Supporting Information

for

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

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1. General Procedure

All manipulations involving air- and moisture-sensitive compounds were carried out under argon using the standard Schlenk technique or argon-filled glovebox. Niobioum complexes 1 and 2 were prepared according to the literature procedure.\textsuperscript{1} NbCl\textsubscript{3} was prepared by reduction of NbCl\textsubscript{5} with 1 equiv of 1-methyl-3,6-bis(trimethylsilyl)-1,4-cyclohexadiene.\textsuperscript{1} Anhydrous hexane and toluene were purchased from Kanto Chemical and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.\textsuperscript{2} Alkyl!halides and silanes were purchased and, if necessary, purified by distillation over CaH\textsubscript{2}. Benzene-\textit{d}_6 was distilled over CaH\textsubscript{2} and degassed before use. \textsuperscript{1}H NMR (400 MHz) and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz) spectra were measured on BRUKER AVANCEIII-400 spectrometers and JEOL JNM-ECS400 (400 MHz) spectrometers.

2. Screening of hydrogen sources for catalytic hydrodehalogenation of 1,1,1,3-tetrachloropropane (Table 1)

To a solution of 1,1,1,3-tetrachloropropane (0.300 mmol), hydrogen source (0.300 mmol), and hexamethylbenzene (2.4 mg, 15.0 \textmu mol) in C\textsubscript{6}D\textsubscript{6} (0.10 mL) as an internal standard in C\textsubscript{6}D\textsubscript{6} (0.20 mL) was added catalyst 1 (9.00 \textmu mol) in C\textsubscript{6}D\textsubscript{6} (0.10 mL) in a J-Young NMR tube. The NMR sample of the reaction mixture was kept in 120 °C oil bath. After the reaction time, the sample was measured by \textsuperscript{1}H NMR.
Figure S1. Hydrodehalogenation of 1,1,1,3-tetrachloropropane catalyzed by 1 (Table 1, entry 1)
3. Substrate scope for catalytic hydrodehalogenation of alkyl halides with PhSiH₃ in Table 2.

**Figure S2.** ¹H NMR spectrum for hydrodehalogenation reaction of dibromomethane.
Figure S3. $^1$H NMR spectrum for hydrodehalogenation reaction of allyl bromide.
Figure S4. $^1$H NMR spectrum for hydrodehalogenation reaction of 4-methylbenzyl bromide.
Figure S5. $^1$H NMR spectrum for hydrodehalogenation reaction of 4-trifluoromethylbenzyl bromide.
Figure S6. $^1$H NMR spectrum for hydrodehalogenation reaction of cyclohexyl chloride.
Figure S7. $^1$H NMR spectrum for hydrodehalogenation reaction of cyclohexyl bromide.
**Figure S8.** $^1$H NMR spectrum for hydrodehalogenation reaction of cyclopropylmethyl bromide.
**Figure S9.** $^1$H NMR spectrum for hydrodehalogenation reaction of (2,2-dichlorocyclopropyl)benzene.
Figure S10. $^1$H NMR spectrum for hydrodehalogenation reaction of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane.
Figure S11. $^1$H NMR spectrum for hydrodehalogenation reaction of 7,7-dichlorobicyclo[4.1.0]heptane.
4. Kinetic Study for Hydrodehalogenation

**Figure S12.** Reaction progress with different concentration of 1 as the catalyst for the hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane with PhSiH₃

**Figure S13.** Dependence of $k_{\text{obs}}$ with the concentration of 1 as the catalyst for the hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane with PhSiH₃
Catalytic hydrodehalogenation of 1,1,1,3-tetrachloropropane was carried out in the presence of complex 1 (3 mol%) and excess PhSiH$_3$ (10 equiv) in C$_6$D$_6$ at 100 °C. The amount of the product was determined by integral ratios of signals for 1,1,3-trichloropropane and the internal standard, and the time dependence for the product formation was fitted to the first-order plot.

![Figure S14](image)

**Figure S14.** A pseudo first-order kinetic behavior on the concentration of 1,1,1,3-tetrachloropropane (S) for the hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane with PhSiH$_3$.

Catalytic hydrodehalogenation of 1,1,1,3-tetrachloropropane was carried out in the presence of complex 1 (3 mol%) and excess 1,1,1,3-tetrachloropropane (10 equiv) with PhSiH$_3$ (1 equiv) in C$_6$D$_6$ at 100 °C. The reaction progress was followed by integral ratios of signals for PhSiH$_3$ and the internal standard, and the time dependence for the consumption of PhSiH$_3$ was fitted to the first-order plot.
Figure S15. A pseudo first-order kinetic behavior on the concentration of PhSiH$_3$ (S) for the hydrodehalogenation reaction of 1,1,1,3-tetrachloropropane with PhSiH$_3$

Catalytic hydrodehalogenation of 1,1,1,3-tetrachloropropane was carried out in the presence of complex 1 (3 mol%) and Ph$_2$SiH$_2$ or Ph$_2$SiD$_2$ in C$_6$D$_6$ at 100 °C. The $k_{obs}$ for two reactions were $k_{obs}$(H) = 3.77 and $k_{obs}$(D) = 2.00, and the KIE value was 1.89, suggesting that the H-abstraction was involved in the rate-determining step.

Figure S16. Kinetic isotope effect for hydrodehalogenation reaction
5. References
