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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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# Etheric C−O Bond Hydrogenolysis Using a Tandem Lanthanide Triflate/Supported Palladium Nanoparticle Catalyst System

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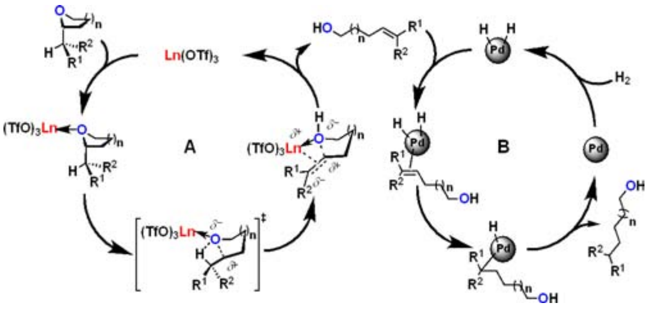
*Supporting Information*

**ABSTRACT:** Selective hydrogenolysis of cyclic and linear ether C−O bonds is accomplished by a tandem catalytic system consisting of lanthanide triflates and sinter-resistant supported palladium nanoparticles in an ionic liquid. The lanthanide triflates catalyze endothermic dehydroalkoxylation, while the palladium nanoparticles hydrogenate the resulting intermediate alkenols to afford saturated alkanols with high overall selectivity. The catalytic C−O hydrogenolysis is shown to have significant scope, and the C−O bond cleavage is turnover-limiting.

Efficiently converting abundant lignocellulosic biomass and coal into liquid fuels and commodity chemicals presents a grand research challenge.[1] In principle, such processes could increase sustainable liquid fuel supplies to satisfy near-term energy demands and decrease reliance on petroleum. However, progress is currently hindered by a lack of energy-efficient/cost-effective catalytic routes,[2] and by the product oxygen content which lowers energy density and complicates processing.[1d,3] Since aliphatic and aromatic ethers and furans constitute a significant component of biomass materials and cross-link many of the structures, we sought mechanistic understanding-based selective C−O cleavage strategies that could ultimately facilitate conversion of these feedstocks into liquid fuels.[4] Moreover, selective C−O bond cleavage processes also have significant potential in organic synthesis;[5] however, these bonds are typically unreactive in the absence of allylic or benzylic junctures. Here we report a new, thermodynamically based tandem strategy for catalytic ether hydrogenolysis which builds on a transformation typically employed to achieve the microscopic reverse, C−O fusion.

To catalyze C−O bond hydrogenolysis, we focused on coupling endothermic C−O bond scission via the microscopic reverse of well-documented alkene hydroalkoxylation processes (Scheme 1, Cycle **A**; Δ*H* ≈ +14 kcal/mol) with exothermic C═C hydrogenation (Δ*H* ≈ −25 kcal/mol) to yield saturated alcohols (Scheme 1, Cycle **B**). We previously demonstrated[6] that solutions of easily recycled, electrophilic lanthanide triflates[7] in ionic liquids are efficient and selective catalysts for C−O fusion via intramolecular alkene hydroalkoxylation[8] (reverse of Scheme 1, Cycle **A**).[9,10] From microscopic reversibility, this catalytic system should, in principle, be ideally competent for the reverse but to date undocumented and endothermic C−O scission to yield alkenols (Scheme 2, step ***i***). Coupling to an effective hydrogenation catalyst would then close the catalytic cycle to produce saturated alkanols (Scheme 2, step ***ii***).[11]

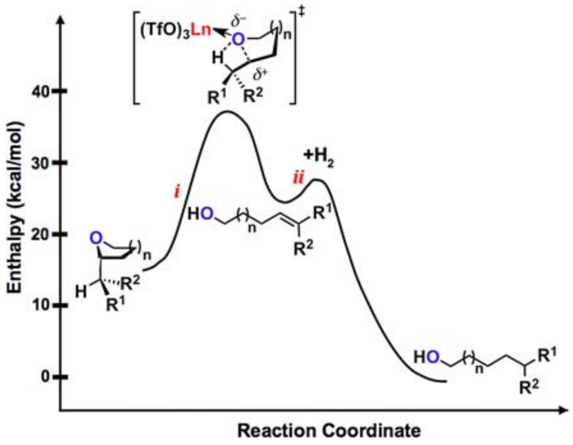
**Scheme 1. Proposed Tandem Pathway for Lanthanide Triflate/Pd Nanoparticle-Mediated Etheric C−O Bond Hydrogenolysis**[a]



[a]Ln = lanthanide; R1, R2 = organic functional group.

The use of room temperature ionic liquids (RTILs) as catalytic reaction media has advanced dramatically.[12] These robust, recyclable, nonvolatile, polar, typically aprotic solvents often provide unique reaction efficiencies and selectivities (as in

**Scheme 2. Approximate Reaction Coordinate Showing: (*i*) Conversion of a Cyclic Ether into an Intermediate Alkenol, Followed by (*ii*) Hydrogenation of the Alkenol to Yield a Saturated Alcohol**

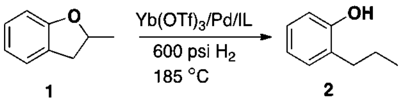


**Received:** June 28, 2012
**Published:** August 13, 2012

dx.doi.org/10.1021/ja306309u | *J. Am. Chem. Soc.* 2012, 134, 14682−14685

lanthanide-mediated hydroalkoxylations),[6] as well as environmental attractions and facile product separation.[13] While metal nanoparticles and various organometallic complexes are effective olefin hydrogenation catalysts in RTILs near room temperature, preliminary studies with such catalysts and allylphenol as a model dehydroalkoxylation product in [EMIM][OTf] (ethylmethyl-imidazolium triflate) revealed significant catalyst deactivation via agglomeration and/or thermal decomposition at temperatures affording useful dehydroalkoxylation rates (≥100 °C).

As an example, commercially available Pd supported on $BaSO_4$ was found to be stable in [EMIM][OTf] and to readily hydrogenate allylphenol at room temperature. However, in tandem catalytic experiments with 2,3-dihydro-2-methylbenzofuran (**1**) in [EMIM][OTf] using $Yb(OTf)_3$ and the aforementioned Pd catalyst at 185 °C/600 psi $H_2$, only slow C−O cleavage and hydrogenation to *n*-propylphenol (**2**) is observed, with a maximum yield of 45% in 22 h (eq 1). In marked contrast, Pd nanoparticles deposited on $Al_2O_3$ via atomic layer deposition (Pd@ALD), are exceptionally resistant to thermal sintering.[14] When this catalyst is used in conjunction with $Yb(OTf)_3$ in [EMIM][OTf] under the same reaction conditions, *n*-propylphenol is formed cleanly at 185 °C/600 psi $H_2$ with any hydrogenated arene byproducts below the detection limits.

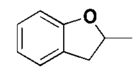
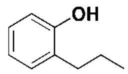
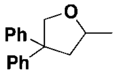
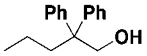
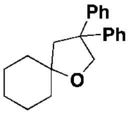
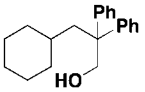
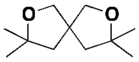
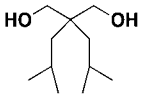
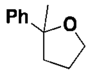
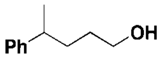
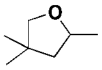
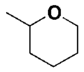
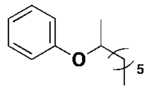
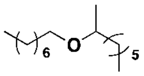


**1** **2** (1)

The scope of this tandem catalytic process was next investigated over the range 110−185 °C and 100−600 psi $H_2$, under anhydrous conditions, with final products isolated either by simple quantitative ether extraction or vacuum transfer, thus allowing efficient catalyst and ionic liquid recycling. Results are summarized in Table 1, with $^1H/^{13}C$ NMR product characterization detailed in the Supporting Information. Importantly, these conversions proceed cleanly (>95% selectivity) to the indicated products. In general, etheric bond cleavage is favored at more substituted C−O junctures, with the C−O bonds of acyclic ethers cleaved more rapidly than those of cyclics (entries 8,9). The latter observation is consistent with the entropic advantage of creating more particles/degrees of freedom that accompanies C−O scission, and with kinetic parameters for the corresponding cyclization process.[6] Negligible C−O cleavage is observed under the present conditions for substrates such as di-*n*-octylether and tetrahydropyran, which lack a H atom $\beta$ to the etheric O atom. That such a substitution pattern is beneficial for rapid hydrogenolysis is in good agreement with the regiochemistry of the reverse hydroalkoxylation process (Scheme 1, cycle ***A***),[6,8a,9] while encumbered substrates such as $\alpha$-*t*-butyl-THF are unreactive. Furthermore, the present turnover frequency ($N_t$) dependence on $Ln^{3+}$ ionic radius/electrophilicity (Table 1) closely parallels that of the microscopic reverse reaction,[6] with $Yb^{3+} > Sm^{3+} > La^{3+}$, again arguing that the same reaction coordinate is traversed.

Additional support for the proposed pathway of Scheme 1 is provided by control experiments indicating negligible turnover in the absence of either the $Ln(OTf)_3$ or Pd nanoparticle catalysts. Note from Table 1, entry 1 that turnover is far slower when 1.0 equiv HOTf is substituted for $Yb(OTf)_3$ in these reactions. Similar observations were made in studies of the corresponding hydroalkoxylation processes,[6] where free HOTf could not be detected in, or vacuum transferred from, $Ln(OTf)_3$-based catalytic reaction mixtures. Note that these observations are consistent with quantum chemical calculations on the $Al(OTf)_3$-catalyzed hydroalkoxylation reaction coordinate,[10c] as well as B3LYP DFT calculations on the present systems.[15] Furthermore, it was found previously that $N_t$ for the $Ln(OTf)_3$-catalyzed ring closure process is depressed on addition of an arylsilane proton trap,[6a,16] arguing that abstractable $H^+$ ions (e.g., from a coordinated alcohol)[10c] are involved in the cyclization; see Scheme 1, cycle ***A*** where a C−H proton is transferred to an evolving Ln-alkoxide group. In the present hydrogenolysis experiments, the same effects are observed when 1.0 equiv $PhSiMe_3$ is added to the $Yb(OTf)_3$ + Pd@ALD mediated **1** → **2** ether cleavage, and the yield of alkanol is depressed by ~95%, with benzene and $Me_3SiOTf$ observed in $^1H$ and $^{19}F$ NMR analysis of the reaction mixture.

**Table 1. Catalytic C−O bond Hydrogenolysis Mediated by $Ln(OTf)_3$ + Pd@ALD in [EMIM][OTf]**

| | $Ln^{3+}(H^+)$ | Substrate | Product | $N_t\,(h^{-1},°C)^a$ |
|---|---|---|---|---|
| 1 | Yb<br>Sm<br>La<br>HOTf |  **1** |  **2** | 0.55(185)<br>0.20(185)<br>0.17(185)<br>0.03(185) |
| 2 | Yb |  **3** |  **4** | 3.45(185) |
| 3 | Yb |  **5** |  **6** | 2.80(185) |
| 4 | Yb |  **7** |  **8** | 0.61(185) |
| 5 | Yb |  **9** |  **10** | 1.29(185) |
| 6 | Yb |  **11** |  **12** | 2.71(185) |
| 7 | Yb |  **13** | 1-hexanol | 0.35(185) |
| 8 | Yb |  **14** | Phenol + Octane | 3.72(110) |
| 9 | Yb |  **15** | 1-Octanol + Octane | 3.25(110) |

[a] Turnover frequencies determined from aliquots taken during the initial stages of the reaction with $^1H$ NMR spectroscopic integration vs internal standard. Reaction conditions: 600 psi $H_2$; $[La(OTf)_3] = 1$ mM; [substrate] = 0.01 M. For further experimental details, see the Supporting Information.

As shown in Figure 1, kinetic analysis of the **1** → **2** process in Table 1, entry 1 with $Yb(OTf)_3$ reveals first-order dependence

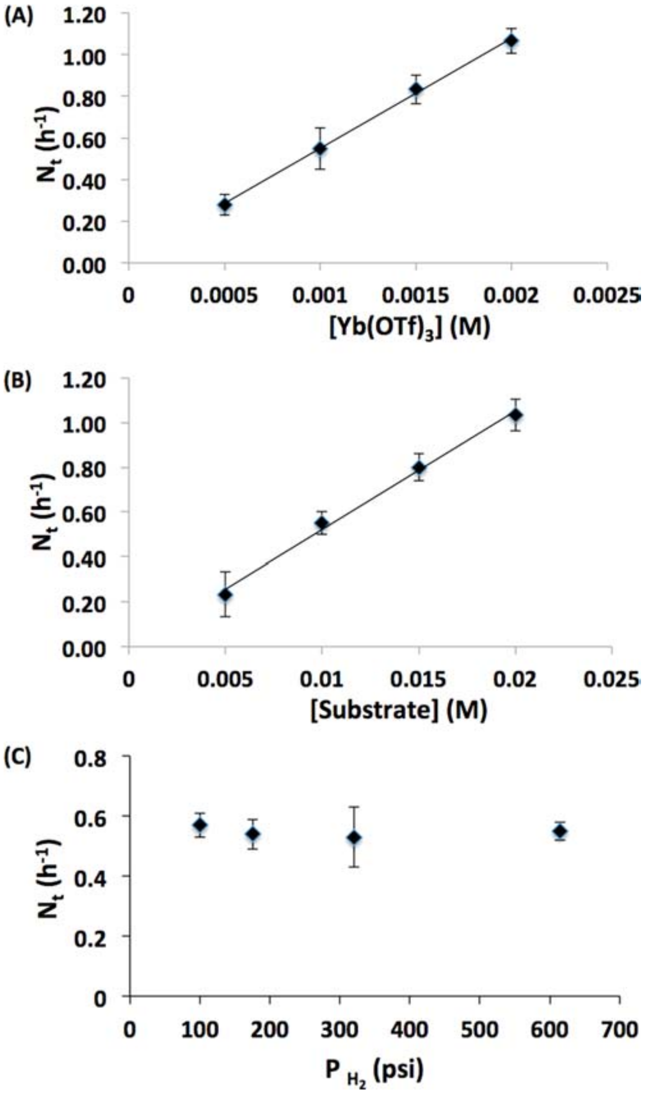


**Figure 1.** Dependence of **1** → **2** conversion turnover frequency on: (A) Yb(OTf)$_3$ concentration, (B) substrate concentration, (C) $H_2$ pressure.

of $N_t$ on [Yb(OTf)$_3$] and [substrate **1**], which mirrors the rate law of the microscopic reverse[6] and is consistent with the aforementioned trends in $Ln^{3+}$ ionic radius. No induction periods are observed as early as 20 min into the **1** → **2** conversion, and addition of 5 equiv of alcohol **2** does not significantly affect $N_t$. The first-order dependence on [Yb(OTf)$_3$] also argues that rapid pre-equilibrium dissociation of oligomeric lanthanide species prior to the turnover-limiting step is not important here. Furthermore, the zero-order dependence of $N_t$ on $H_2$ pressure over the 100−600 psi range (Figure 1C) and on the quantity of Pd@ALD used (not shown) is consistent with dehydroalkoxylation (Scheme 1, Cycle **A**) being turnover-limiting, followed by more rapid alkenol hydrogenation, in agreement with the energetics portrayed in Scheme 2.

In summary, these results demonstrate a selective Ln(OTf)$_3$/Pd nanoparticle mediated catalytic etheric C−O bond hydrogenolysis process in ionic liquid media. This atom-economical route is clean, thermodynamically and mechanistically understandable, and benefits from catalyst and reaction medium recyclability. Current efforts are focusing on scope and mechanism in terms of substrate and catalyst.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details and product characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This material is based upon work supported as part of the Institute for Atom-efficient Chemical Transformations (IACT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under contract DE-AC02-06CH11357 (catalytic C−O cleavage processes) and by the NSF under grant CHE-0809589 (basic lanthanide chemistry).

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