **2**, **3**, and **4**. The crystal structures have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers 720372 (**2**), 720371 (**3**), 720373 (**4**).

	(dipic)V(O)(pinOMe) ( <b>2</b> )	(dipic)V(O)(OPE) ( <b>3</b> )	(dipic)V(O)(DPME) ( <b>4</b> )
Empirical formula	C <sub>14</sub> H <sub>18</sub> NO <sub>7</sub> V	C <sub>15</sub> H <sub>12</sub> NO <sub>7</sub> V	C <sub>22</sub> H <sub>18</sub> NO <sub>7</sub> V
FW	363.23	369.20	459.31
T(K)	120(1)	120(2)	120(1)
Wavelength (Å)	0.71073	0.71073	0.71073
crystal description	yellow needle	yellow block	orange cube
space group	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P 2 <sub>1</sub> /n
unit cell dimensions (Å, deg)	a = 10.444(3) b = 9.690(3) c = 15.041(4) α = 90 β = 98.100(3) γ = 90	a = 8.7744(10) b = 12.1686(14) c = 13.4618(16) α = 90 β = 90 γ = 90	a = 6.4966(7) b = 20.740(2) c = 14.6977(15) α = 90 β = 95.119(1) γ = 90
V(Å <sup>3</sup> )	1507.0(8)	1437.3(3)	1972.5(4)
Z, ρ(Mg/m <sup>3</sup> )	4, 1.601	4, 1.706	4, 1.547
μ(mm <sup>-1</sup> )	0.695	0.731	0.550
F(000)	752	752	944
crystal size	0.12 x 0.08 x 0.06 mm	0.20 x 0.10 x 0.08 mm	0.22 x 0.16 x 0.06
Θ range (deg)	1.97 to 25.30	2.26 to 25.33	1.96 to 25.27
index ranges	-12 ≤ h ≤ 12 -11 ≤ k ≤ 11 -17 ≤ l ≤ 17	-9 ≤ h ≤ 10 -14 ≤ k ≤ 11 -16 ≤ l ≤ 16	-7 ≤ h ≤ 7 -24 ≤ k ≤ 24 -17 ≤ l ≤ 17
reflections collected, unique	13696, 2729	9244, 2626	18756, 3578
completeness to Θ	[R(int) = 0.0910] 99.8%	[R(int) = 0.0594] 100.0%	[R(int) = 0.0674] 100.0 %
refinement method	full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
goodness of fit on F <sup>2</sup>	S = 1.007	S = 0.984	S = 1.168
R <sub>1</sub>	0.0438	0.0370	0.0379
wR (I > 2σI)	0.1082	0.0766	0.0886

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