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Communication

Vanadium Pyridonate Catalysts: Isolation of Intermediates in the Reductive Coupling of Alcohols

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ABSTRACT: The reductive coupling of alcohols using vanadium pyridonate catalysts is reported. This attractive approach for C(sp^3)−C(sp^3) bond formation uses an oxophilic, earth-abundant metal for a catalytic deoxygenation reaction. Several pyridonate complexes of vanadium were synthesized, giving insight into the coordination chemistry of this understudied class of compounds. Isolated intermediates provide experimental mechanistic evidence that complements reported computational mechanistic proposals for the reductive coupling of alcohols. In contrast to previous mononuclear vanadium(V)/vanadium(III)/vanadium(IV) cycles, this pyridonate catalyst system is proposed to proceed by a vanadium(III)/vanadium(IV) cycle involving bimetallic intermediates.

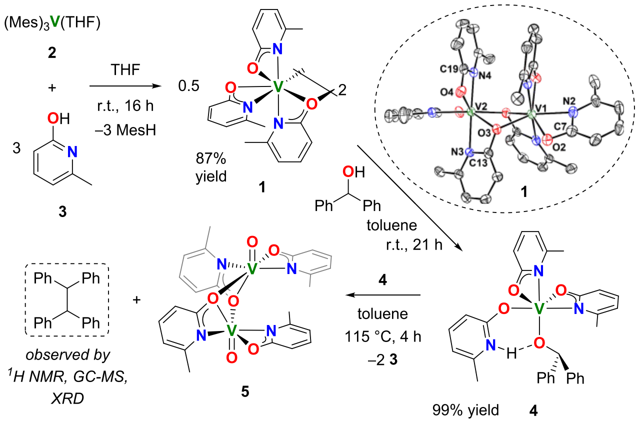
The conversion of oxygen-rich, biomass-derived feedstocks to alternatively functionalized chemicals has gained growing interest because of its potential as a renewable source of fuels and chemicals.[1−3] Numerous strategies have been developed to this end, including polyol dehydration,[4−6] deoxygenation,[7−16] and deoxydehydration.[1,17−19] Each of these methods effects C−O bond cleavage to produce valuable chemical feedstocks for further functionalization.

While the majority of deoxygenation reactions require the use of noble-metal catalysts, the use of earth-abundant and inexpensive 3d metal catalysts is desirable. Recently, Nicholas and co-workers have reported promising advances in the catalytic reductive coupling of alcohols using oxorhenium and oxovanadium catalysts.[20−23] This allows for both C−O bond cleavage and subsequent C−C bond formation using readily available monoalcohols as the carbon source.[23] While a reductant for O-atom transfer is required in the rhenium system,[20,22] the alcohol itself acts as the reductant in the vanadium system, producing the corresponding ketone and water as the byproducts.[21,23] Avoiding the use of an external reductant makes the vanadium-catalyzed reaction attractive, although a recent report has shown that hydrazine can be used as a terminal reductant for the reaction.[24] Using earth-abundant vanadium as a catalyst for deoxygenation reactions is both appealing and counterintuitive; oxygen is often deleterious to early-transition-metal catalysts because of their oxophilic nature.

Given our understanding of 1,3-N,O-chelated early-transition-metal catalysts for the functionalization of abundant feedstocks,[25−27] we anticipated that such complexes would be well suited for the reductive coupling of alcohols, taking advantage of the established metal−ligand cooperativity of pyridonates for E−H bond activations.[28−31] Moreover, vanadium pyridonate complexes are rare,[32] and their fundamental coordination chemistry is unexplored. Herein we demonstrate that vanadium(III) pyridonate complex **1** can mediate the catalytic and stepwise stoichiometric reductive coupling of benzyl alcohol derivatives. The stoichiometric reactivity allowed for the isolation of relevant catalytic intermediates to furnish key insights into the mechanism of this transformation.

Tris(pyridonate)vanadium(III) complex **1** was synthesized from trimesityl complex **2**[33] and pyridone **3** (Scheme 1).

Scheme 1. Synthesis of Vanadium Pyridonate Complexes



Complex **2** is a reliable precursor to vanadium(III) complexes[34−36] and allows direct access to the reactive vanadium(III) species needed for the reductive coupling of alcohols. Overall, complex **1** was produced in 87% yield and fully characterized including by X-ray crystallography, NMR, mass spectrometry (MS), and elemental analysis. Although assignment of the ^{1}H NMR chemical shifts is ambiguous for

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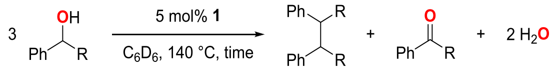
this paramagnetic complex (Figure S1), the identity of **1** was confirmed using X-ray crystallography.

Crystals of **1** obtained from a saturated tetrahydrofuran (THF) solution were suitable for X-ray diffraction, and the solid-state molecular structure is depicted (Scheme 1). Dimeric complex **1** is C_2-symmetric, with each V being seven-coordinate and having distorted pentagonal-bipyramidal geometry. All six pyridonates are κ^2-bound, with the two central ligands also bridging through the O to the adjacent V center (μ_2-O), exhibiting a κ^2:κ^1 bridging mode.[37−39] The μ_2-O interaction is unsymmetrical [V2−O3, 2.184(3) Å; V1−O3, 2.078(3) Å]. The oxidation state of V in **1** can be definitively assigned as V^{III}, as verified using Evan's method,[40−42] where paramagnetic **1** gives μ_{eff} = 2.89 μ_B (C_6D_6 solution, 25 °C), consistent with two unpaired d electrons ($\mu_{spin\text{-}only}$ = 2.83 μ_B). Thus, complex **1** is primed for the reductive coupling of alcohols.

Next, the reductive coupling of benzhydrol was attempted using **1** as the catalyst. Reaction conditions similar to those employed by Nicholas and co-workers were used.[21] Gratifyingly, heating a C_6D_6 solution of benzhydrol with 5 mol % of dimer **1** provides full conversion to the desired product with concomitant formation of benzophenone (Table 1, entry 1).

Table 1. Catalytic Reductive Coupling of Alcohols



entry	R	time (h)	product yield (%)[a]	carbonyl yield (%)[a]
1	Ph	24	>99	88
2	Me	48	65[b]	66
3	H	48	34	31

[a] Yields determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [b] A 1:1 mixture of meso/racemic diastereomers was observed.

This is confirmed by the ^{1}H NMR spectrum after the reaction (Figure S4), in which a singlet is observed at 4.68 ppm and a doublet is observed at 7.71 ppm; these signals are diagnostic for the methine H atoms of 1,1,2,2-tetraphenylethane and the *o*-H atoms of benzophenone, respectively.[21] Observation of the ketone byproduct suggests that the reaction proceeds through the previously reported mechanism in which the alcohol acts as a reductant. This reaction can be successfully extended to other benzyl alcohol derivatives (Table 1, entries 2 and 3, and Figures S5 and S6), an attractive class of substrates that can be derived from lignin biomass.[43,44] In the case of 1-phenylethanol, a 1:1 mixture of a racemic/meso product is observed. No ether byproducts were observed by gas chromatography (GC)−MS.

Previous work has shown that 1,3-N,O chelating ligands can be used to promote the isolation and characterization of reactive intermediates in catalysis.[45−49] Reported mechanistic studies of vanadium-catalyzed reductive coupling have used density functional theory to predict intermediates in the catalytic cycle.[23] Here we can use the vanadium pyridonate complex to our advantage to complete stoichiometric studies and gain complementary mechanistic information.[23]

First, the interaction of bimetallic complex **1** with 2 equiv of benzhydrol was investigated. Within 21 h at room temperature, the reaction in THF or toluene produced a green solution, which upon removal of volatiles afforded the alkoxide complex **4** as a green powder in near-quantitative yield (Scheme 1). The solid-state molecular structure of **4** (Figure 1, left) was obtained by X-ray crystallography using dark-green crystals grown from a saturated toluene solution. This structure shows that the hemilability of the pyridonate ligand is advantageous to promote coordination of the alcohol substrate and facilitate deprotonation of the alcohol. A short hydrogen-bonding interaction with the alkoxide [O4−H3, 1.914 Å (calcd)] is present, giving a six-membered vanadacycle within the distorted octahedral complex. Paramagnetic complex **4** has C_1 symmetry, consistent with the observation that the ^{1}H NMR spectrum of **4** (Figure S2) shows an increased number of signals compared to that of the more symmetric complex **1**. Most importantly, **4** provides experimental evidence for the analogous species predicted computationally.[23] Notably, deprotonation of an alcohol by a pyridonate ligand is the first step in iridium-catalyzed acceptorless alcohol dehydrogenation,[29] and here we show that similar metal−ligand cooperativity is relevant to early-transition-metal reactivity. Evan's method of **4** confirms a d^2 metal (μ_{eff} = 2.62 μ_B; C_6D_6 solution, 25 °C), as expected for this redox-neutral reaction.

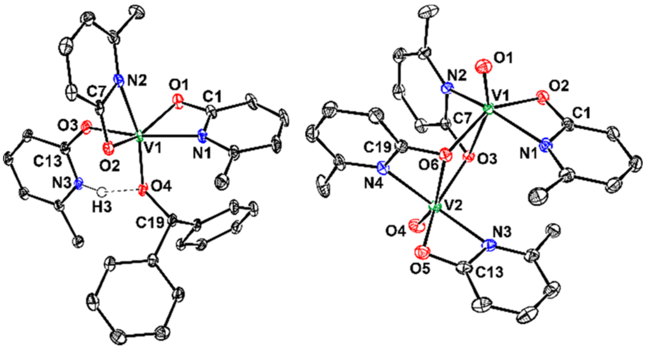


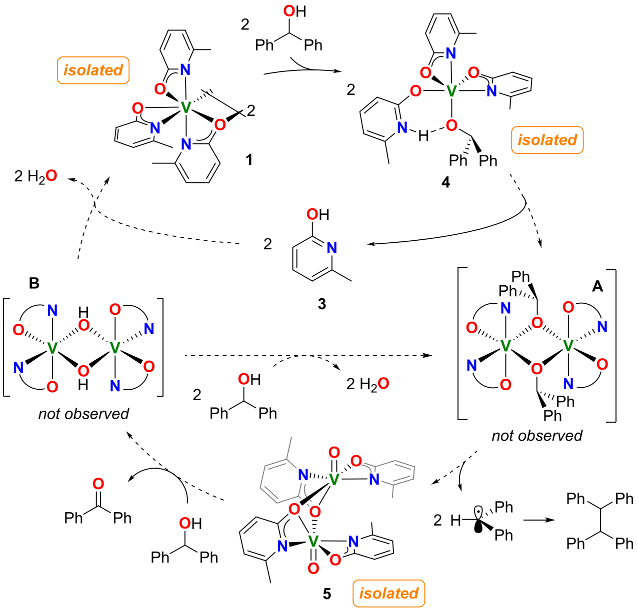
Figure 1. ORTEP representations of complexes **4** (left) and **5** (right) with ellipsoids shown at 50% probability and H atoms omitted for clarity. Selected bond lengths for **4** (Å): O4−H3, 1.914 (calcd). Selected bond lengths for **5** (Å): V1−O1, 1.5931(14); V1−O3, 2.4520(14); V2−O3, 2.0039(15); V2−O4, 1.5954(15).

Complex **4** was then heated in toluene to achieve reductive coupling of the bound alcohol (Scheme 1). After 4 h, the dark-green solution turned turquoise. Following removal of the volatiles and subsequent recrystallization from toluene, blue crystals of **5** suitable for X-ray diffraction studies (Figure 1, right) and some colorless crystals (vide infra) were obtained. Dimeric terminal oxo complex **5** is C_2-symmetric, with each V atom being six-coordinate and having distorted octahedral geometry. Similar to **1**, all pyridonates bind κ^2, with two having the κ^2:κ^1 bridging mode through a μ_2-O to the other V center. The μ_2-O−V interaction is more unsymmetrical in **5** compared to **1** [V1−O3, 2.4520(14) Å; V2−O3, 2.0039(15) Å] due to the strong trans influence of the oxo ligand. Additionally, the V−O distances [V1−O1, 1.5931(14) Å; V2−O4, 1.5954(15) Å] are in good agreement with a reported pyridine-2-thiolate oxovanadium complex [V−O_{oxo}, 1.583(6) Å].[50] The ^{1}H NMR spectrum of **5** (Figure S3) gives a diagnostic signal at 13.91 ppm, consistent with increased symmetry relative to **4**.

Paramagnetic **5** contains two V^{IV} d^1 metal centers, as predicted from the solid-state molecular structure. Thus, each V atom is oxidized by one electron upon going from **4** to **5**, consistent with reductive coupling. Indeed, 1,1,2,2-tetraphenylethane was observed by ^{1}H NMR spectroscopy when the reaction was performed in toluene-d_8 (Figure S11). Furthermore, the colorless crystals isolated from the reaction were confirmed to be 1,1,2,2-tetraphenylethane.[51] Homolysis of the C−O bond to give the benzhydryl radical (which would dimerize to form the reductively coupled product) and a vanadium(IV) complex was predicted to occur computationally; thus, the isolation of **5** is consistent with the computationally predicted mechanistic proposal. Notably, the pyridone released during reductive coupling was observed by ^{1}H NMR spectroscopy in both the stoichiometric and catalytic reactions. The only vanadium-based signals observed in the ^{1}H NMR spectrum of the catalytic reaction were those of **5**, suggesting that **5** is the catalyst resting state. Importantly, when crude **5** is used as the catalyst, the system achieves catalytic turnover (46% yield in 24 h; see Figure S9). Thus, **5** is catalytically relevant, although the lower conversion may suggest that a third equiv of free pyridone is important for catalysis. However, adding 10 mol % of pyridone to crude **5** prior to catalysis shows no improvement (see the Supporting Information, SI). Alternatively, **5** may be an off-cycle species that can slowly reenter the cycle.

Given these results, a plausible mechanism for the reductive coupling of benzhydrol with this system is proposed (Scheme 2). In the presence of benzhydrol, complex **1** is first converted to **4**, as observed within minutes at room temperature by ^{1}H NMR spectroscopy. Dissociation of pyridone would give the alkoxide complex **A**, which would undergo C−O homolysis to release a benzhydryl radical and **5**. The benzhydryl radical would then dimerize to give the coupled product. Importantly, no intermediate is observed during the formation of **5** from **4**, and efforts to isolate **A** have been unsuccessful. Thus, the nature of **A** is unknown, and it is proposed to be a bridged species based on the observed tendency of these complexes to aggregate. A mechanism in which C−O homolysis occurs at **4** prior to pyridone dissociation cannot be ruled out. After reductive coupling, complex **5** could undergo reduction with 1 equiv of alcohol to give the benzophenone byproduct and a putative bridged vanadium(III) hydroxide species **B**. We propose a bimetallic pathway. Nicholas and co-workers propose oxidation of benzhydrol via a monomeric vanadium(V) species.[23] No vanadium(V) species have been observed in our system, and NMR studies on the reaction of **1** with 4 equiv of benzhydrol show that benzophenone is produced (see the SI). Similar to **A**, the true nature of **B** is unknown, and this species has not been observed. Nevertheless, we propose that complex **B** could undergo protonolysis with free pyridone to produce water as a byproduct and regenerate **1**. Alternatively, complex **B** could undergo protonolysis with benzhydrol and proceed directly to complex **A**.

Scheme 2. Proposed Mechanism of Reductive Coupling



Evidence for the involvement of radical species has been obtained. A cyclopropyl-substituted alcohol undergoes ring opening under catalytic conditions, as evidenced by the formation of 1,2-dihydronaphthalene (see the SI).[21] The observed mixture of 1:1 meso/racemic diastereomers for the C−C coupled product using 1-phenylethanol as the substrate (Table 1, entry 2) also supports a radical mechanism. However, the radical-trapping agent fluorene does not intercept the benzhydryl radical during the reaction (see the SI). Additionally, a crossover experiment between benzhydrol and fluorenol gave very little heterocoupled product rather than the anticipated statistical mixture of homo- and heterocoupled products one would see for free radicals (expect the SI). These latter two results contrast observations by Nicholas and co-workers,[23] suggesting that C−C coupling of benzhydryl radicals may occur via a pathway different from that in their system. For example, the benzhydryl radicals may combine rapidly within the solvent cage of the proposed dinuclear intermediate **A**. Further studies are needed to elucidate the mechanism of this process.

In summary, the catalytic reductive coupling of alcohols by vanadium pyridonate complexes is reported. Complex **1** was found to be catalytically active for the reductive coupling of benzyl alcohols, showing vanadium(III) to be a viable starting point for the catalytic cycle. Intermediates **4** and **5** were isolated, providing experimental evidence for bimetallic intermediates in this vanadium-catalyzed transformation, complementary to previous mechanistic studies. On the basis of these stoichiometric reactions and radical-trap experiments, a vanadium(III)/vanadium(IV) redox cycle is proposed for this system. This work proposes a new design strategy for developing catalysts for this transformation: the involvement of bimetallic species, coupled with ligand hemilability and metal−ligand cooperativity. These features enable deoxygenative transformations of renewable feedstocks with oxophilic 3d early transition metals. Future directions will focus on related systems for expansion of the catalyst substrate scope in the redox disproportionation of alcohols.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00071.

> Experimental procedures, ^{1}H NMR spectra for NMR tube reactions and all complexes, and crystallographic data for all complexes (PDF)

Accession Codes

CCDC 1939764−1939766 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The

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Notes

The authors declare no competing financial interest.

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