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α-Diimine-Niobium Complex-Catalyzed Deoxychlorination of Benzyl Ethers with Silicon Tetrachloride

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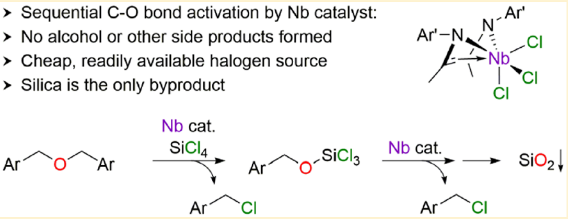
Supporting Information

ABSTRACT: α-Diimine niobium complexes serve as catalysts for deoxygenation of benzyl ethers by silicon tetrachloride (SiCl$_4$) to cleanly give two equivalents of the corresponding benzyl chlorides, where SiCl$_4$ has the dual function of oxygen scavenger and chloride source with the formation of a silyl ether or silica as the only byproduct. The reaction mechanism has two successive trans-etherification steps that are mediated by the niobium catalyst, first forming one equivalent of benzyl chloride along with the corresponding silyl ether intermediate that undergoes the same reaction pathway to give the second equivalent of benzyl chloride and silyl ether.



■ INTRODUCTION

Ether linkages are one of the most fundamental bonds in organic chemistry and are present in a huge range of both natural and synthetic molecules. The Williamson ether synthesis is a classic reaction discovered in the mid-19th century, which is the synthesis of ethers by a simple substitution reaction of alkyl halides. Since then, hundreds more reactions have been developed to synthesize ethers; current goals are improving the selective synthesis under mild reaction conditions with high selectivity, high functional group tolerance, and using cheaper reagents.[1−3]

In sharp contrast, the reverse reaction is considered to be significantly more difficult, since deoxygenation of ethers back to alkyl halides is generally thermodynamically unfavorable due to the strength of the C−O bond and relative weakness of the C−X bond formed in the alkyl halide products, as shown in selected examples in Figure 1.[4,5] One notable application of such ether cleavage reactions has been the deprotection of phenol derivatives;[6] boron tribromide is a classic reagent for the cleavage of methyl ethers of phenols as well as certain other ethers.[6,7] Other reactions with milder reagents or conditions for the cleavage of dimethyl ether and similar ethers have also been developed that tolerate a wider range of functional groups.[8,9] In addition to deprotection reactions, ether cleavage can be used in its own right in synthesis and semisynthesis from ether natural products and substrates, such as in the depolymerization of lignin, which is a critical step in biomass conversion to liquid fuels.[10−12] In a similar manner, the treatment and recycling of ethereal solvents, including benzyl ether, by deoxygenation reactions are used to produce useful chemical products from what would otherwise be waste material.[13,14]

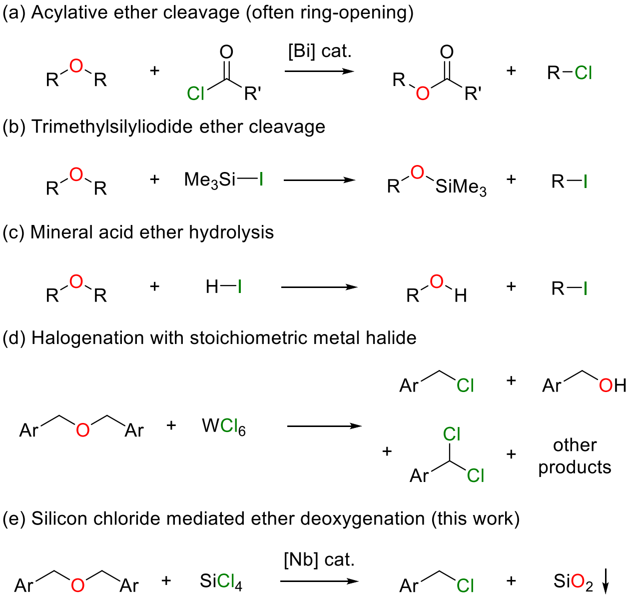


Figure 1. Selected ether deoxygenation reactions to alkyl halide products.

Metal halides have also been reported as reagents for ether cleavage to give alkyl halides, where the metal acts as a halogen transfer reagent. For example, bismuth can transfer a chlorine atom to 2-methyl- and 2,5-dimethyltetrahydrofurans, where the ring is preactivated with an acyl chloride (Figure 1a).[15,16] Numerous other acylative metal-catalyzed ring-opening re-

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actions are known that rely on relieving ring strain, giving esters rather than completely deoxygenated products.[17,18] Tungsten hexachloride has been used to stoichiometrically cleave many ethers, including benzyl ether, to form alkyl chlorides (Figure 1d); a variety of other products including alcohols and overhalogenated compounds are invariably produced as well.[19] Simple halogenating reagents such as trimethylsilyl iodide or concentrated hydrobromic or hydroiodic acid are generally effective (Figure 1b and c), but these aggressive reagents are typically required in excess and can form a variety of different products depending on the conditions used.[3,20,21]

Here, we present an ether cleavage reaction in which silicon tetrachloride ($SiCl_4$) or another silicon halide is used both as a halogen source as well as an oxygen atom scavenger (Figure 1e). A niobium complex bearing a redox-active α-diimine ligand catalyzes this reaction, although it can react stoichiometrically with ether substrates as well. The use of $SiCl_4$ in this role is especially attractive, as it forms silica as the only major byproduct, which is inert and easily removed by filtration. This reaction is selective for benzyl ethers, especially dibenzyl ethers. The reaction takes place through two successive transetherification reactions to silicon driven by Si−O bond formation, both of which are catalyzed by niobium.

■ RESULTS AND DISCUSSION

Catalyst and Additive Screening. We have previously reported that α-diimine complexes of niobium and tantalum cleave activated carbon−halogen bonds, promoted by the redox-active α-diimine ligand.[22−25] A variety of niobium and tantalum complexes with α-diimine ligands were screened for their effectiveness as catalysts in ether deoxygenation (Figure 2, Table 1), in which 4-methoxybenzyl ether was used as the model substrate due to its high reactivity at room temperature. Several variants of the α-diimine (DAD) ligand with different substituents suggest that a sterically bulky ligand is optimal, and the similar naphthalene-based BIAN ligand (**1d**) is also effective. Analogous complexes of the other group 5 metals tantalum (**2**) and vanadium (**3**) can catalyze the reaction as well but are less effective, and side reactions are observed.

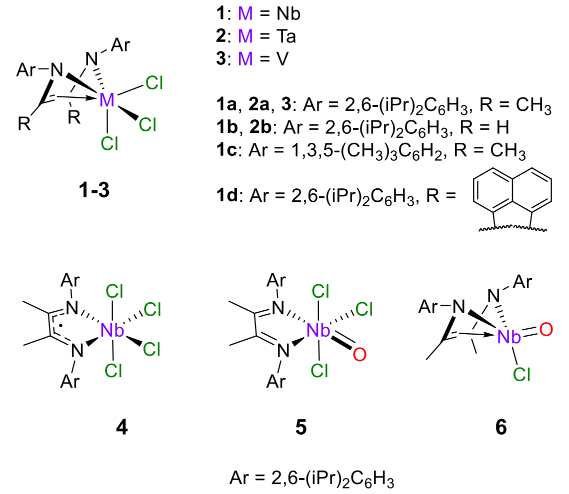
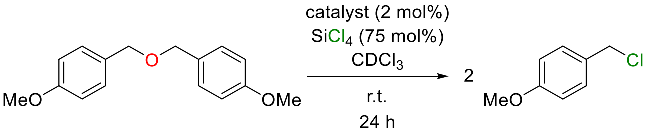


Figure 2. α-Diimine metal catalyst structure.

Having identified the optimal α-diimine ligand bearing methyl substituents on the imine carbons and diisopropylphenyl substituents on the nitrogen atoms, similar complexes with different atoms directly bonded to the niobium were also tested. The tetrachloride complex (**4**), trichloro-oxo complex (**5**), and monochloro-oxo complex LNbOCl (**6**) all likely function as precatalysts, first forming **1**, although lower yields arise due to the inefficiency of these steps.

Table 1. Catalyst Screen for Benzyl Ether Deoxygenation



entry	catalyst	yield[a]
1	**1a**	88%
2	**1b**	18%
3	**1c**	20%
4	**1d**	72%
5	**2a**	36%
6	**2b**	24%
7	**3**	78%
8	**4**	80%
9	**5**	57%
10	**6**	43%
11	**1a**[b]	47%
12	$NbCl_5$	37%
13	$TaCl_5$	20%
14	$NbCl_3{\cdot}2DME$	57%
15	none	NR

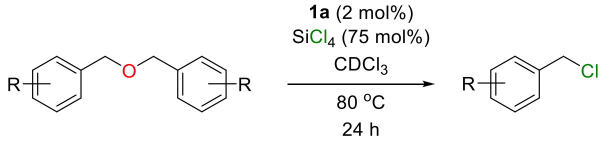
[a] All yields are NMR yields. NR = no reaction. [b] 50 mol % $SiCl_4$.

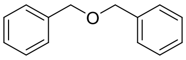
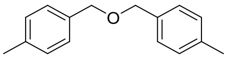
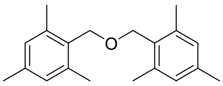
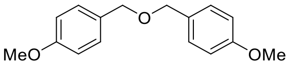
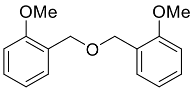
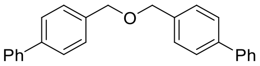
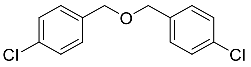
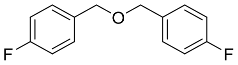
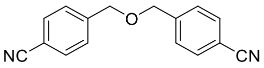
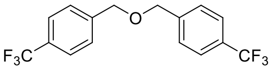
Group 5 metal salts were also tested for their reactivity (entries 12−14). Benzyl chloride is produced in low yields in these reactions, and a mixture of metal and silicon alkoxides are observed also. The lower solubility of these salts is another limitation for these reactions, and some oxychlorides that may form during the reaction are also expected to be insoluble. This reactivity is reminiscent of the reported reaction of ethers with WCl_6 and $SbCl_5$, where the Lewis acidic metal alone acts as the halogen source and oxygen acceptor.[9,19] In the case of tungsten, the reaction was stoichiometric, but it can be made catalytic with the addition of $SiCl_4$. Reactions with simple metal salts are straightforward but less effective than the ligand-supported catalysts (see Supporting Information, Table S1), due to low solubility, incomplete reactions, and requiring higher catalyst loadings.

Different solvents and conditions were examined to determine optimal conditions for this deoxygenation reaction (see Supporting Information, Table S2). Many noncoordinating solvents are suitable, with the reaction working in benzene, toluene, chlorobenzene, dichloromethane, and chloroform; unlike the others, the latter two performed well at room temperature. In contrast, coordinating solvents including THF, acetonitrile, and 1,4-dioxane are ineffective as they coordinate to the niobium center, suppressing reactivity. In the case of THF and acetonitrile, this manifests as a color change, indicating a change of geometry upon their binding.[22] Mixtures of THF and noncoordinating solvents show diminished activity rather than complete suppression of the reaction, confirming that this binding is reversible and that such solvents do not compete with benzyl ether or otherwise react with the catalyst.

Substrate Scope and Limitations. A wide variety of substrates were tested under the optimized deoxygenation reaction conditions to determine substrate scope and discover reactivity patterns. The reaction rate and yield strongly depend on the substituents on the benzyl group, where electron-donating substituents (Table 2, entries 2−5) increase the reaction rate, while electron-withdrawing groups on the aromatic ring (entries 7−9) hinder the reaction, resulting in either lower yields or no reaction. The trifluoromethyl-substituted benzyl ether substrate (entry 10) undergoes side reactions, resulting in multiple unidentified products. Similar niobium complexes are known to be effective at defluorination of CF_3 groups, although in the present case the fluorine-containing products have not been identified.[26]

Table 2. Substrate Scope of Symmetric Benzyl Ethers

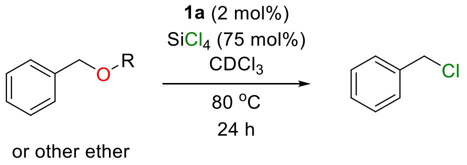


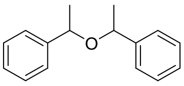
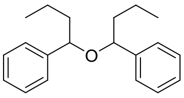
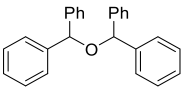
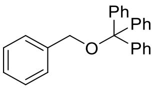
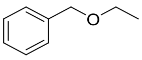
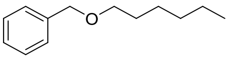
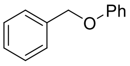
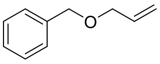
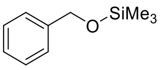
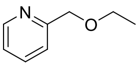
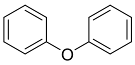
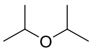
Entry	Ether	Yield
1		52% (40%)
2		68%
3		95%
4(a)		88% (85%)
5(a)		69%
6		79%
7		49%
8		90%
9		NR
10		0% (b)

[a]Reaction performed at room temperature. [b]No product, side reactions occur. [c]Yields are NMR yields (isolated yields in parentheses). NR = no reaction.

Unsymmetrical substrates containing only one benzyl group (Table 3, entries 4−8) also react, although generally with slower reaction rates and lower product yields. The initial activation step of the first C−O bond appears to proceed normally, but the reaction may then need to proceed through an alternate pathway to form side products containing nonbenzylic alkoxide groups (see below for details). Diaryl and nonbenzylic dialkyl ethers show no reactivity, even with prolonged heating or in a neat substrate. This unusually high selectivity suggests that the benzyl group plays a unique role such as radical stabilization, consistent with ethers bearing substituents on the α-carbon showing much higher reactivity, most notably α-propylbenzyl ether (Table 3, entry 2), where the reaction is very rapid, forming silica at room temperature within minutes.

Table 3. Substrate Scope of Other Ethers



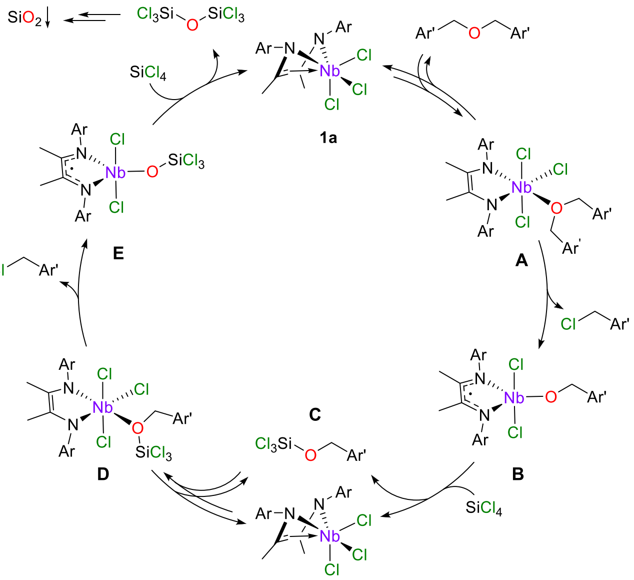
Entry	Ether	Benzyl chloride yield
1 (a)		59%
2 (a,b)		96%
3		73%
4		57%
5		70%
6		16%
7		18%
8		9%
9		93%
10		NR
11		NR
12		NR

[a]Mixture of (±) and meso substrate. [b]Reaction performed at room temperature. [c]All yields are NMR yields. NR = no reaction.

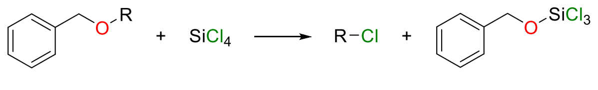
The other reagent that is critical to this reaction is the silicon halide. Silicon tetrachloride was found to be superior to other silicon halides tested, including dichlorodimethylsilane, trimethylsilyl chloride, and others (see Table S3 in Supporting Information). The silicon halide is both the source of the halogen atom that is incorporated into the product (trimethylsilyl bromide can be used to form the analogous benzyl bromide) as well the oxygen atom acceptor, forming strong Si−O bonds to give the only byproduct of the reaction. When $SiCl_4$ is used, silica precipitates in the reaction mixture, leading to simplified workup and purification procedures. An excess of $SiCl_4$ is needed for high yields and a smooth reaction, due to the trapping of some unreacted halogen atoms in the solid as it is formed. Therefore, a 50% excess of $SiCl_4$ was used in reactions (corresponding to 75 mol % with respect to substrate or 300 mol % Cl atoms), leading to the satisfactory results. The nominal product of one reaction cycle is one unit of the silyl ether $(Cl_3Si)_2O$ from two equivalents of $SiCl_4$; however, once formed, the mixed oxygen-chlorine species rearrange and continue reacting to ultimately form variable composition silicon oxyhalide oligomers, polymers, and network solids. This type of product mixture has been previously reported as the byproduct of phosphine oxide deoxygenation and other partial hydrolysis and condensation reactions.[27]

Proposed Reaction Mechanism. On the basis of observations of this deoxygenation reaction with a variety of different substrates and conditions, we propose a reaction pathway as shown in Scheme 1. Dibenzyl ethers are activated in two steps, each effectively a trans-etherification reaction to form a silyl ether. In both of these steps, the ether reversibly coordinates to the niobium, although the coordinated ether is labile due to steric hindrance. This can be observed as a color change as well as by NMR, but only at very large [ether]/[Nb] ratios (see Supporting Information Figures S1 and S2). The niobium species **A** then performs an intramolecular C−O bond cleavage (the rate-determining step), to release one equivalent of benzyl chloride, leaving the alkoxide **B**. Byproducts arising from radical coupling, H$^\bullet$ abstraction, or reaction with the solvent are never observed, suggesting that no free radicals are formed in this process. Subsequently, $SiCl_4$ reacts to form a silyl ether, releasing the alkoxide and regenerating the initial niobium trichloride complex **1a**. The second trans-etherification proceeds in the same manner to form a second equivalent of benzyl chloride via silyl ether-coordinated species **D** and siloxyniobium species **E**.

Scheme 1. Proposed Catalytic Cycle of Benzyl Ether Deoxygenation



Benzyl-trimethylsilyl ether and benzyl-trityl ether (Table 3, entries 3 and 8), both containing Lewis acid-labile C−O bonds, are protected benzyl alcohols.[28] These react with $SiCl_4$ at room temperature in the absence of any catalyst (eq 1) to form the benzyl-O-$SiCl_3$ ether **C**, in the same way as the first step of the proposed catalytic cycle (**C** cannot be isolated pure as it disproportionates into the bis(benzyl) product $(BnO)_2SiCl_2$ and $SiCl_4$; see Supporting Information Figures S3 and S4). However, the rate of this process is greatly increased when the niobium catalyst is present, and the silyl ether **C** formed at this point in the reaction does not proceed to form benzyl chloride in the absence of a catalyst.



(1)

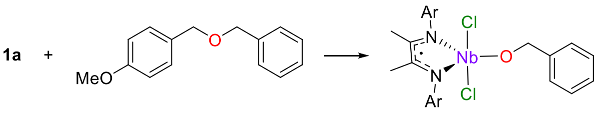
R = $SiMe_3$, CPh_3

C

Observation of Reaction Progress. Reactions were monitored over time by NMR spectroscopy, using unsubstituted benzyl ether and heating to 80 °C with varying concentrations of reagents and catalysts (see Supporting Information Figures S5−S7). The reaction is first-order with respect to the catalyst; however, it shows no dependence on both the substrate and silicon reagent concentrations. This is supportive of a unimolecular rate-determining step, where an initial activation or coordination of the substrate takes place before the C−O bond cleavage.

To elucidate the mechanism for the C−O bond activation step, a "one-pot Hammett" analysis was attempted, using a mixture of two substrates.[29] Unsubstituted benzyl ether and a substituted benzyl ether in approximately equal molar amounts were allowed to react for a short period of time and the product yields measured. Although some substrates show the trend that electron-withdrawing substituents decrease the reaction rate and electron-donating ones increase it, other substrates do not follow a typical Hammett free energy relationship. Notably, 4-phenylbenzyl ether reacts almost one order of magnitude faster than the unsubstituted ether; however, it is expected to have virtually no effect on an ionic mechanism (see Supporting Information Table S4). Consequently, we propose that the intramolecular C−O activation step does not easily fall into a simply ionic or radical mechanism, and the benzyl ether sterics probably play an important role as well in orienting the ether, which is not accounted for in the Hammett analysis.

Alkoxide complex **B**, here denoted as compound **7**, is unstable and decomposes over several hours. Further proof that the two C−O bond activation reactions are independent from each other came from their reactivity of some asymmetric ethers such as the mono(4-methyoxy) substituted benzyl ether (eq 2). Only 4-methoxybenzyl chloride was produced cleanly, then the reaction stopped and the other benzyl chloride was not immediately observed.



(2)

7

The isolation of **7** was attempted, including by trapping with other ligands or using several chelating ethers as substrates; however, in all cases, **7** is unstable at room temperature, decomposing within several hours at most. However, its reactivity is consistent with the assigned structure (Scheme 2). The addition of $SiCl_4$ and heat is needed to continue the reaction and produce the Bn-O-$SiCl_3$ ether, with similar reactivity to other silyl halides. Additionally, when a solution containing **7** was quenched with a small amount of water,

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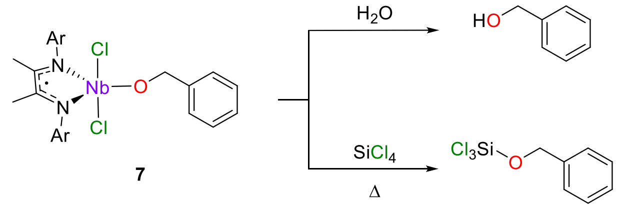
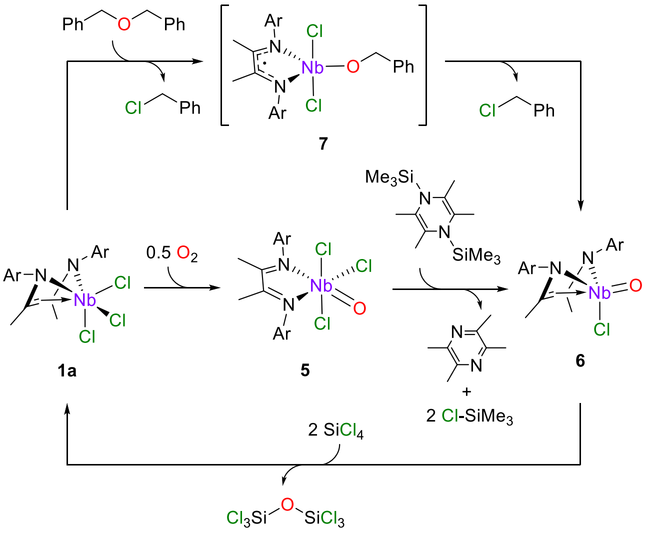
Scheme 2. Reactivity and Decomposition of 7



benzyl alcohol was produced and isolated from the product mixture. The similar 4-methoxy/4-cyano substituted asymmetric ether reacts in the same way, but the cyano-substituted **7** is even less reactive.

The stoichiometric reaction of the symmetric benzyl ether with the niobium complex in the absence of $SiCl_4$ does produce approximately 1.8 equiv of benzyl chloride over 48 h along with the niobium oxomono(chloride) **6** along with other niobium oxido species, Nb_2O_5, as well as a free and partially hydrolyzed DAD ligand.[30] Compound **6** can also be synthesized from **5**, the niobium oxotrichloride, using our group's silicon-based reducing agents (Scheme 3).[22,31] When an excess of $SiCl_4$ is added to **6** or mixtures containing **6** from either source, deoxygenation occurs to regenerate **1a**. However, this step is slow, and several unidentified side reactions also take place throughout this pathway. Although it could contribute to the overall catalytic reaction, it is much slower and less efficient and does not play a meaningful role in the catalytic cycle.

Scheme 3. Formation of 6 from 7 (top) and Independent Synthesis of 6 (Middle) and Deoxygenation Back to 1a



Ligand Participation. Throughout the catalytic cycle, the transformations taking place at the niobium atom are all redox-neutral, and no formal oxidation state changes occur. However, the geometry and redox-active nature of the DAD ligand play a critical role in the reaction by varying the extent of electron donation from the ligand (Figure 3). In the niobium trichloride catalyst **1a**, niobium is in the +5 oxidation state with a dianionic ligand, with additional π-donation from the ligand.[22] When the ether coordinates to form intermediate **A**, the ligand reverts to simple κ^2 coordination to make a 6-coordinate complex with a corresponding color change to yellow; after C—O bond cleavage to form **7**, the Nb atom and ligand are best described as Nb(IV) and $L^{\bullet -}$, where the ligand donates less electron density to niobium due to the electron-rich alkoxide (see Supporting Information Figure S1). This is seen as a color change to a deep emerald-green color and lack of an NMR signal, consistent with the previously reported $LNbCl_4$ complex **4** with a radical anion on the ligand as the source of the green color.[22,23]

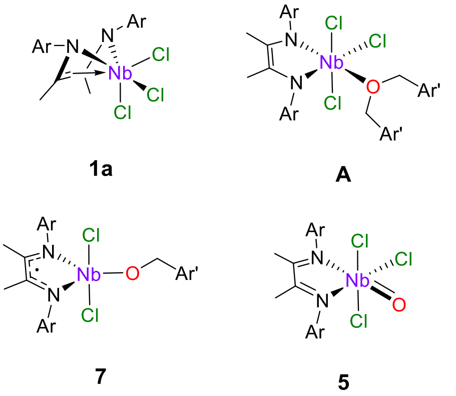


Figure 3. Geometry and oxidation state changes at niobium.

Since the precise mechanisms for the important reaction steps are not known, the effect of different alkyl groups on the ligand (Figure 2) is not obvious. However, larger groups on both the backbone and nitrogen atoms are important for high yields (**1a** and **1d**). The increased electron-donating ability of these ligands may help stabilize **7** and favor the formation of the Nb(IV) center, as **1a** has shown to be especially reactive in other redox-active roles.[22,25] However, steric protection afforded by these ligands may play a more significant role in suppressing side reactions such as radical addition to the ligand backbone or H-abstraction from the ligand.[23] In addition, ligand lability appears to be a source of side reactions as the free ligand has been observed in reaction mixtures at long reaction times (see above).

The deoxygenation reaction is typically very clean, forming only benzyl chloride under the optimized catalytic conditions with excess $SiCl_4$. In control experiments, when stoichiometric (50 mol %; 200 mol % Cl atoms per benzyl ether) or substoichiometric amounts are used, side reactions are observed at long reaction times. Most of these decomposition products are unidentified, but a few of them are known to arise from ligand hydrolysis or H-abstraction of the backbone methyl group, both of which are reported for these types of ligands.[23,32−34] By using an excess of the cheap silicon reagent, these reactions are effectively suppressed.

■ CONCLUSIONS

α-Diimine supported niobium complexes are efficient catalysts for the deoxygenation of benzyl ethers to two equivalents of benzyl chloride, either stoichiometrically or catalytically with silicon tetrachloride or another silicon halide as the halogen source and oxygen scavenger. The use of $SiCl_4$ is especially advantageous as the only byproduct of the reaction is silica, which is easily separated by simple filtration. The reaction is selective for benzyl ethers, with those containing electron-withdrawing groups showing reduced reactivity and ones with electron-donating groups or α-carbon substituents showing faster reaction rates and yields.

Through kinetic observations and substrate reactivity patterns, the deoxygenation reaction normally takes place through two successive trans-etherification steps, where the first C−O bond is activated to form benzyl chloride and a silyl ether with $SiCl_4$. The other C−O bond is activated in the same way, although these steps occur at different rates for asymmetric ethers. Although no formal redox transformations occur throughout the catalytic cycle, the redox-active ligand enables these steps to take place by changing its geometry and electron donation to the niobium.

Ongoing work is aimed at exploring further halogenation reactions using $SiCl_4$ as a convenient, inexpensive halogen source, further examining the mechanism of the steps and its applicability to other diimine complex reactivities, and exploring the chemistry of analogous complexes of vanadium and other metals, as they may show different redox behavior at the metal.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01784.

> Catalyst screening and reaction condition optimization, interactions of complex **1a** with benzyl ether, benzyl-O-$SiCl_3$ intermediate (C) spectra, kinetic studies and one-pot Hammett analysis, NMR spectra of catalytic reaction mixtures or products, experimental section (PDF)

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Notes

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