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Hydrodehalogenation of Alkyl Halides Catalyzed by a Trichloroniobium Complex with a Redox Active α-Diimine Ligand†

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A high-valent d[0] niobium(V) complex, (α-diimine)NbCl₃ (1), bearing a dianionic redox-active α-diimine ligand served as a catalyst for a hydrodehalogenation reaction of alkyl halides in the presence of PhSiH₃. During the catalytic reaction, the redox-active α-diimine ligand allowed the complex to reversibly release and accept one-electron through switching its coordination mode between a dianionic folded form and a monoanionic planar one.

Replacement of a halogen atom in organic compounds by a hydrogen atom, a so-called hydrodehalogenation reaction, is one of the straightforward methods to decompose useful but toxic organic halides, whose disposal is otherwise problematic due to their high resistance to degradation under ambient conditions.[1] Alkaline metals and alkaline earth metals as well as their corresponding organometallic reagents have been typically utilized for converting the carbon-halogen bond to a carbon-hydrogen bond in the presence of organic and inorganic hydrogen sources, from which a stoichiometric amount of metal salt is inevitably generated. Organotin hydrides, typically ⁿBu₃SnH, are effective for metal-salt free hydrodehalogenation in the presence of a radical initiator; however, both organotin hydrides and their reaction by-products such as ⁿBu₃SnX are highly toxic.[2,3] As an environmentally friendly and less toxic hydrodehalogenation reaction, heterogeneous precious metal catalysts show high activity for hydrodehalogenation in combination with dihydrogen gas.[4,5] Recent requirements have favoured the use of cheap and earth abundant non-noble metal catalysts,[6] and some early transition metal catalysts also exhibited activity for the hydrodehalogenation reaction due to their high reactivity in reductively cleaving carbon-halogen bonds.[7] We recently reported the catalytic application of group 5 metal complexes with redox active α-diimine ligands for radical addition of alkyl halides to alkenes,[8] in which the α-diimine ligand assisted the reductive cleavage of the carbon-halogen bonds as well as the *in situ*-generated metal-halogen bonds *via* reversibly transferring one-electron between the metal center and the α-diimine ligand. Herein, we report that a hydrodehalogenation reaction of alkyl halides is catalyzed by a niobium complex bearing a redox active α-diimine ligand (*N,N'*-bis(2,6-diisopropylphenyl)-1,4-diaza-2,3-dimethyl-1,3-butadiene) in the presence of 1 equiv of PhSiH₃, in which the α-diimine ligand plays an important role for assisting the cleavage of the carbon-halogen bonds of organic halides to the carbon-hydrogen bond by safety silanes, though the handling of this needs under strictly anaerobic conditions.

We started searching for the optimal catalyst system by treating 1,1,1,3-tetrachloropropane, as a model substrate, with 1 equiv of different silanes in the presence of (α-diimine)NbCl₃ (1, 3 mol%) in C₆D₆ at 120 °C for 2 hours, and the results are summarized in Table 1. The reaction with PhSiH₃ (1 equiv) gave a hydrodehalogenated product, 1,1,3-trichloropropane, in 85% yield along with PhSiH₂Cl and PhSiHCl₂ as byproducts (entry 1). Other secondary and tertiary silanes such as Ph₂SiH₂, Ph₃SiH, and Et₃SiH were less effective hydrogen sources (entries 2—4). The yield of the hydrodehalogenated product increased upon using 3 equiv of Et₃SiH (entry 5). NaBH₄ has been reported as a hydrogen source for early transition metal-catalyzed hydrodehalogenation, but was ineffective here (entry 6).[7a] Another borane, HB(pin) (entry 7), was also checked, producing only a trace amount of product. When 3 equiv of 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (*Si*-Me-CHD)[9-11] was used as a masked silane instead of PhSiH₃, 1,1,3-trichloropropane was obtained in 45% yield along with the formation of chlorotrimethylsilane and trimethylsilyl-toluene (entry 8), although *Si*-Me-CHD served as an effective hydrogen source for the hydrodehalogenation of 1,1,1,3-tetrachloropropane catalyzed by paddlewheel dimolybdenum complexes.[7f] As a result, we selected the best reaction conditions of PhSiH₃ (1 equiv) at 120 °C for hydrodehalogenation.

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Table 1 Hydrodehalogenation of 1,1,1,3-tetrachloropropane

entry	H source	yield (%)[a]	entry	H source	yield (%)[a]
1	PhSiH$_3$	85	5	Et$_3$SiH[b]	73
2	Ph$_2$SiH$_2$	66	6	NaBH$_4$	n.d.
3	Ph$_3$SiH	44	7	HB(pin)	trace
4	Et$_3$SiH	47	8	Si-Me-CHD[b]	45

[a] Determined by ^{1}H NMR with respect to an internal standard (C$_6$Me$_6$). [b] 3 equiv.

We found that the catalytic hydrodehalogenation reaction is applicable to polyhaloalkanes, allyl bromide, and benzyl bromide derivatives in combination with PhSiH$_3$ as a reductant in C$_6$D$_6$ in sealed J-young NMR tubes, and the results are shown in Table 2. Debromination of dibromomethane afforded bromomethane in 72% yield. Allyl bromide was selectively converted to propene in good yield, in which no hydrosilylation of the C=C moiety was observed. Hydrodehalogenation of benzyl bromide derivatives produced the corresponding aromatic compounds in moderate yield; 4-methylbenzyl bromide was reduced to *p*-xylene, and 4-trifluoromethylbenzyl bromide was transformed to 4-trifluoromethyltoluene after 14 h without defluorination from the CF$_3$ moiety, although the products were contaminated with radical coupling dimers. For these benzyl bromide derivatives, using of *Si*-Me-CHD as the hydrogen source instead of PhSiH$_3$, *p*-xylene and 4-trifluoromethyltoluene were obtained in better yield without forming any radical coupling dimers. Both cyclohexyl chloride and bromide were converted to cyclohexane in 62% and >99% yield, respectively. Cyclopropylmethyl bromide was converted to 1-butene in 43% yield, in which the initially formed cyclopropylmethyl radical was transformed to the corresponding ring-opening isomer,[12] with no contamination with the ring-opened isomer of cyclopropylmethyl bromide, 4-bromo-1-butene (*vide infra*). Hydrodehalogenation of *gem*-dihalocyclopropanes gave the monodehalogenated halocyclopropanes in moderate to good yield.

**Table 2** Substrate scope of hydrodehalogenation reaction [a]

[a] All reactions were carried out in J-young NMR tubes, and yields was determined with respect to an internal standard (1,4-dioxane) in the ^{1}H NMR spectra. [b] *Si*-Me-CHD (3 equiv) was used. [c] 10 mol% catalyst and 5 equiv of PhSiH$_3$ were used for 0.5 h. [d] 6 mol% catalyst was used.

When NbCl$_3$ was used as the catalyst instead of **1** for the hydrodehalogenation of bromomethylcyclopropane, NbCl$_3$ acted as an initiator for the radical reaction to afford 4-bromobutene and 1-butene. This mixture arises from a radical chain reaction of the butenyl radical, generated by the ring-opening of a free cyclopropymethyl radical, which then abstracts either a bromine atom from a second (bromomethyl)cyclopropane molecule or a hydrogen atom from the silane (Scheme 1). This is in sharp contrast to the selective formation of 1-butene catalyzed by **1** as shown in Table 2, where the catalyst moderates the reactivity and suppresses free radical reactivity instead of just initiating a radical chain reaction. A similar result was observed for NbCl$_3$(DME).
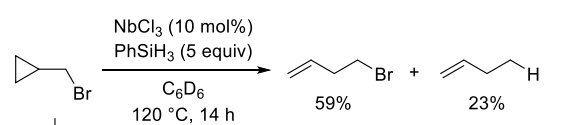
Scheme 1 Hydrodehalogenation reaction of bromomethylcyclopropane catalyzed by NbCl$_3$

Next, we carried out kinetic studies for the hydrodehalogenation reaction.[13] Under the optimized conditions, k_{obs} for the reaction progress indicated a linear dependence on the concentration of the catalyst **1**. In the presence of a large excess of PhSiH$_3$, 1,1,1,3-tetrachloropropane showed pseudo first-order kinetic behavior. Similarly, pseudo first-order kinetics was also

observed for $PhSiH_3$ in the presence of large excess 1,1,1,3-tetrachloropropane. The reaction progress followed overall second-order kinetics with respect to the concentrations of both substrates (Figure 1). We further analyzed the rate dependence on the reaction temperature to estimate the activation parameters for the reaction of 1,1,1,3-tetrachlropropane and $PhSiH_3$ catalyzed by **1**. Eyring analysis derived from the kinetic data gave the thermodynamic parameters of $\Delta H^{\ddagger} = 126(7)$ kcal/mol, $\Delta S^{\ddagger} = 2.18(5)$ e.u., and $\Delta G^{\ddagger}$ (298 K) = 123(13) kcal/mol. The entropy value was nearly zero, suggesting no involvement of a free radical during the catalytic cycle. In addition, the reaction using Ph_2SiH_2/Ph_2SiD_2 showed a KIE of 1.72, corresponding to the rate-determining step involving H-abstraction by organic radicals.
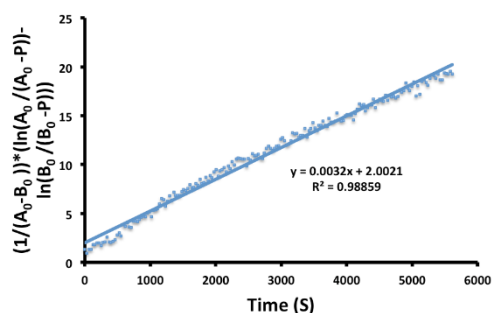

Fig. 1 A second-order kinetic behavior on the concentration of 1,1,1,3-tetarachlropropane and $PhSiH_3$ for the hydrodehalogenation reaction of 1,1,1,3-tetrachlropropane with $PhSiH_3$ (A = $PhSiH_3$, B = 1,1,1,3-tetrachlropropane, P = product).

Based on the kinetic study, we propose a mechanism for the hydrodehalogenation reaction catalyzed by **1**. As shown in Scheme 2, the initial step is the coordination of the alkyl halide to the niobium center of **1** to afford a niobium(IV) species **A**, in which one electron is transferred from the α-diimine ligand to the niobium(V) center. This behaviour of the redox-active ligand is similar to our previous results on radical addition reactions.[8b] Subsequent reductive cleavage of the carbon-halogen bond in **A** *via* a one-electron transfer from the niobium(IV) center to the alkyl halide affords a niobium(V) species **B**. A hydrogen atom is then abstracted from $PhSiH_3$ to form the dehalogenated product as well as the niobium(V) species **C**, which is consistent with first-order rate dependence on both alkyl halides and phenylsilane. Finally, disproportionation of **C** produces $XSiPhH_2$ and regenerates **1**. During the catalytic reaction, the redox-active α-diimine ligand accelerates the disproportionation of **C** by accepting one electron. The observed primary kinetic isotope effect for deuterated and non-deuterated silanes is consistent with the involvement of hydrogen abstraction in the overall rate-determining step.
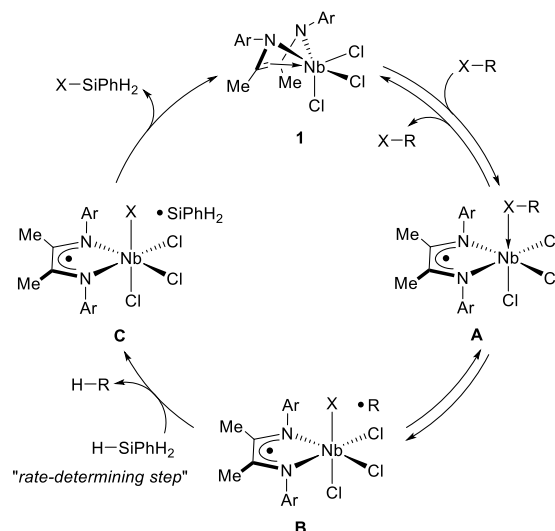
Scheme 2. Proposed catalytic cycle.

We alternatively prepared a tetrachloroniobium complex **2** with a monoanionic α-diimine ligand by treating $NbCl_5$ with the α-diimine ligand in the presence of *Si*-Me-CHD (0.5 equiv) (eq 1).[7b] Since the complex **2** is analogous to the tetrachloroniobium moiety of **C** in Scheme 2, we treated **2** with $PhSiH_3$ (3 equiv) in C_6D_6 to give **1** in 80% yield (determined by ^{1}H NMR) together with the formation of $ClSiH_2Ph$ (eq 2), indicating that $PhSiH_3$ worked as not only a hydrogen source for the hydrodehalogenation reaction but also a reductant for the niobium complex **2**. Under the reaction condition, further transformation of **1** by the remaining $PhSiH_3$ was not observed.
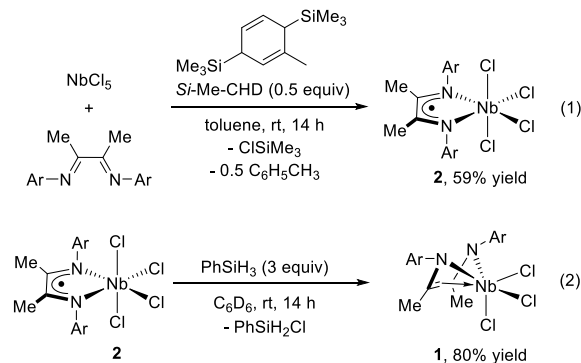
In summary, we have developed a hydrodehalogenation reaction of haloalkanes using $PhSiH_3$ as a reductant as well as a hydrogen source. Although the catalyst **1** contained a high-valent d^0 niobium center, the α-diimine ligand played an important role in releasing one electron from the dianionic ligand to the alkyl halides to a generate carbon radical as the initial step of the catalytic reaction. Further study on the reductive transformation of organic compounds by **1** and similar niobium complexes bearing an α-diimine ligand is ongoing in our laboratory.

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13   Details for the kinetic study, see ESI.

TOC used only:

We have developed a hydrodehalogenation reaction of haloalkanes using $PhSiH_3$ as a reductant as well as a hydrogen source. The α-diimine ligand on the niobium center plays an important role in releasing one electron from the dianionic ligand to the alkyl halides to a generate carbon radical as the initial step of the catalytic reaction.

$$R{-}X \xrightarrow[\text{C}_6\text{D}_6,\ 120\ °\text{C}]{\substack{\textbf{1}\ (3\ \text{mol\%}) \\ \text{PhSiH}_3\ (1\ \text{equiv})}} R{-}H$$