

Mechanistic Insights into the ReIO₂(PPh₃)₂-Promoted Reductive **Coupling of Alcohols**

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Supporting Information

ABSTRACT: A mechanistic investigation of the reductive coupling of $\stackrel{\mathsf{R}}{\longrightarrow}$ -OH + PPh₃ $\xrightarrow{\mathsf{RelO}_2(\mathsf{PPh}_3)_2}$ $ReIO_2(PPh_3)_2$ (1) is disclosed utilizing (1) stoichiometric reaction studies of 1 with alcohols, with PPh₃ and with $OPPh_3$; (2) rate law determination of the reaction of benzhydrol with PPh_3 catalyzed by 1; (3) substrate structure-



dependent reactivity/selectivity studies; and (4) DFT computational analysis of various potential reaction pathways in the benzyl alcohol/PPh₃ reaction. In situ NMR monitoring of reactions of 1 with PPh₃ and various alcohols demonstrate (a) facile, reversible PPh₃ dissociation from 1; (b) association of various alcohols to form Re-alcohol/alkoxide complexes, $(Ph_3P)IReO_2(ROH)$ and $(Ph_3P)IReO(OH)(OR)$; and (c) thermal conversion of these alcohol(ate)-rhenium complexes to $Ph_2CH-CHPh_2$ and OPPh₃ at >50 °C. Under pseudo-first-order conditions, the initial rate kinetics of reductive coupling of Ph₂CHOH/PPh₃ catalyzed by 1 shows (a) a reaction rate that is first-order each in ROH, catalyst and first-order (or higher) in PPh₃ and (b) the reaction is inhibited by OPPh₃. Alcohol structure effects show (a) relative reactivity of sec-, tert-benzylic = allylic > prim-benzylic/allylic \gg sec-, prim-alkyl and (b) low regioselectivity of the dimers from unsymmetrical allylic alcohols. A DFT computational study of the reaction of benzyl alcohol/PPh₃ with 1 reveals a preferred pathway involving: (a) formation of rhenium-alcohol and -alkoxide intermediates, (Ph₃P)IReO₂(ROH) and (Ph₃P)IReO(OH)(OR); (b) reduction of the latter by PPh₃ to form $(OPPh_3)(Ph_3P)IRe(OH)(OBn)(E)$; (c) association of a second BnOH with E to give $(Ph_3P)IRe(OBn)_2(K)$; (d) facile dissociation of a benzyl radical from K by C-O homolysis; and (e) a second rhenium-O-Bn homolysis from $(PPh_3)IRe(H_2O)(OBn)$ (O), giving bibenzyl via benzyl radical recombination and regenerating $(PPh_3)ReIO_2$.

INTRODUCTION AND BACKGROUND

The search for efficient processes to convert abundant, renewable resources to chemicals and fuels has spurred recent efforts to develop selective chemical transformations of biomass-derived, oxygen-rich feedstocks by refunctionalizing C-O bonds.¹ Besides dehydration and oxidation, reductive processes that give products with reduced oxygen (and increased energy) content and/or different functionality are receiving particular attention. Hydrodeoxygenation (HDO, Scheme 1) is one such reaction that is practiced in chemical

Scheme 1. Hydrodeoxygenation (HDO) and Deoxydehydration (DODH) of Alcohols

$$H_{2}/Cat \xrightarrow{R} R$$

$$H_{0}/Cat \xrightarrow{R} R$$

$$H_{0}/(H_{2}O) \xrightarrow{R} R$$

industry and in the laboratory,² typically with activated (benzylic, alylic) alcohols using $H_2/Pd-C_1^3$ Lewis acid/ silanes,⁴ and for unactivated alcohols with heterogeneous metal and metal oxide catalysts,⁵ but HDO of unactivated alcohols typically require severe conditions and often have limited product selectivity. Recently, the selective HDO of aryl ethers⁶ and phenols,⁷ having strong C_{sp}^2 -O bonds, has been disclosed, catalyzed by nickel and iridium complexes.

An alternative reductive process, deoxydehydration (DODH), involving vicinal hydroxyl group elimination to give unsaturated products (Scheme 1), has been developed more recently⁸ and has been catalyzed primarily by oxorhenium compounds and an expanding set of reductants including PPh_{3} ,⁹ H_{2} ,¹⁰ secondary and activated alcohols,¹¹ sulfite,¹² elements,¹³ and hydroaromatics.¹⁴ We reported the first DODH reactions catalyzed by nonprecious oxo-vanadium complexes,¹⁵ while others have recently disclosed oxomolybdenum catalyzed DODH with alcohol reductants.¹⁶ A catalytic cycle involving a reduced metalloglycolate species that undergoes olefin extrusion by concerted C-O bond cleavage appears to be a common feature of the DODH reactions.¹

The ability of oxo-metal complexes to activate C-O bonds in the dehydration¹⁸ and deoxydehydration⁸ of alcohols prompted us to investigate their potential for the deoxygenation of monoalcohols. In our initial study we discovered that activated alcohols such as benzylic, allylic and α -keto are deoxygenated by reaction with PPh_3 catalyzed by $(PPh_3)_2ReIO_2$ (1) (Scheme 2).¹⁹ Remarkably, however, for most of the alcohols tested, alkane dimers were the exclusive

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Scheme 2. Re-Catalyzed Deoxygenation (DO) and Reductive Coupling (RC) of Alcohols



reduction products, the result of reductive coupling (RC). Very recently, we have reported that oxo-vanadium complexes catalyze a related reductive coupling of alcohols in which the alcohol (rather than phosphine) serves as the reductant producing ketones as coproducts.²⁰

The deoxygenation and particularly the reductive coupling (RC) of alcohols promoted by soluble transition metal compounds is little known. The deoxygenation of activated alcohols (to alkanes) has been effected stoichiometrically using alcohols (to alkalies) has been enceded output Cp_2TiCl^{21} and $WCl_2(PMe_3)_4^{22}$ as reagents and catalytically by polymethylhydrosiloxane/PdCl₂.²³ Stoichiometric reductive coupling of activated alcohols by reduced Ti compounds² and La/Me₃SiCl,²⁵ and a Cu-catalyzed La/Me₃SiCl variant has also been reported.²⁶ The formation of bibenzyl as a minor product in the recently reported molybdate-catalyzed HDO of benzyl alcohol by isopropanol is also noted.¹⁶ The Recatalyzed, phosphine-mediated catalytic RC system that we discovered recently provides a means to convert alcohols to higher hydrocarbons under neutral and relatively mild conditions, while avoiding prefunctionalization of the alcohol. It thus has potential use for conversion of biomass-derived alcohols to chemicals as an alternative to the unselective Guerbet reaction.²⁷

Our initial report of oxo-rhenium-promoted reductive coupling of alcohols was suggestive but inconclusive as to the nature of reactive intermediates involved in the process. The RC reaction was observed only with activated alcohols, i.e., benzylic and allylic alcohols which have weaker C-O bonds,²⁸ suggesting that C–O bond breaking is likely the ratelimiting step. The reaction showed little regioselectivity in the coupling of unsymmetrical allylic alcohols, which could be explained by the involvement of a nearly symmetrical intermediate, e.g., carbocation/radical, but oxo-metal-catalyzed isomerization of the allyl alcohol substrate²⁹ also could explain this result. While the formation of hydrocarbon dimers and alkane C-H reduction products are suggestive of carbon free radical intermediates, attempted trapping of radicals with H atom donating hydroaromatic compounds failed to produce Hdonor derived products¹⁹ and thus could not conclusively implicate free radical intermediates. These mechanistic ambiguities, together with the novelty and potential synthetic utility of the RC reactions prompted a follow-up study to address these issues, which is reported herein.

RESULTS AND DISCUSSION

Stoichiometric Reactivity Studies of IReO₂(PPh₃)₂ (1). Solution Behavior of 1. A benzene- d_6 solution of IRe-O₂(PPh₃)₂ (1)³⁰ undergoes color changes from purple to crimson to yellow over 1–2 days. When monitoring this process by ³¹P NMR spectroscopy, the signal for 1 at 4.6 ppm diminished over time with concomitant growth of peaks at -5.0 (for free PPh₃) and at -12.0 ppm. These color and spectroscopic changes were completely suppressed when 1 was combined with 5 equiv of triphenylphosphine. Additionally, adding excess PPh₃ to a 3 day old yellow benzene solution of ReIO₂(PPh₃)_{1,2} caused the sample to return to the purple color of 1; the ³¹P NMR spectrum of the final solution showed the signal of 1 at 4.6 ppm to be predominant again and the -12.0 ppm signal to have nearly vanished. These observations are indicative of a room temperature equilibrium between 1 and a monophosphine derivative, tentatively formulated as (PPh₃)-ReIO₂ (2) (Scheme 3). As suggested by a reviewer, monophosphine derivative 2 could exist in part or entirely as an iodide-bridged dimer.

e	-			
0	 PPh₃ 0 ↓ Re ↓ 0	+	PPh_3	
PPh ₃ 1 purple	2 yellow			

Scheme 3. Ligand Dissociation Equilibrium for Precatalyst 1

Interaction of 1 with Alcohols. A series of stoichiometric reactivity experiments was conducted to elucidate the transformations of 1 in the presence of various alcohols at room temperature. ¹H NMR monitoring of a room temperature solution of 1 in benzene- d_6 containing 5 equiv of benzhydrol showed after 1-2 days two new low intensity singlets shifted downfield from those of the free alcohol at 6.3 and 5.5 ppm (approximate ratio 2:1; Figure 1). HSQC NMR spectra indicated that these signals correlate with ¹³C peaks at 35 and 75 ppm, indicative of H-CPh2-ORe moieties. In the ³¹P NMR spectrum of the mixture, free PPh_3 (-8.0 ppm) and additional signals at -9.0 and at -11.5 ppm (ReO₂IPPh₃, 2) were detected. The new species were tentatively assigned as Re-alcohol and Re-alkoxo-hydroxo species, e.g., A-D (Scheme 4). This assignment was supported by NMR monitoring of the reaction of $\text{ReO}_2 I(\text{PPh}_3)_{1,2}$ with other alcohols and computational reaction modeling (vide infra).

We also examined the NMR spectra of 1:5 mixtures of complex 1 with other alcohols, including ethanol, benzyl alcohol, 1-phenylethanol, and cinnamyl alcohol (PhCH= CHCH₂OH). All of these solutions changed color over 1-2days and exhibited changes in their NMR spectra. The ¹H NMR spectra of the aged samples with the first three alcohols showed, besides the signals of the free alcohol, two new sets of signals appearing substantially upfield from the free alcohol, Δ (ppm) from 1.1 to 1.7. The spectrum of the reaction mixture with ethanol is shown in Figure 2; see the Supporting Information for others. The integrated ¹H NMR signals for these two pairs of peaks were about 1:2 (and about 1:5 with cinnamyl alcohol). The two unequal intensity sets of alcoholderived proton signals correlated with the presence of a large ^{31}P NMR signal at -10.5 to -10.9 ppm and a smaller one at -7 to -6 ppm in the region for coordinated PPh₃, indicating the formation of two major PPh3-containing product complexes.

Up to four alcohol/alkoxide adduct structures arising from the interaction of 1 with excess alcohol can be envisioned: A-D in Scheme 4, mono- or bis-adducts, as either alcohol complexes, M(ROH) (A, C) or metal hydroxo–alkoxides (HO)MOR (B, D). To distinguish among these possibilities we reasoned that the mono-/bis-adduct equilibrium should be affected by the ROH/Re ratio, so the ratio of ethanol to rhenium complex 1 was varied at 2:1 and 10:1 in two samples.



Figure 1. ¹H (left) and ³¹P (right) NMR spectra of 5:1 Ph₂CHOH/1 at room temperature over 35 days in CDCl₃, then at 50 °C for 1 day.







Figure 2. ¹H NMR spectrum of 5:1 $CH_3CH_2OH + 1$ (CDCl₃, 20 °C).

After 24 h, the integrated ratio of the two new CH_2 quartet signals was not appreciably different for these samples, showing the independence of the product ratio to the ROH/1 ratio. This result is best explained in terms of a coordinated alcohol/ alkoxide mixture, e.g., A/B or C/D, rather than a mono/bisequilibrium mixture (Scheme 5). The electronically different nature of alcohol vs alkoxide coordination is also consistent with the very different chemical shifts for the two sets of signals in the ¹H and ¹³C NMR spectra.

Although a number of rhenium–alkoxide complexes have been reported,³¹ very few alcohol complexes of any metal have

been well-characterized;³² hence, NMR data comparable to the present results are insufficient to definitively assign structures to the detected rhenium alcohol/alkoxide species. In our DFT computational modeling of the Re-catalyzed reductive coupling pathways, we find support for the energetic viability of both types of complexes.

A role of the alcohol/alkoxide adducts in the catalytic reductive coupling is implicated by the result of heating solutions containing these species. When a 35 day aged sample derived from mixing 5 equiv of Ph₂CHOH with 1 was warmed to 50 °C, the NMR signals from the Re-OCHPh₂ species gradually disappeared and Ph₂CH–CHPh₂ was detected after about 24 h (Figure 1), along with a ³¹P NMR signal at ~27–24 ppm, assigned to the coproduct, OPPh₃ (Scheme 5).

Formation of a (PPh₃)Re(OPPh₃) Species under Ambient Conditions. Another rhenium-phosphine complex was detected in the NMR experiments that could be relevant to the catalytic mechanism. After many days at room temperature, solutions of 1 and Ph₂CHOH displayed a pair of equal intensity doublets in the ³¹P NMR spectrum at 50.7 and -11.5 ppm (J = 15 Hz), which is typical of a two- or three-bond phosphorus-phosphorus coupling (see the Supporting Information).³³ The 50 ppm signal is downfield of that of free O=PPh₃ (25 ppm), in the region of reported phosphine oxide metal complexes.³⁴ These features suggest that the species has a Ph₃P-O-Re-PPh₃ subunit. To further clarify its composition an NMR sample was prepared with a 1:5 ratio of IReO₂(PPh₃)₂ (1) to O=PPh₃. After 24 h at room temperature, this solution was yellow and exhibited the same

Scheme 5. Formation and Conversion of Alcohol-Alkoxide Adducts to Products



pair of doublets in its ³¹P NMR spectrum as produced after several hours in the reaction of Ph_2CHOH with 1. We therefore identify this species as $(PPh_3)ReO_2I(OPPh_3)$ (3) (Scheme 6). The formation of 3 from the reaction of 1 with

Scheme 6. Formation of Mixed Phosphine Oxide-Rhenium-Phosphine Complex 3



 $OPPh_3$ shows the rapid ligand substitution of 1 as indicated in the earlier NMR studies. The generation of 3 during long-term interaction of 1 with benzhydrol may be the result of Re(V) to Re(III) reduction by dissociated PPh_3 (or Ph_2CHOH , see below) and subsequent rhenium reoxidation by adventitious oxygen or during slow reductive coupling of the alcohol.

PPh₃/ReO₂I(PPh₃)₂ Reactivity. To further evaluate the viability of generating a Re(III) species by phosphine reduction of $ReO_2I(PPh_3)_{1,2}$ in the catalyzed RC reaction, a solution of 1 and PPh₃ in C_6D_6 was monitored by ³¹P NMR at r.t. for 6 days, then at 150 °C for 30 min. The NMR spectra (see the Supporting Information) showed gradual formation of OPPh₃ and, eventually, the complete disappearance of 1; the Re-containing product was not identified (Scheme 6). This result demonstrates the ready reducibility of 1 by PPh₃ and thus the viability of producing a reduced presumably Re(II or III) species at the higher temperature of the catalyzed reactions. The reducibility of other $LRe(V)O_2$ species by phosphines has been noted in a number of reports,³ and the reduction of a Re(V)-diolate to a Re(III)-diolate by secalcohols has been suggested in the MeReO3-catalyzed deoxydehydration of glycols.³⁶

Substrate Structure/Reactivity Effects. A few substrate structure-based reactivity probes were also evaluated to gain additional insights into the nature of the C-O bond cleavage step. From our preliminary study, we observed selective formation of dimeric hydrocarbon products from the most activated alcohols; less activated substrates, e.g., BnOH and PhCHOH-C(O)Ph, gave significant amounts of H-transfer reduction products, i.e., toluene and PhCH₂COPh, respectively.¹⁹ Additionally, in our initial study the reductive coupling of unsymmetrical allylic substrates, e.g., cinnamyl alcohol and its isomer, produced essentially the same mixture of isomeric diene dimers.¹⁹ Although this could be taken as evidence for the formation of a common isomerizing or symmetrical intermediate, e.g., allylic radicals, the proven ability of oxometal species to catalyze the facile isomerization of the substrate allylic alcohols,²⁹ renders this result inconclusive.

An alcohol substrate that could implicate a radical intermediate by the formation of ring-opened products, cyclopropyl carbinol 4,³⁷ also proved inconclusive because this compound was quite unreactive under our typical conditions, achieving little conversion after 5 days and failing to provide an adequate amount of a characterizable product.



A substrate stereochemical probe was also considered, homochiral PhCH(OH)CH₃ (**5**), for which the question was whether the resulting chiral *anti* hydrocarbon dimer would be nonracemic. If so, then it would indicate a concerted or stereodefined replacement of the C–O bond by the C–C bond of the dimer. Unfortunately, the decisiveness of this test was also undermined by the discovery that the homochiral alcohol was substantially racemized under the reaction conditions (150 °C), indicating that C–O bond cleavage is reversible with this substrate. These substrate-based probes thus failed to identify the character of the C–O bond cleavage.

Kinetics Study. We sought to determine the reaction order in each component, i.e., the precatalyst, $\text{ReO}_2\text{I}(\text{PPh}_3)_2$ (1), the alcohol substrate and PPh₃ in the reductive coupling of benzhydrol (Scheme 7). NMR spectroscopy was used to

Scheme 7. Reductive Coupling of Benzhydrol for Kinetic Analysis



collect concentration/time data for the product dimer, $Ph_2CH-CHPh_2$; with chlorobenzene as the solvent at 125 °C, dimer yields of 75–80% were obtained. Reactions were monitored with hexamethylbenzene as an internal integration reference, sampling every minute to determine initial reaction rates (conversion $\leq 15\%$). Sets of reactions varying only the concentration of one component were run under pseudo-first-order conditions. Keeping the alcohol and phosphine at a fixed concentration (0.10 M) the catalyst concentration was varied at 0.010, 0.005, and 0.0010 M, and the initial reaction rates were determined (Figure 3). Plotting the initial rate versus the catalyst concentrations gave a value of the reaction order (*n*) in catalyst of approximately one (Figure 4).



Figure 3. Initial rate data for $Ph_2CHCHPh_2$ formation at various concentrations of precatalyst 1.

¹H NMR sampling of the Ph₂CHOH/PPh₃/ReO₂I(PPh₃)₂ reaction was also carried out with various concentrations of benzhydrol at a fixed concentration of catalyst (0.01 M) and excess PPh₃ (0.50 M). Under these conditions the reaction rate had an apparent first-order dependence on the alcohol concentration (Figure 5), but at 0.10 M PPh₃ (typical of catalytic conditions) increasing the benzhydrol concentration from 0.050 to 0.2 M actually resulted in a lower reaction rate (Table 1, entries 1 and 2). This apparent substrate inhibition



Figure 4. Reductive coupling rate dependence on the catalyst 1 concentration.



Figure 5. Reductive coupling rate dependence on the benzhydrol concentration at 0.50 M PPh_3 .

has been observed in enzyme kinetics and suggests the formation of a "dead-end" (inactive) intermediate.³⁸

Table 1. Initial Rates of Reductive Coupling Showing Substrate Inhibition at High Concentrations of PPh_3 and Ph_2CHOH

entry	$[Ph_2CHOH]$ (M)	$[PPh_3]$ (M)	initial rate ($\mu M/min$)
1	0.05	0.10	0.0026
2	0.20	0.10	0.0021
3	0.10	0.05	0.0029
4	0.10	0.20	0.0024
4	0.10	0.20	0.0024

To determine the reaction order in the reductant the PPh₂ concentration was varied between 0.05-0.2 M at a fixed concentration of Ph₂CHOH (0.1 M) and the typical catalyst concentration of 1 (0.01 M). These conditions led to a substantial increase in the formation of the ether Ph₂CH-O-CHPh₂ from alcohol dehydration and more scatter of the data points in the concentration versus time plots. The rate versus [PPh₃] plot showed a positive phosphine concentration dependency (see Supporting Information) but gave only a moderate fit with a first-order dependence $(R^2 = 0.82)$. Additionally, at high [PPh₃] (0.2 M) the overall reaction rate was slower (Table 1, entries 3 and 4), similar to that observed with increasing [Ph₂CHOH] at moderate [PPh₃]. As for a possible explanation in the present system, high PPh₃ concentrations favor the coordinatively saturated $(PPh_3)_2 ReIO_2$ (1) (Scheme 3), limiting binding and activation of the alcohol substrate. Conversely, an excess of alcohol would favor the formation of bis-alcohol/alcoholate-rhenium species that could be less reactive toward reduction by PPh₃ for steric or electronic reasons. These concentration-dependent effects on the kinetic behavior provide evidence of mutual substrate inhibition and are consistent with a ping-pong type reaction

mechanism³⁹ in which one substrate, e.g., PPh_3 , is converted to product (OPPh₃) while generating a different catalyst species, e.g., Re(III), which then turns over the other substrate (alcohol) to the dimeric hydrocarbon, i.e., ROH to R–R.

Considering that triphenylphosphine oxide, OPPh₃, is a coproduct of the reductive coupling, that phosphine oxides are established ligands for higher oxidation state metals, ^{34,40} and the evidence for a mixed phosphine oxide–rhenium– phosphine complex species in the stoichiometric reactivity study (*op cit*), we sought to determine if OPPh₃ is also a product inhibitor of the RC reaction. An experiment was conducted in which 5 equiv of triphenylphosphine oxide was added to the standard reaction mixture (Ph₂CHOH/PPh₃/1); dimer formation was monitored by NMR at 125 °C. A 60% decrease of the reaction rate was observed (Figure 6),



Figure 6. Effect of added OPPh₃ on the initial rate of $Ph_2CH-CHPh_2$ formation at 125 °C. squares: [PPh₃] = [Ph₂CHOH] = 0.10 M, [1] = 0.010 M, no added OPPh₃; triangles: 0.50 M OPPh₃, [PPh₃] = [Ph₂CHOH] = 0.10 M, [1] = 0.010 M.

demonstrating an inhibitory effect of triphenylphosphine oxide in the reaction. The presence of high concentrations of the phosphine oxide may disfavor an equilibrium step in which it decoordinates or its coordination forms a less reactive complex.

Summarizing, under pseudo-first-order conditions the approximate empirical rate law derived is rate = $k[\text{cat}]^1[\text{Ph}_2\text{CHOH}]^1[\text{PPh}_3]^{\geq 1}$. However, at concentrations used for the catalytic reaction runs ([ROH] = [PPh_3] = 10[1]), we see departures from this rate law, apparently the result of catalyst saturation and/or competitive substrate binding and inhibition. With these provisos in mind the kinetics results are consistent with a catalytic pathway in which a monometallic catalyst reacts with at least one alcohol and one phosphine molecule in or before the turnover-limiting step. The inhibitory effect of phosphine oxide suggests that OPPh₃ production via coordinated OPPh₃ is reversible.

Computational Reaction Modeling. In our initial report of the ReIO₂(PPh₃)₂-catalyzed reductive coupling¹⁹ a preliminary DFT study of the deoxygenation of PhCH₂OH by the model catalyst MeReO₃ supported the viability of a mechanistic pathway involving PPh₃ reduction of MTO to MeReO₂, condensation of the latter with BnOH to give MeReO(OCH₂Ph)(OH), ReO-CH₂Ph bond homolysis to benzyl radical, and radical dimerization. The PhCH₂-ORe bond was suggested to be much weaker than typical, with a calculated dissociation energy of only 35 kcal for the intermediate, PhCH₂-ORe(O)Me(OH)(PMe₃), compared to that for PhCH₂-OH homolysis (81 kcal/mol, B3LYPcalculated; 82 kcal/mol, experimental).²⁷



Figure 7. B3LYP-optimized, M06(benzene) single point free energy profile of the $ReIO_2(PPh_3)_2$ -catalyzed reductive coupling of PhCH₂OH via a monoalkoxide pathway A; transition states are shown in blue.

In light of the observations in the stoichiometric reactivity and kinetics studies, we carried out a more thorough and experimentally more realistic DFT computational analysis of the ReO₂I(PPh₃)₂-catalyzed reductive coupling reaction, selecting PPh₃ as the ligand and reductant and benzyl alcohol as the substrate. As a starting point and benchmark, the B3LYP calculated structure of ReO₂I(PPh₃)₂ was compared to its Xray structure.³⁰ There is good overall agreement between the two trigonal bipyramidal structures with trans phosphine ligands, and the bond lengths and angles (±0–4%), with the largest variances in the Re-heavy atom distances, e.g., Re–O: X-ray 1.74 Å, B3LYP calcd 1.74 Å; Re–P: X-ray 2.49 Å, B3LYP calcd 2.54 Å; Re–I: X-ray 2.66 Å, B3LYP calcd 2.77 Å.

The favorable PPh₃ dissociation from 1, established experimentally, was also modeled computationally. We note that the energy for dissociation of PMe₃ from $ReO_2I(PMe_3)_2$ has been estimated at 7.3 kcal/mol.⁴¹ On the basis of B3LYPcalculated electronic energies (0 K, vacuum) a substantial energy penalty of 16.9 kcal/mol for the PPh3 ligand dissociation from 1 (\rightarrow ReIO₂(PPh₃) (A) + PPh₃) was found. When corrected for solvation (benzene) and temperature (293 K), the free energy of reaction was approximately thermoneutral, $\Delta G \sim 0.2$ kcal/mol. The ΔG_{rxn} using the M06 functional (single point with solvation and temperature correction) gave $\Delta G = 10.6$ kcal, a poorer agreement with the experimentally observed favorable dissociation. The inaccuracies of these DFT methods for calculating metalphosphine dissociation energies are acknowledged.⁴² In light of the generally better accuracy of the M06 method for TS energies⁴³ and our experimental observation of substantial PPh₃ dissociation and alcohol coordination at room temperature, we have set ΔG to zero for the monophosphine complex $ReO_2I(PPh_3)$ (A) in the calculated relative energy profiles.

The coordination of benzyl alcohol with ReIO₂(PPh₃) to form (PPh₃)ReIO₂(BnOH) (C) is calculated (M06/benzene, 298 K) to be nearly thermoneutral, $\Delta G = -0.7$ kcal. Alcohol complex C is found to be of similar energy to the corresponding alkoxo-hydroxo-complex (PPh₃)ReIO(OH)-(OBn) (D), $\Delta G = -0.4$ kcal. The isomeric alcohol and alkoxo-hydroxo adduct pairs of other aliphatic alcohols, e.g., ethanol, methanol, and benzyhydrol, also have comparable thermodynamic stabilities (see Supporting Information) and thus should exist in similar amounts in a tautomeric equilibrium. The energetic viability of such rhenium– alcohol/alkoxide species is demonstrated by their NMR detection from the interaction of various alcohols with $ReIO_2(PPh_3)_2$ (1).

We have considered two subsequent reaction pathways from the monoalkoxide complex $(PPh_3)ReIO(OH)(OBn)$ (D): (1) O-transfer reduction of D by PPh₃, followed by R-ORe cleavage processes (pathway A) or (2) association of a second ROH to give a dialkoxo-rhenium species, followed by reduction by PPh₃ and then R-ORe cleavage (pathways B and C). The calculated energy profile for the first of these is presented as scheme A in Figure 7. Oxo-rhenium attack by PPh₃ on the alkoxo-hydroxo species D has a substantial free energy of activation barrier (28.2 kcal/mol) via TS_{D-E} to produce the Re(III)-phosphine oxide species E in a nearly thermoneutral step in a singlet manifold. The d^4 -Re(III) species, e.g., E, could potentially exist as a low- or high-spin species, and examples of both spin states are documented, depending on the ligand set.⁴⁴ B3LYP calculations for the closed shell singlet and open shell triplet for the model $ReIPPh_3(OMe)_2$ found the singlet species to be approximately 30 kcal more stable. On this basis, the other Re(III) species evaluated in our study were also optimized as closed shell singlets. The substantial activation barrier in the phosphine reduction of **B** is derived from the counterbalancing enthalpic contributions of P-O bond-making and Re=O bondbreaking, and the considerable entropic cost of an associative process. In transition state TS_{D-E} (Figure 8), the P–O and Re-O distances are both much longer than for typical O-PR₃ and Re=O lengths.⁴⁵ The electronic character of the transformation may be simply viewed as an electron pair transfer from the HOMO of the nucleophile PPh3 to the LUMO of the electrophile $O = Re(V)I(OH)(OBn)(PPh_3)$ (D). This picture is in accordance with other computational



Figure 8. Transition state for the PPh₃ reaction with D.

and experimental studies of phosphine O-transfer reactions of oxo-metal complexes.⁴⁶

Considering the most likely options for O–C bond cleavage in a nonpolar medium (reaction solvent = benzene), the energetics of homolytic processes were evaluated. A transition state search for the dissociation of E to the spin doublets benzyl radical and (PPh₃)Re(IV)IO(OH) (F), yielded a saddle point TS_{E-F} with open shell singlet having an activation energy of only 26.4 kcal (Figure 9). The O–C bond energy for



Figure 9. Transition state (left) and product (right) structures for C– O homolysis of **E** and their Mulliken spin densities.

dissociation of benzyl radical from E is remarkably low compared to the B3LYP-calculated and experimental C–O dissociation energy of 80–82 kcal for $PhCH_2$ –OH itself.^{28,47} Product oxo-rhenium(IV) species F is calculated to have its unpaired electron delocalized primarily on the Re and oxo centers. The origin of the extraordinarily weak rhenium O–R bond is discussed in more detail subsequently.

Doublet Re(IV) species F thus generated can then undergo a nearly thermoneutral dissociative ligand substitution of OPPh₃ by benzyl alcohol via species G to give benzyl alcohol complex H. Dissociation of benzyl radical from H to give Re(V)-dihydroxo species I is once again found to be facile, with an activation free energy for the open-shell singlet transition state of 26.0 kcal/mol, nearly equal to that for the corresponding dissociation from E. The highly exothermic combination of two benzyl radicals generated from F and H, with expected low barrier, would give the bibenzyl product. Finally, dihydroxo species I can isomerize to modestly less stable aquo complex J, from which water dissociation would regenerate $ReIO_2(PPh_3)$ (B) to re-enter the catalytic cycle.

For the complete reaction sequence of pathway A (Figure 7) the total free energy barrier is 29.2 kcal at TS_{H-L} which is in

the activation energy range estimated by the Arrhenius equation for an experimental reaction rate of approximately 1 turnover/h at 150 °C. In this pathway step H-I is marginally rate-limiting, so a second-order rate dependence in the alcohol would be expected. However, the experimental kinetics study was conducted with benzhydrol as the substrate. Although we did not model the complete reaction pathway with benzhydrol, the B3LYP-calculated electronic dissociation energies for the conversion of $(PPh_3)(OH)(O)IRe-O-R$ to $(PPh_3)(OH)$ -(O)IRe[•] and R[•], for both $R = CH_2Ph$ and $CHPh_2$ were determined. The dissociation energy was 9.8 kcal lower for the benzhydryl relative to the benzyl derivative. One can estimate then that the activation free energies for benzhydryl radical dissociation from a Re-alkoxy species would be at least a few kcal lower than for the benzyl species, which in turn would make the phosphine-O-transfer step (D-E) rate-limiting, consistent with the experimentally determined first-order dependence on the benzhydrol concentration.

Since in the catalytic reductive coupling reaction there is an excess of alcohol substrate relative to catalyst, it is reasonable to consider the formation of bis-alcohol/alkoxide species prior to O-C bond cleavage events (Figure 10, pathway B). From monoalkoxide complex E a second alcohol could coordinate, tautomerize to the bis-alkoxo aquo species, and dehydrate to provide dialkoxy complex K; overall this process is nearly thermoneutral. Dialkoxo complex K could dissociate to benzyl radical and Re(IV) monobenzyloxy complex L. This transformation is calculated to have an activation free energy of only 20.2 kcal/mol via the open-shell singlet transition state and is only mildly endoergic, once again indicating an extraordinarily weak O-C bond in a rhenium(III)-alkoxide species. The transition state structure $TS_{K-Ldissoc}$ (not shown) features a very long O---C distance, indicative of a late transition state and extensive spin delocalization onto primarily the Re-O and benzylic fragments. After the first R-O homolysis, (K-L) monobenzyloxy species L was considered to undergo the second C-O cleavage by either of two processes, dissociative or associative. The transition state for the dissociative process TS_{L-Mdissoc} (Figure 11) features a very long O---C distance, indicative of a late transition state and extensive spin delocalization onto primarily the Re-O and benzylic fragments. A rebound reaction between Re-alkoxide L and the benzyl radical could occur via associative transition state $TS_{K-Lassoc}$ to produce bibenzyl and the original catalyst species $ReO_2I(PPh_3)$ (B); overall, this is a highly excergic transformation. The very long O-C and C-C distances in the cleaving and forming bonds are noteworthy. The electron spin densities in $TS_{L-Massoc}$ are also quite delocalized, being distributed primarily at the Re-O unit, both benzylic carbons, and the aryl rings. This reaction step is a bimolecular radical substitution at carbon, of which there are relatively few verified examples.⁴⁸ The calculated activation energy for the associative process via $TS_{L-Massoc}$ (29.5 kcal) is somewhat higher than that for the dissociative step via $TS_{L-Massoc}$ (24.5), which points to the primary operation of the dissociative process for O-C cleavage. The total calculated energy barrier for the dissociative pathway B is 24.5 kcal, significantly lower than that for pathway A, and thus is considered to be more viable for the catalytic process.

A variation in the dialkoxide pathway B was also considered and is shown in the energy profile of Figure 12 (pathway C). This pathway diverges from Re(IV)-alkoxide species L, which could undergo nearly thermoneutral substitution of phosphine



Figure 10. M06-solvent free energy profile for the $\text{ReO}_2I(\text{PPh}_3)_2$ -catalyzed reductive coupling of PhCH₂OH via a dialkoxide pathway B; shows dissociative and associative TSs for ReO–C bond cleavage, TS_{L-M} ; transition states are shown in blue.



Figure 11. Dissociative and associative transition state structures for C–O homolysis of L and Mulliken spin densities.

oxide by water to give the Re(IV)–alkoxo species **O**. Dissociation of **O** into benzyl radical and dihydroxo species **I** has an activation barrier of only 20.7 kcal via the open shell singlet transition state TS_{O-I} . In pathway C, the total activation barrier, peaking at TS_{O-I} is 23.8 kcal, the lowest among pathways A–C for the second ReO–R cleaving step. We thus consider pathway C to be the most favorable for the reductive coupling reaction. Although pathway C still has the radical-dissociation step (O–I) with a slightly higher energy barrier than the reduction of **D** by phosphine (**D**–**E**), the expected lower barrier for the corresponding radical-forming steps from benzhydrol relative to benzyl alcohol, and the limits of computational accuracy inherent in the B3LYP, M06, and solvation modeling would reconcile the computational and kinetics results.

Alternative Pathways to Reductive Coupling. The possibility of initial reduction of $ReIO_2(PPh_3)_{1,2}$ before the alcohol coordination was also considered. B3LYP-level

calculation shows this as a viable step, but with a substantially higher activation barrier (36.0 kcal) than reduction of (PPh₃)ReOI(OH)OBn) **D** (28.2 kcal). The experimental detection of room-temperature phosphine dissociation and alcohol association with ReO₂I(PPh₃)₂ (1) to produce detectable alcohol/alkoxide intermediates **D** and **E** supports the conclusion that alcohol association is more facile than the reduction of the dioxo species (**A** or **B**) by phosphine.

Could ReIO(OBn)₂(PPh₃) undergo benzyl radical dissociation before reduction? Comparing activation energies (B3LYP, vac, 0 K) for Re(V)IO(OBn)₂(PPh₃) \rightarrow Bn-rad + Re(VI)O₂I(OBn)(PPh₃) (28.3 kcal) versus Re(III)I-(OBn)₂(PPh₃) \rightarrow Bn-rad + Re(IV)IO(OBn)(PPh₃) (23.4 kcal) indicates that benzyl radical dissociates more easily from the more reduced Re(III)-alkoxo species. Since the homolytic dissociation is formally an oxidation of the rhenium center, the more facile homolysis of the reduced rhenium alkoxo species may reflect a lower energy requirement for the Re(III) to Re(IV) versus Re(V) to Re(VI) oxidations.⁴⁹

A few nonradical pathways to the hydrocarbon dimer were also evaluated as shown in Scheme 8. These include concerted oxidative elimination from a bis-alkoxide species (\mathbf{P}) and reductive elimination from a bis-alkyl complex (\mathbf{S}) .

We sought to find a transition state for concerted "oxidative elimination" of the hydrocarbon dimer Bn–Bn from a $ReI(OBn)_2(PPh_3)$ species, e.g., **P**, analogous to the metal–glycolate intermediate verified in the oxo-metal promoted deoxydehydration of glycols.^{8,9,17} However, attempts to approach such a transition state via constrained geometry scans failed to show an inflection point over a wide range of R–R distances (R = Me or PhCH₂) or a tendency toward C–C bonding or significant O–C lengthening even at close contact and at high energy cost. Such a process leading to dimer formation thus appears energetically unfavorable.

Could dialkyl-rhenium complexes, e.g., $(R)_2 ReO_2 I$ (T), arising from O-to-Re alkyl group migration (deinsertion) form the dimeric hydrocarbon by reductive elimination (T-A)? We



Figure 12. Free energy profile for $ReO_2I(PPh_3)_2$ -catalyzed reductive coupling of $PhCH_2OH$ via a dialkoxide pathway (M06-benzene); transition states are shown in blue.





found that reductive elimination of ethane from the model species ReO_2IMe_2 could proceed via a concerted transition state, but with a rather high barrier of 50.4 kcal (B3LYP level). Furthermore, we could not locate a transition state for a concerted migratory deinsertion process to form a dialkyl-rhenium species, e.g., (PhCH₂)₂ReO₂IPPh₃ (S), from ReI-(PhCH₂O)₂PPh₃ (P). We conclude, therefore, that the migratory deinsertion also has a substantial activation barrier probably greater than for homolytic O-R dissociation. Indeed, to our knowledge, proven examples of a metal–alkoxide to oxo-metal alkyl transformation have not been reported.⁵⁰ This conversion has been suggested to account for the formation of small amounts of coupling product in molybdate-catalyzed dehydration of benzylic alcohols.¹⁶

Our study of the oxo-rhenium promoted reductive coupling reaction supports the idea that lower oxidation state metal– alkoxides can be precursors to carbon radicals. There is rather little direct experimental evidence for this concept, however, from prior reports.⁴⁹ Peters and co-workers provided evidence for the generation of t-butyl radicals in the room-temperature decomposition of $(t-BuO)_3Mo(\mu-N)Ti(NRAr)_3$.⁵¹ In the Cp₂Ti(III)Cl-promoted alcohol deoxygenation and coupling reactions, C–O cleavage was suggested to take place via the generation of organic radicals from a reduced Ti–alkoxide complex,²¹ and this hypothesis was supported computationally.⁵² Our recent discovery of oxo-vanadium catalyzed oxidation-reductive coupling of activated alcohols provides additional evidence that reduced vanadium alkoxide species are precursors to C-centered radicals.²⁰ It is also noteworthy that metal–alkoxides have been used as thermolytic precursors to nanoparticle metal oxides,⁵³ but the resulting organic products usually have not been identified. These experimental and computational results raise the question of whether weak C–O bonds are typical of reduced metal–alkoxides. Although additional studies are needed to more fully address this fundamental question, the homolytic bond dissociation energy of the MO–R species should be diminished when the one electron oxidation potential for the metal species is favorable and a delocalized metallo-radical species is formed.

CONCLUSIONS

The key findings of the experimental and computational studies of the oxorhenium-promoted reductive coupling reaction of alcohols include: (1) alcohols that have weaker C–O bonds, i.e., allylic and benzylic, undergo reductive coupling most readily; (2) unsymmetrical allylic alcohols produce regioisomeric dimers; (3) a room temperature equilibrium exists between $\text{ReIO}_2(\text{PPh}_3)_2$ (1) and $\text{Re-IO}_2(\text{PPh}_3)$ by dissociation of a triphenylphosphine ligand; (4) rhenium–alcohol and –alkoxide adducts can be detected by NMR under ambient conditions; (5) these species disappear upon heating with formation of the hydrocarbon dimer and OPPh_3 ; (6) PPh₃ can deoxygenate Re(V)- $\text{IO}_2(\text{PPh}_3)_{1,2}$; (7) under pseudo-first-order conditions the

empirical rate law is approximately first-order in both the catalyst and the alcohol concentrations and first-order or higher in PPh₃; (8) DFT calculations support the viability of both (PPh₃)IRe(V)- and -Re(III)-alkoxide intermediates; and (9) homolytic cleavage of Re(III)-benzyloxide species to benzyl and rhenium-centered radical species is calculated to be facile, with activation energies of 20–25 kcal/mol and dissociation energies of only about 15 kcal/mol.

Taken together, the results from the experimental and computational probes lead us to suggest a preferred reaction pathway for the phosphine-driven reductive coupling of activated alcohols that begins with alcohol coordination to form monoalcohol/alkoxide complex, then reduction of the latter by PPh₃ to give Re(III)-monoalkoxide species E. Association of a second alcohol molecule produces a Re(III)bis-alkoxide which can undergo sequential, facile C-O bond homolysis to generate the hydrocarbon radicals and oneelectron oxidized rhenium oxo-species. The former recombine to form the dimeric hydrocarbon and regenerate the original dioxo-Re(V) species. With less activated alcohols, e.g., benzyl alcohol, benzoin, which lead to more reactive radicals, a greater amount of H atom abstraction product relative to dimer is observed.⁵⁴ Our current efforts seek to expand the range of alcohol substrates for reductive coupling and deoxygenation reactions and to develop more active and economical catalysts and reductants.

EXPERIMENTAL SECTION

Materials and Methods. All reactants and solvents were obtained commercially and used without further purification. ¹H, ³¹P, and ¹³C NMR spectra were collected on Varian V-NMRS at 400 or 500 MHz. The NMR data were processed using MestReNova⁵⁵ and ACD⁵⁶ software. Gas chromatograms were collected on a Shimadzu GC-2014 equipped with an AOC 20i+s auto sampler, with a 3% SE-54 packed column, and a FID detector.

Preparation of RelO₂(PPh₃)₂ (1). Complex 1 was prepared in two steps following a literature procedure.³⁰ Ammonium perrhenate (1.0 g, 3.7 mmol) and triphenylphosphine (5.0 g, 19 mmol) were added to a mixture of 56% hydroiodic acid solution (5 mL) and ethanol (30 mL). The reaction was brought to reflux for 15 min. Green crystals of I₂ReO(OEt)(PPh₃)₂ formed in the mixture. After cooling to room temperature the crystals were filtered off, washed with ethanol, and dried under high vacuum. To a mixture of acetone (50 mL) and water (2 mL) was added ReI₂O(OEt)(PPh₃)₂ (1.00 g, 0.97 mmol). The green suspension was magnetically stirred at room temperature. After an hour the suspended crystals had changed color to violet. The crystals were filtered off and washed with cold acetone. The product was recrystallized from hot 1:1 benzene/hexanes, giving an 80% yield of ReIO₂(PPh₃)₂ which was stored in a desiccator over CaCl₂.

Stoichiometric NMR Experiments Involving 1. Ligand Dissociation. Each sample was prepared with about 1 mL of benzene- d_6 and 4.0 mg of ReIO₂(PPh₃)₂ under nitrogen (5 mM). For the samples in which triphenylphosphine was added, 26 mg was used.

Interaction with Alcohols. ReIO₂(PPh₃)₂ (1) (0.0060 mmol, 5.0 mg) and benzhydrol (60 μ L of 0.06 M solution in benzene- d_6) were added to 0.74 mL of benzene- d_6 in a thick-walled NMR tube. The NMR tube was capped and purged (evacuated, then backfilled) with nitrogen three times. The tube was left at room temperature for several weeks. The changes over time were followed by ¹H and ³¹P NMR. After a month, the sample was placed in an oil bath at 50 °C; the changes were followed by ¹H and ³¹P NMR about every 16 h.

*Reaction of 1 with PPh*₃. A solution of 1 and PPh₃ (1:5 equiv) in C_6D_6 was monitored by ³¹P NMR at 20 °C for 6 days, then at 150 °C for 30 min. The NMR spectra showed gradual disappearance of the signal from 1 (4 ppm) and increasing formation of OPPh₃ (25 ppm; see the Supporting Information).

Kinetics Study. In a 1 dram vial were weighed quantities of complex 1, benzhydrol, and triphenylphosphine, to which was added 0.90 mL of distilled chlorobenzene (stored over molecular sieves 4 Å) and 0.10 mL of hexamethylbenzene (0.1 M). The vial was capped and vortexed for 20 s. The sample was then split and dispensed into 10 NMR tubes (0.10 mL in each tube). After capping the tubes they were placed in a preheated oil bath at 125 °C and a timer was started. An NMR tube was removed from the oil bath every minute starting at 2 min. As soon as the tube was removed it was placed in an ice bath, and 0.50 mL of CDCl₃ was added. The NMR tubes remained in ice or in the freezer until the NMR spectra were acquired.

Computational Methods. The B3LYP⁵⁷ and M06⁵⁸ methods resident in Gaussian 09^{S1} were used to determine the energyminimized structures, vibrational frequencies and electronic energies. For the B3LYP optimizations, the 6-31G(d) basis set was used for H, C, and O atoms, 6-311+G(d,p) was used for P, and LANL2DZ was used for Re and I. For single-point energy (M06) calculations, the basis sets were as follows: 6-311++G(d,p) for H, C, O, and P and SDD for Re and I and the SMD solvent continuum method⁵⁹ was included for modeling the species in the experimental reaction medium (benzene). The Gibbs free energies and enthalpies include zero-point vibrational energies and thermal corrections at 298 K. Transition states were approached by mod-redundant scans and characterized by single imaginary frequencies with displacement along the reaction coordinate. Energy values and Cartesian (x,y,z)coordinates for each of the species are provided in the Supporting Information.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00285.

NMR spectra for the interaction of $\text{ReO}_2\text{I}(\text{PPh}_3)_2$ (1) with alcohols, kinetics data, DFT-calculated energies for the species in the putative reaction pathways (PDF) Cartesian coordinates (XYZ)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Boucher-Jacobs, C.; Nicholas, K. M. Selective Catalysis for Renewable Feedstocks and Chemicals. *Top. Curr. Chem.* 2014, 353, 163. (b) Chheda, J. N.; Huber, G. W.; Dumesic, J. A. Liquid-Phase Catalytic Processing of Biomass-Derived Oxygenated Hydrocarbons to Fuels and Chemicals. *Angew. Chem., Int. Ed.* 2007, 46, 7164–7183. (2) (a) Dutta, S. Deoxygenation of Biomass-Derived Feedstocks: Hurdles and Opportunities. *ChemSusChem* 2012, 5, 2125-2127.
(b) Zacher, A. H.; Olarte, M. V.; Santosa, D. M.; Elliott, D. C.; Jones, S. B. A Review and Perspective of Recent Bio-Oil Hydrotreating Research. *Green Chem.* 2014, *16*, 491-515. (c) Ruppert, A. M.; Weinberg, K.; Palkovits, R. Hydrogenolysis Goes Bio: From Carbohydrates and Sugar Alcohols to Platform Chemicals. *Angew. Chem., Int. Ed.* 2012, *51*, 2564-2601.

(3) (a) Kieboom, A. P. G.; De Kreuk, J. F.; Van Bekkum, H. Substituent Effects in the Hydrogenolysis of Benzyl Alcohol Derivatives over Palladium. *J. Catal.* **1971**, *20*, 58–66. (b) Sawadjoon, S.; Lundstedt, A.; Samec, J. S. M. Pd-Catalyzed Transfer Hydrogenolysis of Primary, Secondary, and Tertiary Benzylic Alcohols by Formic Acid: A Mechanistic Study. *ACS Catal.* **2013**, *3*, 635–642. (c) Tsuji, J.; Mandai, T. Palladium-Catalyzed Hydrogenolysis of Allylic and Propargylic Compounds with Various Hydrides. *Synthesis* **1996**, 1–94.

(4) (a) Larson, G.; Fry, J. Ionic and Organometallic-Catalyzed Organosilane Reductions. In Organic Reactions; John Wiley & Sons, Inc.: Hoboken, NJ, 2008; pp 1-737. (b) McLaughlin, M. P.; Adduci, L. L.; Becker, J. J.; Gagné, M. R. Iridium-Catalyzed Hydrosilylative Reduction of Glucose to Hexane. J. Am. Chem. Soc. 2013, 135, 1225-1227. (c) Yasuda, M.; Onishi, Y.; Ueba, M.; Miyai, T.; Baba, A. Direct Reduction of Alcohols: Highly Chemoselective Reducing System for Secondary or Tertiary Alcohols Using Chlorodiphenylsilane with a Catalytic Amount of Indium Trichloride. J. Org. Chem. 2001, 66, 7741-7744. (d) Mayr, H.; Dogan, B. Selectivities in Ionic Reductions of Alcohols and Ketones with Triethylsilane/Trifluoroacetic Acid. Tetrahedron Lett. 1997, 38, 1013-1016. (e) Adlington, M. G.; Orfanopoulos, M.; Fry, J. L. A Convenient One-Step Synthesis of Hydrocarbons from Alcohols through Use of the Organosilane-Boron Trifluoride Reducing System. Tetrahedron Lett. 1976, 17, 2955-2958. (5) (a) Hong, Y.-K.; Lee, D.-W.; Eom, H.-J.; Lee, K.-Y. The Catalytic Activity of Pd/WOx/γ-Al2O3 for Hydrodeoxygenation of Guaiacol. Appl. Catal., B 2014, 150-151, 438-445. (b) de Souza, P. M.; Rabelo-Neto, R. C.; Borges, L. E. P.; Jacobs, G.; Davis, B. H.; Sooknoi, T.; Resasco, D. E.; Noronha, F. B. Role of Keto Intermediates in the Hydrodeoxygenation of Phenol over Pd on Oxophilic Supports. ACS Catal. 2015, 5, 1318-1329. (c) Martin, A.; Armbruster, U.; Gandarias, I.; Arias, P. L. Glycerol Hydrogenolysis into Propanediols Using in Situ Generated Hydrogen - A Critical Review. Eur. J. Lipid Sci. Technol. 2013, 115, 9-27. (e) Murru, S.; Nicholas, K. M.; Srivastava, R. S. Ruthenium (II) Sulfoxides-Catalyzed Hydrogenolysis of Glycols and Epoxides. J. Mol. Catal. A: Chem. 2012, 363-364, 460-464. (f) Schlaf, M.; Ghosh, P.; Fagan, P. J.; Hauptman, E.; Bullock, R. M. Catalytic Deoxygenation of 1,2-Propanediol to Give n-Propanol. Adv. Synth. Catal. 2009, 351, 789-800. (d) Tomishige, K.; Nakagawa, Y.; Tamura, M. Selective Hydrogenolysis of C-O Bonds Using the Interaction of the Catalyst Surface and OH Groups. Top. Curr. Chem. 2014, 353, 127-162.

(6) Sergeev, A. G.; Webb, J. D.; Hartwig, J. F. A Heterogeneous Nickel Catalyst for the Hydrogenolysis of Aryl Ethers without Arene Hydrogenation. J. Am. Chem. Soc. 2012, 134, 20226-20229.

(7) Kusumoto, S.; Nozaki, K. Direct and Selective Hydrogenolysis of Arenols and Aryl Methyl Ethers. *Nat. Commun.* **2015**, *6*, 6296.

(8) (a) Boucher-Jacobs, C.; Nicholas, K. M. Deoxydehydration of Polyols. *Top. Curr. Chem.* **2014**, 353, 163–184. (b) Petersen, A. R.; Fristrup, P. New Motifs in Deoxydehydration: Beyond the Realms of Rhenium. *Chem. - Eur. J.* **2017**, 23, 10235–10243. (c) Mao, G.; Jia, B.; Wang, C. Recent Progress in Re-Catalyzed Dehydroxylation Reactions. *Youji Huaxue* **2015**, 35, 284–293.

(9) Cook, G. K.; Andrews, M. A. Toward Nonoxidative Routes to Oxygenated Organics: Stereospecific Deoxydehydration of Diols and Polyols to Alkenes and Allylic Alcohols Catalyzed by the Metal Oxo Complex $(C_5Me_5)ReO_3$. J. Am. Chem. Soc. **1996**, 118, 9448–9449.

(10) (a) Ziegler, J. E.; Zdilla, M. J.; Evans, A. J.; Abu-Omar, M. M. H_2 -Driven Deoxygenation of Epoxides and Diols to Alkenes Catalyzed by Methyltrioxorhenium. *Inorg. Chem.* **2009**, *48*, 9998–10000. (b) Gopaladasu, T. V.; Nicholas, K. M. Carbon Monoxide and

Hydrogen-Driven, Vanadium-Catalyzed Deoxydehydration of Glycols. *ACS Catal.* **2016**, *6*, 1901–1904.

(11) (a) Arceo, E.; Ellman, J. A.; Bergman, R. G. Rhenium-Catalyzed Didehydroxylation of Vicinal Diols to Alkenes Using a Simple Alcohol as a Reducing Agent. J. Am. Chem. Soc. 2010, 132, 11408–11409.
(b) Shiramizu, M.; Toste, F. D. Expanding the Scope of Biomass-Derived Chemicals through Tandem Reactions Based on Oxorhenium-Catalyzed Deoxydehydration. Angew. Chem., Int. Ed. 2013, 52, 12905–12909. (c) Boucher-Jacobs, C.; Nicholas, K. M. Catalytic Deoxydehydration of Glycols with Alcohol Reductants. ChemSusChem 2013, 6, 597–599.

(12) (a) Vkuturi, S.; Chapman, G.; Ahmad, I.; Nicholas, K. M. Rhenium-Catalyzed Deoxydehydration of Glycols by Sulfite. *Inorg. Chem.* **2010**, *49*, 4744–4746. (b) Ahmad, I.; Chapman, G.; Nicholas, K. M. Sulfite-Driven, Oxorhenium-Catalyzed Deoxydehydration of Glycols. *Organometallics* **2011**, *30*, 2810–2818.

(13) McClain, J. M.; Nicholas, K. M. Elemental Reductants for the Deoxydehydration of Glycols. *ACS Catal.* **2014**, *4*, 2109–2112.

(14) Boucher-Jacobs, C.; Nicholas, K. M. Oxo-Rhenium-Catalyzed Deoxydehydration of Polyols with Hydroaromatic Reductants. *Organometallics* **2015**, *34*, 1985–1990.

(15) Chapman, G.; Nicholas, K. M. Vanadium-Catalyzed Deoxydehydration of Glycols. *Chem. Commun.* **2013**, *49*, 8199.

(16) (a) Dethlefsen, J. R.; Lupp, D.; Teshome, A.; Nielsen, L. B.; Fristrup, P. Molybdenum-Catalyzed Conversion of Diols and Biomass-Derived Polyols to Alkenes Using Isopropyl Alcohol as Reductant and Solvent. ACS Catal. 2015, 5, 3638–3647. (b) Larsen, D. B.; Petersen, A. R.; Dethlefsen, J. R.; Teshome, A.; Fristrup, P. Mechanistic Investigation of Molybdate-Catalysed Transfer Hydrodeoxygenation. Chem. - Eur. J. 2016, 22, 16621–16631.

(17) (a) Gable, K. P.; Zhuravlev, F. A. Kinetic Isotope Effects in Cycloreversion of Rhenium (V) Diolates. J. Am. Chem. Soc. 2002, 124, 3970–3979. (b) Nunes, D.; Domingos, Â.; Paulo, A.; Patrício, L.; Santos, I.; Fermanda, M.; Carvalho, N. N.; Pombeiro, A. J. L. Synthesis, Characterization and Study of the Redox Properties of Rhenium (V) Diolates. Inorg. Chim. Acta 1998, 271, 65–74.

(18) (b) Zhu, Z.; Espenson, J. H. Organic Reactions Catalyzed by Methylrhenium Trioxide: Dehydration, Amination, and Disproportionation of Alcohols. *J. Org. Chem.* **1996**, *61*, 324–328. (c) Korstanje, T. J.; Jastrzebski, J. T. B. H.; Klein-Gebbink, R. J. M. Mechanistic Insights into the Rhenium-Catalyzed Alcohol-to-Olefin Dehydration Reaction. *Chem. - Eur. J.* **2013**, *19*, 13224–13234.

(19) Kasner, G. R.; Boucher-Jacobs, C.; McClain, J. M.; Nicholas, K. M. Oxo-Rhenium Catalyzed Reductive Coupling and Deoxygenation of Alcohols. *Chem. Commun.* **2016**, *52*, 7257–7260.

(20) Steffensmeier, E.; Nicholas, K. M. Oxidation-reductive Coupling of Alcohols Catalyzed by Oxo-Vanadium Complexes. *Chem. Commun.* **2018**, *54*, 790–793.

(21) Diéguez, H. R.; López, A.; Domingo, V.; Arteaga, J. F.; Dobado, J. A.; Herrador, M. M.; Quílez del Moral, J. F.; Barrero, A. F. Weakening C–O Bonds: Ti(III), a New Reagent for Alcohol Deoxygenation and Carbonyl Coupling Olefination. J. Am. Chem. Soc. 2010, 132, 254–259.

(22) Crevier, T. J.; Mayer, J. M. C–O Bond Homolysis in a Tungsten Alkoxide: The Mechanism of Alcohol Deoxygenation by $WCl_2(PMe_3)_4$ and $WH_2Cl_2(PMe_3)_4$. J. Am. Chem. Soc. 1997, 119, 8485–8491.

(23) Wang, H.; Li, L.; Bai, X.-F.; Shang, J.-Y.; Yang, K.-F.; Xu, L.-W. Efficient Palladium-Catalyzed C-O Hydrogenolysis of Benzylic Alcohols and Aromatic Ketones with Polymethylhydrosiloxane. *Adv. Synth. Catal.* **2013**, 355, 341–347.

(24) (a) van Tamelen, E. E.; Schwartz, M. A. Reductive Coupling of Alcohols to Hydrocarbons. J. Am. Chem. Soc. 1965, 87, 3277-3278.
(b) McMurry, J. E.; Silvestri, M. A Simplified Method for the Titanium(II)-Induced Coupling of Allylic and Benzylic Alcohols. J. Org. Chem. 1975, 40, 2687-2688. (c) Isakov, V. E.; Kulinkovich, O. G. The Head-to-Head ReductiveCoupling of Homoallylic Alcohols Promoted by Titanium(II)-Olefin Complexes. Synlett 2003, 967-970.
(d) Karunakar, G. V.; Periasamy, M. A Simple Method for the Conversion of Propargyl Alcohols to Symmetrical 1,5-Diynes Using Low Valent Titanium Reagents. *Tetrahedron Lett.* **2006**, *47*, 3549– 3552.

(25) Nishino, T.; Nishiyama, Y.; Sonoda, N. Deoxygenative Dimerization of Benzylic and Allylic Alcohols, and Their Ethers and Esters Using Lanthanum Metal and Chlorotrimethylsilane in the Presence of a Catalytic Amount of Iodine and Copper(I) Iodide. *Bull. Chem. Soc. Jpn.* **2003**, *76*, 635–641.

(26) Nishino, T.; Nishiyama, Y.; Sonoda, N. Lanthanum Metal-Assisted Deoxygenative Coupling of Alcohols. *Tetrahedron Lett.* **2002**, 43, 3689–3691.

(27) Gabriëls, D.; Hernández, W. Y.; Sels, B.; Van Der Voort, P.; Verberckmoes, A. Review of Catalytic Systems and Thermodynamics for the Guerbet Condensation Reaction and Challenges for Biomass Valorization. *Catal. Sci. Technol.* 2015, *5*, 3876–3902. (b) Aitchison, H.; Wingad, R. L.; Wass, D. F. Homogeneous Ethanol to Butanol Catalysis - Guerbet Renewed. ACS Catal. 2016, *6*, 7125–7132.
(c) Kozlowski, J. T.; Davis, R. J. Heterogeneous Catalysts for the Guerbet Coupling of Alcohols. ACS Catal. 2013, *3*, 1588–1600.

(28) Luo, Y.-R. Handbook of Bond Dissociation Energies in Organic Compounds; CRC Press, 2003.

(29) (a) Bellemin-Laponnaz, S.; Gisie, H.; Le Ny, J. P.; Osborn, J. A. Mechanistic Insights into the Very Efficient [ReO₃OSiR₃]-Catalyzed Isomerization of Allyl Alcohols. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 976–978. (b) Herrmann, A. T.; Saito, T.; Stivala, C. E.; Tom, J.; Zakarian, A. Regio- and Stereocontrol in Rhenium-Catalyzed Transposition of Allylic Alcohols. *J. Am. Chem. Soc.* **2010**, *132*, 5962–5963. (c) Jacob, J.; Espenson, J. H.; Jensen, J. H.; Gordon, M. S. 1,3-Transposition of Allylic Alcohols Catalyzed by Methyltrioxorhenium. *Organometallics* **1998**, *17*, 1835–1840.

(30) Ciani, G. F.; D'Alfonso, G.; Romiti, P. F.; Sironi, A.; Freni, M. Rhenium(V) Oxide Complexes. Crystal and Molecular Structures of the Compounds *trans*-ReI₂O(OR)(PPh₃)₂ (R = Et, Me) and of Their Hydrolysis Derivative ReIO₂(PPh₃)₂. *Inorg. Chim. Acta* **1983**, 72, 29–37.

(31) (a) Shcheglov, P. A.; Drobot, D. V. Rhenium Alkoxides. Russ. Chem. Bull. 2005, 54, 2247-2258. (b) DuMez, D. D.; Mayer, J. M. Rhenium(V) Oxo-Alkoxide Complexes: Syntheses and Oxidation to Aldehydes. Inorg. Chem. 1995, 34, 6396-6401. (c) Paulo, A.; Domingos, A.; Marcalo, J.; Pires de Matos, A.; Santos, I. Reactivity of a Tetrakis(Pyrazolyl)Borate Oxorhenium Complex. Inorg. Chem. 1995, 34, 2113-2120. (d) Seisenbaeva, G. A.; Shevelkov, A. V.; Tegenfeldt, J.; Kloo, L.; Drobot, D. V.; Kessler, V. G. Homo- and Hetero-Metallic Rhenium Oxomethoxide Complexes with a $M_4(\mu$ - $O_2(\mu$ -OMe)₄ Planar Core—a New Family of Metal Alkoxides Displaying a Peculiar Structural Disorder. Preparation and X-Ray Single Crystal Study. J. Chem. Soc. Dalt. Trans. 2001, 2762-2768. (e) Erikson, T. K. G.; Bryan, J. C.; Mayer, J. M. Low-Valent Oxo Compounds. 5. Low-Valent Rhenium Oxo Alkoxide Complexes. Synthesis, Characterization, Structure, and Ligand Exchange and Carbon Monoxide Insertion Reactions. Organometallics 1988, 7, 1930-1938. (f) Matano, Y.; Northcutt, T. O.; Brugman, J.; Bennett, B. K.; Lovell, S.; Mayer, J. M. Tp* Rhenium(V) Oxo-Halide, -Hydride, -Alkyl, -Phenyl, and -Alkoxide Complexes: Syntheses and Oxidations. Organometallics 2000, 19, 2781-2790.

(32) (a) Casey, C. P.; Guan, H. Cyclopentadienone Iron Alcohol Complexes: Synthesis, Reactivity, and Implications for the Mechanism of Iron-Catalyzed Hydrogenation of Aldehydes. J. Am. Chem. Soc. **2009**, 131 (7), 2499–2507. (b) Appelt, A.; Ariaratnam, V.; Willis, A. C.; Wild, S. B. Alcohol Complexes of Platinum(II). Syntheses and Crystal Structures of $[S-(R^*,R^*)]-(+)589-[Pt(OSO_2CF_3)_2[1,2-C_6H_4(PMePh)_2]$ and $[S-(R^*,R^*)]-(+)589-[Pt(HOCH_2CH_2OH)]$ $[1,2-C_6H_4(PMePh)_2](CF_3SO_3)_2$. Tetrahedron: Asymmetry **1990**, 1, 9–12. (c) Bakhmutov, V. I.; Vorontsov, E. V.; Antonov, D. Y. NMR Evidence for Formation of New Alcohol Rhenium Complexes as Intermediates in Ionic Hydrogenations of Carbonyl Groups with Systems Composed of ReH₂(NO)(CO)(PR₃)₂ (R = Pr-i, CH₃, OPri) and CF₃COOH. Inorg. Chim. Acta **1998**, 278, 122–126. (33) Kühl, O., Ed. The Range of Chemical Shifts, Coupling Constants, and What Influences Each. In *Phosphorus-31 NMR Spectroscopy*; Springer: Berlin Heidelberg, 2008; pp 7–23.

(34) (a) Dean, P. A. W.; Phillips, D. D.; Polensek, L. A 31P Nmr Spectroscopic Study of Complexation of Tin(II) and Lead(II) by Some Phosphines, Phosphine Oxides, and Related Ligands, with the 31P Nuclear Magnetic Resonance Spectra of Two Tetratertiary Phosphine Tetraoxides and the Analogous Tetra-Sulfides An. *Can. J. Chem.* **1981**, *59*, 50–61. (b) Hursthouse, M. B.; Levason, W.; Ratnani, R.; Reid, G. Synthesis and Spectroscopic Properties of Mo(VI) Complexes with Phosphine Oxide Ligands and the Crystal Structures of $[MoO_2X_2(OPMe_3)_2]$ (X = Cl or Br) and $[MoO_2Br_2\{o-C_6H_4(P(O)Ph_2)_2\}] \cdot 2CH_2Cl_2$. *Polyhedron* **2004**, *23*, 1915–1921.

(35) (a) Saucedo Anaya, S. A.; Hagenbach, A.; Abram, U. Reactions of Phenylbis(2-Pyridyl)Phosphine with Oxorhenium(v) Complexes. *Inorg. Chem. Commun.* **2009**, *12*, 128–130. (b) Machura, B.; Jankowska, A.; Kruszynski, R.; Kłak, J.; Mroziński, J. Structural and Spectroscopic Studies on Rhenium(III) Diphenyl(2-Pyridyl)-Phosphine Oxide Complexes. *Polyhedron* **2006**, *25*, 2663–2672.

(36) Liu, S.; Senocak, A.; Smeltz, J. L.; Yang, L.; Wegenhart, B.; Yi, J.; Kenttämaa, H. I.; Ison, E. A.; Abu-Omar, M. M. Mechanism of MTO-Catalyzed Deoxydehydration of Diols to Alkenes Using Sacrificial Alcohols. *Organometallics* **2013**, *32*, 3210–3219.

(37) (a) Newcomb, M. Radical Kinetics and Clocks. In *Encyclopedia* of *Radicals in Chemistry, Biology and Materials*; John Wiley & Sons, Ltd: Chichester, U.K., 2012. (b) Griller, D.; Ingold, K. U. Free-Radical Clocks. *Acc. Chem. Res.* **1980**, *13*, 317–323.

(38) (a) Reed, M. C.; Lieb, A.; Nijhout, H. F. The Biological Significance of Substrate Inhibition: A Mechanism with Diverse Functions. In *BioEssays*; Wiley-Blackwell, 2010; pp 422–429.
(b) Jones, L. Substrate Inhibition. http://what-when-how.com/molecular-biology/substrate-inhibition-molecular-biology/.

(39) (a) Shearer, J. Insight into the Structure and Mechanism of Nickel-Containing Superoxide Dismutase Derived from Peptide-Based Mimics. Acc. Chem. Res. 2014, 47, 2332–2341. (b) Boone, C. D.; Pinard, M.; McKenna, R.; Silverman, D. Catalytic Mechanism of α -Class Carbonic Anhydrases: CO₂ Hydration and Proton Transfer. Subcell. Biochem. 2014, 75, 31–52. (c) Cook, P.; Cleland, W. W. Enzyme Kinetics and Mechanism; Garland Science, 2007.

(40) Walker, B. J., Hobbs, J. B., Walker, B. J., Eds.Phosphines Oxides and Related Compounds. In *Organophosphorus Chemistry*; Royal Society of Chemistry: Cambridge, 1989; pp 72–86.

(41) Chung, L. W.; Lee, H. G.; Lin, Z.; Wu, Y.-D. Computational Study on the Reaction Mechanism of Hydrosilylation of Carbonyls Catalyzed by High-Valent Rhenium(V)–Di-Oxo Complexes. J. Org. Chem. 2006, 71, 6000–6009.

(42) (a) Zhang, S.; Katz, A.; Gates, B. C.; Dixon, D. A. Structures, Relative Energies, and Ligand Dissociation Energies of Iridium Carbonyl Phosphine Clusters. *Comput. Theor. Chem.* **2015**, *1069*, 18– 35. (b) Chen, M.; Craciun, R.; Hoffman, N.; Dixon, D. A. Ligand Bond Energies in Cis- and Trans-[LPd(PH₃)₂Cl]+ Complexes from Coupled Cluster Theory (CCSD(T)) and Density Functional Theory. *Inorg. Chem.* **2012**, *51*, 13195–13203.

(43) Wang, Y.; Jin, X.; Yu, H. S.; Truhlar, D. G.; He, X. Revised M06-L Functional for Improved Accuracy on Chemical Reaction Barrier Heights, Noncovalent Interactions, and Solid-State Physics. *Proc. Natl. Acad. Sci. U. S. A.* **2017**, *114*, 8487–8492.

(44) (a) Erikson, T. K. G.; Bryan, J. C.; Mayer, J. M. Low-Valent Oxo Compounds. 5. Low-Valent Rhenium Oxo Alkoxide Complexes. Synthesis, Characterization, Structure, and Ligand Exchange and Carbon Monoxide Insertion Reactions. *Organometallics* **1988**, *7*, 1930–1938. (b) Tang, H.; Brothers, E. N.; Hall, M. B. The Distinctive Electronic Structures of Rhenium Tris(Thiolate) Complexes, an Unexpected Contrast to the Valence Isoelectronic Ruthenium Tris(Thiolate) Complexes. *Inorg. Chem.* **2017**, *56*, 583– 593. (c) Palion-Gazda, J.; Gryca, I.; Machura, B.; Lloret, F.; Julve, M. Synthesis, Crystal Structure and Magnetic Properties of the Complex [ReCl₃(Tppz)]·MeCN. *RSC Adv.* **2015**, *5*, 101616–101622. (d) MacHura, B.; Wolff, M.; Gryca, I.; Mroziński, J. Two Novel

Organometallics

Rhenium Complexes Derived from $[ReO(OMe)Cl_2(dpphen)]$ -Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties. *Polyhedron* **2011**, *30*, 354–363. (e) Machura, B.; Kruszynski, R.; Mroziński, J.; Kusz, J. Synthesis, Spectroscopic Characterization, X-Ray Structure and DFT Calculations of Rhenium(III) Complex with 1-Isoquinolinyl Phenyl Ketone. *Polyhedron* **2008**, *27*, 1739–1746.

(45) (a) Machura, B.; Wolff, M.; Gryca, I.; Kruszynski, R. Syntheses, Structures, Spectroscopic Properties and DFT Calculations of Re(V)-Benzothiazole and 2-(2-Aminophenyl)Benzothiazole Complexes. *Polyhedron* **2012**, 40, 93–104. (b) Machura, B.; Wolff, M.; Świtlicka, A.; Kruszynski, R.; Mroziński, J. Synthesis, X-Ray Studies, Spectroscopic Investigation, and DFT Calculations of [ReBr₃(dppt)-(OPPh₃)]. *Struct. Chem.* **2010**, 21, 761–769. (c) Machura, B.; Świetlicka, A.; Wolff, M.; Kruszynski, R. Novel Rhenium Oxocomplexes of Indazole-3-Carboxylic Acid - Synthesis, X-Ray Studies, Spectroscopic Characterization and DFT Calculations. *Polyhedron* **2010**, 29, 2061–2069. (d) MacHura, B.; Kusz, J.; Tabak, D. Synthesis, Spectroscopic Characterization, X-Ray Structure, and DFT Calculations of [ReOBr₂(Hmquin-7-COOH)(AsPh₃)]. *Struct. Chem.* **2009**, 20, 361–368.

(46) (a) Kail, B. W.; Pérez, L. M.; Zarić, S. D.; Millar, A. J.; Young, C. G.; Hall, M. B.; Basu, P. Mechanistic Investigation of the Oxygen-Atom-Transfer Reactivity of Dioxo-Molybdenum(VI) Complexes. *Chem. - Eur. J.* **2006**, *12*, 7501–7509. (b) Millar, A. J.; Doonan, C. J.; Smith, P. D.; Nemykin, V. N.; Basu, P.; Young, C. G. Oxygen Atom Transfer in Models for Molybdenum Enzymes: Isolation and Structural, Spectroscopic, and Computational Studies of Intermediates in Oxygen Atom Transfer from Molybdenum(VI) to Phosphorus(III). *Chem. - Eur. J.* **2005**, *11*, 3255–3267.

(47) Li, X.-H.; Yin, G.-X.; Zhang, X.-Z. Theoretical studies on bond dissociation energies for some aliphatic alcohol compounds by density functional theory and cbs-q method. *J. Theor. Comput. Chem.* **2011**, *10*, 179–189.

(48) Walton, J. C. Homolytic Substitution: A Molecular Ménage à Trois. *Acc. Chem. Res.* **1998**, *31*, 99–107.

(49) (a) Sugimoto, H.; Sasaki, Y. Oxorhenium(V) Complex of Amidophenolate: Structure and Redox Characteristics. *Chem. Lett.* **1998**, 27, 197–198. (b) Bennett, B. K.; Crevier, T. J.; DuMez, D. D.; Matano, Y.; McNeil, W. S.; Mayer, J. M. Electrochemical and Reactivity Comparisons among Isoelectronic Oxo, Imido, and Nitrido Complexes of Rhenium and Osmium. *J. Organomet. Chem.* **1999**, 591, 96–103.

(50) Mayer, J. M. Not Solely a Spectator: Exploring the Chemistry of the CO Bond in Alkoxide and Related Ligands. *Polyhedron* **1995**, *14*, 3273–3292.

(51) Peters, J. C.; Johnson, A. R.; Odom, A. L.; Wanandi, P. W.; Davis, W. M.; Cummins, C. C. Assembly of Molybdenum/Titanium μ -Oxo Complexes via Radical Alkoxide C–O Cleavage. *J. Am. Chem. Soc.* **1996**, *118*, 10175–10188.

(52) Prieto, C.; González Delgado, J. A.; Arteaga, J. F.; Jaraíz, M.; López-Pérez, J. L.; Barrero, A. F. Homocoupling versus Reduction of Radicals: An Experimental and Theoretical Study of Ti(III)-Mediated Deoxygenation of Activated Alcohols. *Org. Biomol. Chem.* **2015**, *13*, 3462–3469.

(53) (a) Niederberger, M.; Garnweitner, G. Organic Reaction Pathways in the Nonaqueous Synthesis of Metal Oxide Nanoparticles. *Chem. - Eur. J.* **2006**, *12*, 7282–7302. (b) Chandran, K.; Kamruddin, M.; Muralidaran, P.; Ganesan, V. Thermal Decomposition of Sodium Propoxides. *J. Therm. Anal. Calorim.* **2013**, *112*, 63–71. (c) Rupich, M. W.; Liu, Y. P.; Ibechem, J.; Hachey, J. P. Synthesis of Superconductors from Soluble Metal Oxo Alkoxide Precursors. *J. Mater. Res.* **1993**, *8*, 1487–1496.

(54) (a) Huang, R. L.; Lee, H. H.; Malhotra, M. S. Abstraction of benzylic hydrogen atoms from dibenzyl ethers by benzyl radicals. *J. Chem. Soc.* **1964**, 5951–6. (b) Bass, K. C. Abstraction by benzyl radicals. *Nature* **1964**, 201, 700–1.

(55) MestReNova Software, V10.0.2–15465; Mestrelab Research, S.L.: Santiago de Compostela, Spain, 2015.

(56) *ACD/Structure Elucidator*; Advanced Chemistry Development, Inc., 2014.

(57) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. **1993**, 98, 5648–5652.

(58) Zhao, Y.; Truhlar, D. G. The M06 Suite of Density Functionals for Main Group Thermochemistry, Thermochemical Kinetics, Noncovalent Interactions, Excited States, and Transition Elements: Two New Functionals and Systematic Testing of Four M06-Class Functionals and 12 Other Functionals. *Theor. Chem. Acc.* 2008, 120, 215–241.

(59) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378–6396.