Reduction of Carboxylic Acids to Alcohols via Manganese(I) Catalyzed Hydrosilylation

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ABSTRACT: The reduction of carboxylic acids to the respective alcohols, in mild conditions, was achieved using [MnBr(CO)₅] as the catalyst and bench stable PhSiH₃ as the reducing agent. It was shown that the reaction with the earth-abundant metal catalyst could be performed either with a catalyst loading as low as 0.5 mol %, rare with the use of [MnBr(CO)₅], or on a gram scale employing only 1.5 equiv of PhSiH₃, the lowest amount of silane reported to date for this transformation. Kinetic data and control experiments have provided initial insight into the mechanism of the catalytic process, suggesting that it proceeds via the formation of silyl ester intermediates and ligand dissociation to generate a coordinatively unsaturated Mn(I) complex as the active species.

KEYWORDS: Carboxylic Acids, Alcohols, Manganese, Homogeneous, Catalysis, Reduction Reactions, Hydrosilylation

INTRODUCTION

The direct reduction of carboxylic acids to alcohols is a more challenging transformation compared to the respective reduction of other carbonyl or carboxyl derivatives. It is traditionally performed using stoichiometric or even excess amounts of strong reducing reagents such as diborane, LiAlH₄, or DIBAL-H. Also, excesses of milder reducers such as NaBH₄ can be used in combination with stoichiometric activating agents (e.g., I₂, catechol, or trifluoroacetic acid). Since alcohols are widely employed in many chemical industries, the development of catalytic methods to reduce carboxylic acids to alcohols continues to be a highly active research field. While the use of hydrogen offers a highly attractive reduction path, there are few reported examples in the literature for catalytic hydrogenation of carboxylic acids to alcohols, usually requiring rather high H₂ pressures. The catalysts are typically based on expensive noble metals and specialized ligands with only one example using an earth-abundant metal catalyst. This scarcity results inter alia from the Brønsted acidity and coordinative ability of carboxylic acids, which can deactivate the catalysts by interfering with the metal, the ligand, and possible metal–ligand cooperative pathways. An alternative route to the use of traditional stoichiometric metal hydrides is offered by easy-to-handle and safe silane reagents. There are many examples reported for the hydrosilylation of esters and recently also for amides. However, only very few examples exist for free carboxylic acids: they require a large excess of the silane reagent; make use of noble metal catalysts like Ru, Rh, and Ir; are performed in halogenated solvents like chloroform; or require a specific experimental apparatus. Therefore, the development of a direct catalytic reduction from free carboxylic acids to their corresponding alcohols still seems highly desirable.

Until recently, only very few earth-abundant base-metal catalysts were known for carboxylic acid hydrosilylation. Lemaire and co-workers reported that Cu(OTf)₂, used in high catalyst loading, was able to reduce a selection of carboxylic acids into their respective alcohols. Two more examples were presented by the groups of Sortais and Darcel, who utilized metal carbonyl complexes activated under photochemical irradiation: the complex [Fe(COD)(CO)₃], which afforded alcohols from aliphatic carboxylic acids in high yields (including only a couple of aromatic substrates in moderate yields); and the complex [Mn₂(CO)₁₀], which was thermally inactive and used under UV light, leading to aldehydes as the products. More recently, our group reported the use of a manganese(I) pincer complex in the hydrosilylative reduction of a range of carbonyl functional groups, including a few carboxylic acid examples. Manganese(I) complexes have been employed in hydrosilylation reactions to reduce carbonyl groups since the work of Cutler and co-workers in 1995 with multiple recent works focusing on similar hydrosilylative transformations catalyzed by Mn(I) complexes as a result of manganese’s high natural abundance, low toxicity, and low price. Since the direct reduction of carboxylic acids to alcohols still remains an underexplored
field, it was decided to further explore the development of an easy to handle and well-performing Mn(I) catalyst for the hydrosilylation of carboxylic acids to alcohols.

## RESULTS AND DISCUSSION

Initially, we chose to study the catalytic performances of several manganese complexes for this transformation (Scheme 1): the commercial carbonyl complex [MnBr(CO)$_5$] $\text{Mn-1}$, previously shown to be active for other hydrosilylation and hydrogenation reactions; the triazole PNN manganese complex $\text{Mn-2}$, recently reported in hydrosilylation reactions by our group; the complex $\text{Mn-3}$, whose ligand framework has been recently reported by Kirchner and co-workers for the hydrosilylation of carbon dioxide; and $\text{Mn-4}$, a manganese-triazine pincer complex active in hydrogenation reactions.

The complexes were screened under identical conditions at a catalyst loading of 2 mol % with 2.5 equiv of PhSiH$_3$ in THF at 80 °C; yields were determined by 1H NMR spectroscopy relative to an internal standard after hydrolysis (for details, see the Supporting Information). Among the pincer complexes, only the manganese triazole complex $\text{Mn-2}$ showed activity for the hydrosilylation of carboxylic acid 1, yielding 77% of the alcohol 2. The PNP ligand frameworks induced no activity in either the cationic or neutral Mn(I) complexes. Only after activation with excess base did $\text{Mn-4}$ convert the starting acid into 42% alcohol. Notably, the commercially available and bench-stable metal carbonyl complex [MnBr(CO)$_5$] ($\text{Mn-1}$), bearing no additional controlling ligand, showed excellent performances, providing a high yield of 83% of alcohol 2 after hydrolysis.

Control experiments confirmed that no reaction took place under the screening conditions in the absence of a manganese complex. Even though there are reports of manganese(II) pincer complexes showing activity in a range of other hydrosilylation reactions, only the manganese(II) and manganese(III) salts like MnCl$_2$, MnBr$_2$, Mn(OAc)$_2$·(H$_2$O)$_4$, and Mn(OAc)$_3$·(H$_2$O)$_2$ did not afford any product. The reaction could be carried out with good to excellent yields in a broad range of solvents, including even neat conditions (Table 1). In the perspective of balancing the solvent’s performance and environmental impact, 2-methyltetrahydrofuran (2-MTHF) was considered the preferred solvent of choice. While significant activity was also observed at lower temperatures, 80 °C was found to be appropriate, yielding 96% alcohol within the 2 h reaction time.

Next, different silanes were tested in different stoichiometric amounts, and the best results for each silane are reported in Table 2. The sequential reduction of the number of hydrides and hydricity strength from the primary silane to the most sterically congested triphenyl silane, Ph$_3$SiH, reduced the overall performance of the reaction. The oxygen-containing silanes, tetramethyldisiloxane (TMDS), and polymethylhydro-siloxane (PMHS) also performed poorly, making PhSiH$_3$ the preferred choice.

The $\text{Mn-1}$ catalyzed hydrosilylation with PhSiH$_3$ in 2-MTHF was then applied to a scope of different carboxylic acids (Scheme 2). From the initial experiments, a silane to substrate ratio of 2.5:1 and a reaction time of 4 h was adopted for aliphatic acids. The respective alcohols were obtained consistently in high yields across a wide range of substrates. Steric properties of the substrates seem to have little influence on the reaction performances: long-chain acids performed well

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**Scheme 1. Screening of Manganese(I) Complexes for the Hydrosilylation of Cyclohexane Propanoic Acid**

![Scheme 1](https://example.com/scheme1.png)

“Yields were determined after hydrolysis by NMR relative to the internal standard added before extraction. The yield obtained after base activation for $\text{Mn-4}$ is given in the brackets (6 mol % KOtBu).

**Table 1. Solvent Selection and Temperature Variation for the Hydrosilylation of Cyclohexane Propanoic Acid (1) Using [MnBr(CO)$_5$] (Mn-1) as the Catalyst**

| entry | solvent | temperature (°C) | yield (%) |
|-------|---------|----------------|----------|
| 1     | THF     | 80             | 83       |
| 2     | neat    | 80             | 79       |
| 3     | neat    | 100            | 87       |
| 4     | toluene | 80             | 92       |
| 5     | heptane | 80             | 92       |
| 6     | cyclohexane | 80 | 95       |
| 7     | chloroform | 80 | >99      |
| 8     | 2-MTHF  | 80             | 96       |
| 9     | 2-MTHF  | 60             | 74       |
| 10    | 2-MTHF  | 40             | 38       |
| 11    | 2-MTHF  | RT             | 3        |

“Yield was determined by NMR relative to ferrocene as the internal standard, added after hydrolysis.

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under the reaction conditions yielding 3–5, and the bulky adamantanecarboxylic acid and the more complex substrate 1-(4-chlorophenyl)-1-cyclopentanecarboxylic acid gave 9 and 10 in very good yields at somewhat elongated reaction times. Interestingly, while [MnBr(CO)\textsubscript{5}] has been reported to be an active catalyst for the hydrosilylation of alkenes,\textsuperscript{37} the reaction proved highly selective for the carboxylic acid moiety, leaving the double bonds of oleic acid and linoleic acid intact to afford oleyl alcohol (6) and linoleyl alcohol (7) in good yields. For phenylacetic acid derivatives, the electronic nature and position of the ring substituents could be varied widely, and products 11 and 14–16 were all obtained in high yields. The reaction also tolerated some heterocycles: 2-thiopheneacetic acid, which retained the stereochemistry at the chiral center.\textsuperscript{45} A variation in the concentrations of phenylsilane and its PHOS catalyst maintained the same molar concentration as 1.5 equiv of PhSiH\textsubscript{3} was found to be sufficient to reach the quantitative conversion of the acid within a reaction time of 24 h, as determined by monitoring the progression of the reaction in a yield/time profile (Figure 1, panel A). Under these improved reaction conditions ([MnBr(CO)\textsubscript{5}] (2 mol %), PhSiH\textsubscript{3} (1.5 equiv), 6 mL of 2-MTHF, T = 80 °C, t = 24 h), 1.63 g of phenylacetic acid was converted successfully to give an isolated yield of 1.35 g (93%) of 2-phenyl ethanol (11). Continuing our studies on phenylacetic acid, we further explored the catalytic performance of [MnBr(CO)\textsubscript{5}] at lower catalyst loading. After a reaction time of 24 h in standard conditions, it was possible to obtain 2-phenyl ethanol in 78% yield with a catalyst loading as low as 0.5 mol %.

A further examination of the reduction of phenylacetic acid was then performed to establish the reaction order of the individual reactive components by the initial rates method (Figure 1, panels B–D). The temperature was reduced to 60 °C for the study to allow for a more accurate determination of yields as a function of time. A variation in the concentration of [MnBr(CO)\textsubscript{5}] while maintaining the same molar concentrations of phenylsilane and phenylacetic acid indicated an apparent first-order dependence of the reduction on the catalyst. A variation in the concentrations of phenylsilane and phenylacetic acid independently also showed linear correlations between the initial rate and concentration, indicating a first-order dependence with respect to both substrates. The same kinetic behavior has been reported previously for manganese catalyzed hydrosilylation reactions of ketones and formates.\textsuperscript{50}

A vigorous gas evolution in the very early stage of the reaction indicated dehydrogenative coupling of PhSiH\textsubscript{3} and the carboxylic acids to silyl esters PhSiH\textsubscript{3}(O_2CR), as the initial reaction step.\textsuperscript{50} The evolved H\textsubscript{2} was identified by GC-TCD analysis of the gas phase for phenylacetic acid as the substrate under standard conditions. The gaseous hydrogen does not contribute to the reduction as ascertained by releasing the atmosphere and flushing with argon immediately after its formation. Interestingly, even the notoriously less reactive tertiary silane PhMe\textsubscript{3}SiH\textsuperscript{51,52} reacted rapidly to give the corresponding silyl ester in 88% yield after 15 min. A blank

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**Table 2. Silane Screening for the Hydrosilylation of Cyclohexane Propanoic Acid**

| entry | silane | quantity (mmol) | yield (%) |
|-------|--------|-----------------|-----------|
| 1     | PhSiH\textsubscript{3} | 1.25 | 96 |
| 2     | Ph\textsubscript{3}SiH | 3.0 | 33 |
| 3     | Ph\textsubscript{2}SiH | 1.25 | 0 |
| 4     | TMDS  | 2.0 | 9 |
| 5     | PMHS  | 5.0\textsuperscript{a} | 31 |

*Yields are the highest obtained for each silane, varying the silane equivalent (all reactions are listed in the Supporting Information). 10 mmol of monomeric units (MeOSiH) was used.*
reaction performed in the same conditions without \([\text{MnBr(CO)}_5]\) did not afford any product, showing the essential role of the Mn complex in catalyzing this step (Scheme 3, panel A). Notably, the tertiary silyl ester 32 was reduced smoothly with phenylsilane under standard conditions leading to 2-phenylethanol in 82% yield (Scheme 3, panel B). While this does not exclude H transfer occurring from PhSiH\(_3\)(O\(_2\)CR), as suggested previously,\(^{20}\) it demonstrates that PhSiH\(_3\) is able to reduce silyl ester intermediates in the presence of \([\text{MnBr(CO)}_5]\) as the catalyst.

The analysis of the gas phase composition of the reaction between phenylacetic acid and phenylsilane under standard conditions also revealed the presence of CO. A constant ratio of approximately 50:1 between H\(_2\)(g) and CO (g) was determined after 15 min and 4 h. When it is assumed that the hydrogen evolved arises from the quantitative Si–O bond

\(^{20}\) Isolated yields are given below each respective alcohol (NMR yield is given in the parentheses where applicable). [a] Standard conditions for the hydrosilylation of carboxylic acids: \([\text{MnBr(CO)}_5]\) (2 mol%), PhSiH\(_3\) (2.5 mmol), \(T = 80^\circ\text{C}\), carboxylic acid (1 mmol), 2-MTHF (0.5 mL), time = 4 h. [b] Conditions for the hydrosilylation of most aromatic carboxylic acids: \([\text{MnBr(CO)}_5]\) (2 mol%), PhSiH\(_3\) (2.0 mmol), \(T = 80^\circ\text{C}\), carboxylic acid (1 mmol), cyclohexane (0.5 mL), time = 2 h. [c] Same conditions as [b] using 2-MTHF (0.5 mL) as the solvent. [d] Time = 2 h; [e] time = 16 h. [f] Same conditions as [a] using PhSiH\(_3\) (3.0 mmol). [g] Half scale reaction.
formation between the R−COOH and H−Si bonds of silane, the amount of CO accounts for one equivalent relative to the employed [MnBr(CO)5] complex. This suggests the dissociation of one CO ligand upon thermal activation to generate a 16-electron complex of type [MnX(CO)4] (X = bromide or carboxylate). The corroboration of catalytic activity with the formation of coordinatively unsaturated manganese carbonyl species is supported further by the 31P{1H}-NMR spectroscopic investigation of the reaction using the ligand modified complexes Mn-2, Mn-3, and Mn-4 (see the Supporting Information). The spectra of the inactive complexes Mn-3 and Mn-4 revealed the signals of the pristine complex as major species after the typical reaction time. In contrast, the spectrum of the active complex Mn-2 showed a signal at −16.1 ppm associated with a free PPh2 group, indicating ligand dissociation. The reported ability of unsaturated Mn(I) carbonyl complexes to activate Si−H bonds via sigma coordination suggests the possibility of a Mn(I) redox neutral Si−H bond activation circumventing the need for a Mn(I)/Mn(III) oxidative addition–reductive elimination process. An outer-sphere mechanistic proposal is suggested in Scheme 4.

**CONCLUSION**

In conclusion, we have shown that the bench stable and commercially available manganese carbonyl complex [MnBr(CO)5] can catalyze the challenging reduction of a wide variety of both aryl and alkyl carboxylic acids to their respective alcohols in high yields via hydrosilylation. The scalable synthetic procedure can be carried out in standard laboratory glassware using benign solvents under mild conditions with only 1.5 equiv of phenylsilane, the lowest amount of silane reported to date for the hydrosilylation of carboxylic acids. Control experiments are consistent with the formation of silyl esters PhSiH2(O2CR) as intermediates and suggest a coordinatively unsaturated 16-electron Mn(I) carbonyl com-
plex as the active species, probably involved in Si–H activation. Notably, this working hypothesis provides a rational explanation of the catalytic activity of [MnBr(CO)₅] compared to related pincer-type complexes due to the easier access of unsaturated species through ligand dissociation. Further investigations to elucidate the mechanistic details for hydride transfer at different Mn(I) coordinative frameworks are underway to broaden the catalytic potential of this earth-abundant and benign transition metal in homogeneous catalysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.1c00140.

General considerations, experimental methods and synthetic details, and copies of NMR spectra (PDF)

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The authors declare no competing financial interest.

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