Supporting Information

Regioselective deuteration of alcohols in D\textsubscript{2}O catalysed by homogeneous manganese and iron pincer complexes

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1. Materials and methods

All deuteration experiments were carried out under an inert atmosphere (with N_2 or Ar). Complexes MnBrPNP\(^{iPr}\)(CO)\(_2\) (C-1) MnBrPNP\(^{Cy}\)(CO)\(_2\) (C-2), and FeHBrPNP\(^{iPr}\)(CO) (C-3) were prepared by previously reported methods.\(^1\)\(^2\) All catalysts were weighed inside an argon filled glove box. Alcohols 1-21 and NaOH were bought from commercial vendors and used without further purification. D\(_2\)O (CIL, D-99.5%) was sparged with N\(_2\) for 1 h prior to use. \(^1\)H, \(^2\)H, \(^31\)P and \(^{13}\)C NMR spectra were recorded on 400 MHz or 500 MHz Varian NMR spectrometers. \(^1\)H and \(^{13}\)C NMR chemical shifts were determined relative to the residual solvent signals (D\(_2\)O, CDCl\(_3\)). The \(^2\)H NMR chemical shift were determined based on external CDCl\(_3\) reference. Mass spectral data were recorded on a Bruker 300-MS TQ Mass Spectrometer at 70 eV for EI.

![Catalytic complexes screened in this study](#)

2. Standard procedure for deuteration reaction

In a J. Young NMR tube (total volume \(\sim\)2.5 mL), catalyst C-1/C-2/C-3 was weighed inside an argon glove box, followed by the addition of pre-dissolved NaOH (5-200 mol% with respect to alcohol) in 0.4 mL D\(_2\)O, and alcohol (0.25-0.5 mmol) under nitrogen atmosphere (10 µL 1,4-dioxane was additionally added in case of ethanol (2), methanol (3), ethylene glycol (13), and isopropanol (20) as an internal standard). The NMR tube was then sealed and a proton NMR spectrum was recorded. Subsequently, the NMR tube was placed in a pre-heated oil bath (100 °C - 140 °C) for a given amount of time (12-60 h). After the reaction, the NMR tube was cooled to room temperature; after which the \(^1\)H and \(^{13}\)C NMR spectra were recorded. The amount of deuteration was calculated from the \(^1\)H (and \(^2\)H, whenever necessary) NMR spectra based on integral ratios of nondeuterable peaks (not \(\alpha/\beta\))/ internal standard peak with deuterated peaks. The deuterated
alcohols were isolated through extraction with CDCl$_3$. Maximum theoretical deuteration achievable were calculated based on the numbers of exchangeable proton and deuterium atoms present in the system. For example, for Table 1, entry 1, total exchangeable H atoms = [0.5x5 (from n-BuOH) + 1.0 (from NaOH)] mmol = 3.5 mmol. Total exchangeable D atom = [400*1.11*2/20] (from D$_2$O; d= 1.11; MW = 20) = 44.4 mmol. So, the theoretical maximum deuteration = [44.4/(44.4+3.5)]*100% = 93%.

3. Selected spectral data for deuteration reactions

3.1. Deuteration of primary alcohols with manganese complex C-1

Figure S2. $^1$H spectra of deuteration of 1 before (A) and after (B) reaction and $^2$H spectra of deuterated n-butanol (C). Reaction conditions: 1 (0.5 mmol), C-1 (1mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.
Figure S3. $^{13}$C spectra of deuterated ($\alpha$, $\beta$) n-butanol (1) in D$_2$O. Reaction conditions: 1 (0.5 mmol), C-1 (1mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.

Figure S4. $^1$H spectra of 4 before (A) and after (B) reaction. Reaction conditions: 4 (0.5 mmol), C-1 (1 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.
Figure S5. $^1$H spectra of deuteration of 5 before (A) and after (B) reaction. Reaction conditions: 5 (0.5 mmol), C-1 (0.5 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.

Figure S6. $^1$H spectra of deuteration of 6 before (A) and after (B) reaction. Reaction conditions: 6 (0.5 mmol), C-1 (0.5 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.
Figure S7. $^1$H spectra of 7 before (A) and after (B) reaction. Reaction conditions: 7 (0.5 mmol), C-1 (1 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.

Figure S8. $^1$H spectra of 9 before (A) and after (B) reaction and $^2$H spectra of deuterated 9 (C). Reaction conditions: 9 (0.5 mmol), C-1 (1 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.
Figure S9. $^1$H spectra of 10 before (A) and after (B) reaction and $^2$H spectra of deuterated 10 (C).
Reaction conditions: 10 (0.5 mmol), C-1 (0.5 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.

Figure S10. $^1$H spectra of 12 before (A) and after (B) reaction. Reaction conditions: 12 (0.5 mmol), C-1 (0.5 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.
Figure S11. $^1$H spectra of 15 before (A) and after (B) reaction. Reaction conditions: 15 (0.5 mmol), C-1 (1 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 120 °C, 12 h.

3.2. Deuteration of primary alcohols with iron complex C-3

Figure S12. $^1$H spectra of $\alpha$-deuterated 1. Reaction conditions: 1 (0.25 mmol), C-3 (2 mol%), NaOH (10 mol%), D$_2$O (0.4 mL), 100 °C, 24 h.
Figure S13. $^1$H spectra of α-deuterated 4. Reaction conditions: 4 (0.25 mmol), C-3 (2 mol%), NaOH (10 mol%), D$_2$O (0.4 mL), 100 °C, 24 h.

Figure S14. $^1$H spectra of α-deuterated 5. Reaction conditions: 5 (0.25 mmol), C-3 (2 mol%), NaOH (10 mol%), D$_2$O (0.4 mL), 100 °C, 24 h.
Figure S15. $^2$H spectra of $\alpha$-deuterated 5. Reaction conditions: 5 (0.25 mmol), C-3 (2 mol%), NaOH (10 mol%), D$_2$O (0.4 mL), 100 °C, 24 h.

Figure S16. $^1$H spectra of $\alpha$, $\beta$-deuterated 12. Reaction conditions: 12 (0.25 mmol), C-3 (2 mol%), NaOH (10 mol%), D$_2$O (0.4 mL), 100 °C, 24 h.
3.2. Deuteration of secondary alcohol

Figure S17. $^1$H spectra of 17 before (A) and after (B) reaction. Reaction conditions: 17 (0.5 mmol), C-1 (2 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 140 °C, 30 h.

Figure S18. $^2$H spectra of 17 after reaction. Reaction conditions: 17 (0.5 mmol), C-1 (2 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 140 °C, 30 h.
Figure S19. $^1$H spectra of 19 before (A) and after (B) reaction. Reaction conditions: 19 (0.5 mmol), C-1 (2 mol%), NaOH (5 mol%), D$_2$O (0.4 mL), 140 °C, 30 h.

4. Control experiments performed to understand the reaction mechanism

Observation of the active catalytic species in the reaction mixture

In a J Young NMR tube (total volume ~2.5 mL), catalyst C-1 was weighed inside an argon globe box, followed by the addition of pre-dissolved NaOH (5 mol% with respect to alcohol) in 0.4 mL D$_2$O, and n-butanol (0.5 mmol) under nitrogen atmosphere. The NMR tube was then sealed and placed in a pre-heated oil bath (120 °C). After 1 h, the NMR tube was cooled to room temperature and 0.2 mL THF was added to the reaction mixture. The resultant homogeneous solution was then analyzed by $^{31}$P NMR spectroscopy.
Figure S20. Active species detected in the reaction mixture through $^{31}$P NMR after 1 h (0.2 mL THF was added to the reaction mixture to form a homogeneous solution)

**Formation of manganese deuteroxide species (C-1B)**

In a 50 mL Schlenk flask, C-1 (0.05mmol) was weighed inside an argon glove box and subsequently dissolved in 5 mL of dry and degassed THF in a nitrogen atmosphere, followed by the addition of 1 mmol of t-BuOK (weighed inside an argon glove box). The formation of the manganese amido complex (C-1A) was observed as a red solution. After stirring the resulting solution for 15 minutes, the red solution was filtered through Celite, and 5 mmol D$_2$O was subsequently added to the filtrate. The solution immediately turned yellow, signifying the formation of a deuteroxide species. The solution was stirred for 30 minutes, after which the solvents were removed *in vacuo*. Benzene-d$_6$ was used as the deuterated solvent for the $^{31}$P NMR analysis of the resulting C-1B.
Figure S21. $^{31}$P spectra of manganese deuteroxide species [Mn(OD)PN$_3$P$_2$(CO)$_2$] (C-1B).

$\alpha$, $\beta$ deuteration of n-butanol with C-1B

Figure S22. Deuteration of 1 by manganese deuteroxy complex (C-1B) without added base, Signifying the ability of C-1B to form C-1A in the solution at 120 °C. (THF peaks suppressed)
5. EI-MS analysis of benzyl alcohol before and after deuteration

Figure S23. EI-MS spectra of benzyl alcohol
Figure S24. EI-MS spectra of α deuterated benzyl alcohol. Reaction conditions: benzyl alcohol (0.5 mmol), C-1 (0.5 mol%), NaOH (5 mol%), D₂O (0.4 mL), 120 °C, 12 h.
6. Recycling studies

Standard procedure:

In a J. Young NMR tube (total volume ~2.5 mL), catalyst C-1 (2 mol%, 0.01 mmol) was weighed inside an argon globe box, followed by the addition of pre-dissolved NaOH (5 mol% with respect to alcohol) in 0.5 mL D$_2$O, and alcohol (0.5 mmol) under nitrogen atmosphere. The NMR tube was then sealed and a proton NMR spectrum was recorded. Subsequently, the NMR tube was placed in a pre-heated oil bath (120 °C) for a given amount of time (12 h). After the reaction, the NMR tube was cooled to room temperature; after which a $^1$H NMR spectra was recorded. Subsequently, in a nitrogen atmosphere, 0.4 mL of degassed chloroform was added to the NMR tube. From the resulting biphasic solution, the top D$_2$O (with NaOH) layer was separated to afford a yellow solution. The catalyst was then recovered by removing the deuterated n-BuOH and CHCl$_3$ in vacuo. The recovered catalyst inside the J. Young NMR tube then recharged with fresh n-BuOH (0.5 mmol), NaOH (5 mol%) and D$_2$O (0.5 mL) for the next cycle.

![Deuteration (%)](image)

**Figure S25. α and β deuteration observed in successive cycles.** n-butanol (0.5 mmol), C-1 (2 mol%), NaOH (5 mol%), D$_2$O (0.5 mL), 120 °C, 12 h.
Figure S26. Image of the recovered catalyst inside the J.Young NMR tube

7. References
