# Diverse Fates of β-Silyl Radical under Manganese Catalysis: Hydrosilylation and Dehydrogenative Silylation of Alkenes



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**ABSTRACT** Manganese-catalyzed hydrosilylation of alkenes has been underdeveloped for a long time. Herein, we describe a general, chemo- and regio-selective hydrosilylation of alkenes by using the  $Mn(CO)_5Br$  catalyst with ample substrate scopes. Meanwhile, dehydrogenative silylation of aryl olefins can be selectively achieved upon the catalysis of dinuclear  $Mn_2(CO)_{10}$ . Mechanistic experiments revealed diverse fates of the common intermediate  $\beta$ -silyl radical, namely, hydrogen atom transfer (HAT) for the hydrosilylation and organometallic  $\beta$ -H elimination for the dehydrogenative silylation of olefins.

**KEYWORDS** manganese, hydrosilylation, dehydrogenative silylation, alkene, homogenous catalysis

#### Introduction

Organosilanes have wide applications in organic synthesis and silicon-based materials owing to their stability, non-toxicity, and versatile transformations.<sup>[1]</sup> Hydrosilylation reactions are particular noteworthy methods to straightforwardly access organosilanes with high atom economy.<sup>[2]</sup> As an earth-abundant transition metal, manganese catalyzed hydrosilylation of carbonyls compounds have made impressive success recently.<sup>[3]</sup> In sharp contrast, only sporadic examples of hydrosilylation of C-C unsaturated bonds were reported (Scheme 1a).<sup>[4,5]</sup> In 1983, Faltynek described Mn(CO)<sub>5</sub>(SiPh<sub>3</sub>)-catalyzed hydrosilylation of 1-pentene under UV irradiation or heating conditions.<sup>[4a]</sup> In 1987, Hilal disclosed  $Mn_2(CO)_{10}$  could catalyze hydrosilylation of 1-hexene, unfortunately in low yields.<sup>[4b]</sup> More than a decade later, the same group showed hydrosilylation of 1-octene with a poly(siloxane)-supported dimeric Mn complex.[4c] Recently, the group of Thomas demonstrated an example of hydrosilylation of 1-octene by the cooperative use of a pincer-Mn(II) complex and NaO<sup>t</sup>Bu.<sup>[5]</sup> Though elegant, the thus-far reported manganese-catalyzed hydrosilylation of alkenes was highlighted with only three substrates of aliphatic olefins.<sup>[5b]</sup> A general Mn-catalyzed hydrosilylation of olefins with broad substrate scopes is still underdeveloped.

As our persistent interest on manganese catalysis, <sup>[6,7]</sup> we has recently developed the first manganese-catalyzed hydrosilylation of alkynes.<sup>[8]</sup> Herein, we report a general Mn-catalyzed hydrosilylation of olefins with ample substrate scopes including aryl, benzyl, alkyl and functionalized ones by using the Mn(CO)<sub>5</sub>Br catalyst under mild conditions (Scheme 1b). Meanwhile, the dehydrogenative silylation of olefins was achieved through the catalysis of binuclear Mn<sub>2</sub>(CO)<sub>10</sub>, which represents the first Mn-catalyzed dehydrosilylation reaction of olefins. Remarkably, mechanistic experiments uncovered a radical HAT and organometallic  $\beta$ -H elimination pathway might account for the hydrosilylation and dehydrogenative silylation respectively. Scheme 1 Mn-catalyzed reactions of silanes with alkenes

a) Mn complexes in hydrosilylation of alkenes: previous work



### **Results and Discussion**

#### Results

We commenced our hydrosilylation study with styrene **1a** and benzyldimethylsilane **2a** as model substrates and  $Mn(CO)_5Br$  as a catalyst (Table 1, entry 1). The hydrosilylation product **3aa** was contaminated with dehydrogenative silylation product **4aa**, formed in 38% and 7% yields respectively.  $Mn_2(CO)_{10}$  showed a decreased chemoselectivity (entry 2). The addition of ligands or bases gave only inferior results (entries 3-4).<sup>[9]</sup> In the survey of solvents, non-polar hexane proved to be the best (entries 5-7). Gratifyingly, further variations on substrate ratios resulted in an almost quantitative yield of **3aa** and excellent chemoselectivity (entry 9). Moreover, the reaction temperature could be lowered to 60 °C with even better outcome (entry 10). In addition, the UV irradiation could also promote the hydrosilylation reaction at room temperature in comparable efficiency (entry 11).

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Table 1 Optimization of anti-Markovnikov hydrosilylation <sup>a</sup>

|   | Ph              | у∕~ + н                            | ocat<br>Sol.      | [Mn]<br>Temp         | Ph      | Si) + F   | -h  | Si      |
|---|-----------------|------------------------------------|-------------------|----------------------|---------|-----------|-----|---------|
|   |                 | 1a 2a                              | ı <b>(Si)</b> = : | SiMe <sub>2</sub> Bn | 3aa     |           | 4aa |         |
|   | Entry           | Cot [Mp]                           | Additivo          | 10:20                | Sal     | Yield (%) |     | 200,400 |
|   | Entry           |                                    | Additive          | 18.28                | 301.    | 3aa       | 4aa | Jaa:488 |
|   | 1               | Mn(CO)₅Br                          |                   | 1:1                  | Toluene | 38        | 7   | 5:1     |
| L | 2               | Mn <sub>2</sub> (CO) <sub>10</sub> |                   | 1:1                  | Toluene | 34        | 20  | 1.7:1   |
|   | 3               | Mn(CO) <sub>5</sub> Br             | $AsPh_3$          | 1:1                  | Toluene | 2         | 6   |         |
| C | 4               | Mn(CO) <sub>5</sub> Br             | NaOAc             | 1:1                  | Toluene | 31        | 8   | 4:1     |
|   | 5               | Mn(CO) <sub>5</sub> Br             |                   | 1:1                  | THF     | 2         | 4   |         |
|   | 6               | Mn(CO)₅Br                          |                   | 1:1                  | Heptane | 55        | 7   | 8:1     |
|   | 7               | Mn(CO) <sub>5</sub> Br             |                   | 1:1                  | Hexane  | 70        | 6   | 12:1    |
|   | 8               | Mn(CO) <sub>5</sub> Br             |                   | 2:1                  | Hexane  | 80        | 21  | 4:1     |
|   | 9               | Mn(CO)₅Br                          |                   | 1:2                  | Hexane  | 95        | 1   | >50:1   |
|   | 10 <sup>b</sup> | Mn(CO)₅Br                          |                   | 1:2                  | Hexane  | 98        | <1  | >100:1  |
|   | 11°             | Mn(CO)₅Br                          |                   | 1:2                  | Hexane  | 95        | <1  | >100:1  |

<sup>a</sup> Reaction conditions unless otherwise noted: **1a** (0.2 mmol), **2a** (0.2 mmol), cat. (0.01 mmol, 5 mol%), additive (0.04 mmol), hexane (0.2 M), 150 °C, 12 h,  $N_2$  atmosphere. Yields were determined by <sup>1</sup>H NMR. <sup>b</sup> 4 h, 60 °C. <sup>c</sup> 4 h, RT, UV (380 nm).

Having the optimized conditions established, we explored the ubstrate scope for hydrosilylation of alkenes (Table 2). The reaction occured smoothly with a wide range of aryl olefins bearing both electron-withdrawing and -donating groups (3aa-3la). Various functionalities like halogen and acetoxy groups remained intact after reaction, which provides handles for further synthetic transformations (3ca-ea, 3ia, 3ka). Apart from the phenyl moiety, other aryl groups, such as 2-naphth, 2-py and pentafluorophenyl were also well tolerated affording 3ma-3oa successfully. Moreover, aliphatic olefins were amenable to this method leading to the hydrosilylated products as expected (3pa-3ra). Electron-biased olefins such as *n*-butyl acrylate was also compatible to this protocol (**3sa**). In addition, variantions on the silyl groups including aliphatic or aromatic silanes delivered the corresponding products in good yields (3ab-3ag). Of note, the use of  $Mn_2(CO)_{10}$  under UV irridiation showed an excellent hydrosilylation reactivity as exeplified by **3af**, **3ag**.<sup>[10]</sup>

We next investigated reaction parameters to selectively ccess dehydrogenative silylation product 4 with  $Mn_2(CO)_{10}$  as the catalyst (Table 3). The screening of silanes revealed that more sterically bulky silanes were favored (entries 1-4).<sup>[9]</sup> A series of additives was further explored, albeit giving no better results (entries 5-8).<sup>[9]</sup> We surmised that styrene 2a might play a crucial role as a hydrogen acceptor in the dehydrogenative silylation reaction. Consequently, we enhanced the amount of 2a and, to our delight, the yield of 4aa increased accordingly (entries 9-11). Finally, we selected the parameters in entry 10 as the optimized conditions. Then, the applicability of the dehydrogenative silylation protocol was investigated (Scheme 2). Aryl alkenes with varied substituents were well tolerated to deliver the corresponding products in good yields. Again, the delicate halogen groups maintained intact under reaction conditions, which presented reaction sites for further elaborations. Unfortunately, aliphatic olefins were ineffective in this protocol.

Table 2 Mn-catalyzed hydrosilylation of alkenes



<sup>*a*</sup> **1** (0.5 mmol), **2** (1.0 mmol), Mn(CO)<sub>5</sub>Br (0.025 mmol), hexane (0.2 M), 60 <sup>o</sup>C, 4 h, N<sub>2</sub> atmosphere. Isolated yields were shown. <sup>*b*</sup> 100 <sup>o</sup>C. <sup>*c*</sup> 150 <sup>o</sup>C. <sup>*d*</sup> **1** (0.5 mmol), **2** (0.5 mmol), Mn<sub>2</sub>(CO)<sub>10</sub> (0.025 mmol), hexane (0.2 M), RT, 4 h, N<sub>2</sub> atmosphere, UV (380 nm).

Table 3 Optimization of dehydrogenative silylation <sup>a</sup>

| Ph + 1a             | H Si<br>2 cat. Mn <sub>2</sub> (C<br>Hexane, T | emp. Ph                            | 3<br>3 | + Pr | 4          |  |
|---------------------|--|------------------------------------|--------|------|------------|--|
| Entry               | Ligand/Add                                     | Silane                             | Yield  | (%)  | 3: 4       |  |
| Liniy               | Eigana//taa.                                   | Chano                              | 3      | 4    |            |  |
| 1                   |  | <b>2a</b> 37                       |        | 55   | 1:1.4      |  |
| 2                   |  | 2b                                 | 55     | 45   | 1.2:1      |  |
| 3                   |  | 2c                                 | 40     | 53   | 1:1.3      |  |
| 4                   |  | 2f                                 | 18     | 56   | 1:3        |  |
| 5                   | $AsPh_3$                                       | 2f                                 | 4      | 25   | 1:6        |  |
| 6                   | AgOAc  | 2f                                 | 15     | 30   | 1:2        |  |
| 7                   | LPO  | 2f                                 | 19     | 44   | 1: 2.3     |  |
| 8                   | NaOAc  | 2f                                 | 31     | 52   | 1:1.7      |  |
| 9 <sup>[b]</sup>    |  | 2f                                 | 16     | 66   | 1:4        |  |
| 10 <sup>[b,c]</sup> |  | 2f                                 | 12     | 81   | 1:7        |  |
| 11 <sup>[b,d]</sup> |  | 2f                                 | 9      | 89   | 1:10       |  |
| Ph H<br>2a          | i´ Ph <sup>_SiҢ</sup><br>2b                    | <br>Ph <sup>´</sup> H<br><b>2c</b> | Ph     | Ph   | _Siң<br>2f |  |

<sup>*a*</sup> Reaction conditions: **1a** (0.2 mmol), **2** (0.2 mmol),  $Mn_2(CO)_{10}$  (0.01 mmol, 5 mol%), ligand/add. (0.04 mmol), hexane (0.2 M), 150 °C, 12 h, N<sub>2</sub> atmosphere. Yields were determined by <sup>1</sup>H NMR. <sup>*b*</sup>  $Mn_2(CO)_{10}$  (10 mol%). <sup>*c*</sup> **1a:2a** = 3:1.<sup>*d*</sup>

#### **1a:2a** = 4:1.

Scheme 2 Mn-catalyzed dehydrogenative silylation of alkenes. Reaction conditions: 1 (1.5 mmol), 2f (0.5 mmol),  $Mn_2(CO)_{10}$  (0.05 mmol), hexane (0.2 M), 150 °C, 12 h, N<sub>2</sub> atmosphere. Isolated yields were shown.

 $\begin{array}{c} R \stackrel{||}{=} \\ H \stackrel{||}{=} \\ SiH \\ Ph & 2f \end{array} \begin{array}{c} Mn_2(CO)_{10} (10 \text{ mol}\%) \\ Hexane (0.2 \text{ M}) \\ 150 \,^{\circ}\text{C}, 12 \text{ h} \end{array} \begin{array}{c} R \stackrel{||}{=} \\ R \stackrel{||}{=} \\ H \stackrel{||}{=} \\$ 

To shed light on the mechanisms of these two Mn-catalyzed reactions of alkenes with silanes, we firstly carried out a series of deuterium-labeling experiments (Scheme 3). Treatment of deuterated alkenes  $[D_3]$ -**1e** with silane **2a** under hydrosilylation conditions gave the desired product  $[D_3]$ -**3ea**, in which the hydrogen atom from **2a** was transferred to the benzylic position (Scheme 3a). Meanwhile, the reaction of  $[D_3]$ -**1e** with silane **2f** under dehydrogenative silylation conditions afforded product  $[D_2]$ -**4ef** where one terminal deuterium was replaced by the silyl group (Scheme 3b). When reactions of styrene **1a** with deuterated silane [D]-**2f** were conducted under either hydrosilylation or dehydrogenative silylation conditions, similar phenomena were found (Schemes 3c, d). These results indicated that there was no H-D scrambling in the reactions.



To further probe the mechanistic details of Mn-catalyzed hydrosilylation of olefins, we prepared Mn-Si complex **Mn-I** and Mn-H complexes **Mn-II** and examined stoichiometric reactions of alkene **1a**, silane **2a** with the above manganese complexes (Scheme 4a).<sup>[9]</sup> While the Mn-Si species **Mn-I** gave negative results, the hydrosilylation product **3aa** was detected in a quantitive yield when Mn-H species **Mn-II** was used. It clearly suggested that the Mn-Si complex **Mn-II** wasn't the active intermediate, whereas the Mn-H species **Mn-II** played an essential role in the hydrosilylation reaction. Furthermore, a deuterium labeling stoichiometric reaction was carried out (Scheme 4b), which indicated that the Mn-H species **Mn-II** participated in the C-H/D bond formation of **3af**. The addition of a

radical scavenger, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), had an obvious inhibitory effect on the reaction (Scheme 4c). Moreover, highly selective formation of hydrosilylation products (Table 2, **3af**, **3ag**) was achieved by the use of dinuclear  $Mn_2(CO)_{10}$  under UV irradiation, which was known to deliver manganese radicals (CO)<sub>5</sub>Mn·.<sup>[10]</sup> Additionally, when vinyl cyclopropane **1u** was used, only the ring-opening product **3ua** was detected (Scheme 4d), indicating again a radical pathway. In view that HMn(CO)<sub>5</sub> **Mn-III** could produce (CO)<sub>5</sub>Mn·.<sup>[11]</sup> a plausible mechanism based on a radical pathway is proposed in Scheme 4e. The reaction starts with the generation of HMn(CO)<sub>5</sub> from Mn(CO)<sub>5</sub>Br and silane **2a**. The (CO)<sub>5</sub>Mn· (**Mn-IV**), originating from HMn(CO)<sub>5</sub>. Next, the silyl radical attacks alkene **1** accessing a  $\beta$ -silyl alkyl radical **6a**, which undergoes HAT with HMn(CO)<sub>5</sub>

Scheme 4 Mechanistic studies on anti-Markovnikov hydrosilylation



To obtain more information on mechanism of Mn-catalyzed dehydrogenative silylation of olefins, a sequence of experiments was performed.<sup>[9]</sup> Firstly, the hydrogenation byproduct, ethylbenzene 5a, was ascertained to form in 82% yield, which was consistent with the yield of 4af and conformed the role of styrene 1a as the hydrogen acceptor (Scheme 5a). Next, the stoichiometric reaction of Mn-H species Mn-II with alkenes 1a was examined at high temperature, which demonstrated the generation of 5a (Scheme 5b vs Scheme 4a). Meanwhile, in Scheme 5c, the ratios of H-contents in two positions of byproduct 5t indicated that the Mn-H species participated in the formation of both vicinal C-H bonds of 5t. Consequently, a proposed mechanism for dehydrogenative silvlation is shown in Scheme 5d. Similar to the mechanism of hydrosilylation, the early steps of the dehydrogenative silvlation also lead to the generation of the  $\beta$ -silyl-alkyl radical **6b** from the addition of a silyl radical to the alkene 1a. At this stage, the recombination of the  $\theta$ -silyl-alkyl radical 6b and (CO)<sub>5</sub>Mn· gave an organomanganese species Mn-V, which releases the desired product 4af via a  $\beta$ -H elimination and regenerates HMn(CO)5. Of note, the manganese-phenyl  $\pi$ -interaction may attribute to the formation of **Mn-V**. Meanwhile, the reduction of styrene **1a** by HMn(CO)<sub>5</sub> delivers the byproduct, ethylbenzene **5a**.

 $\label{eq:scheme 5} \begin{array}{l} \mbox{Scheme 5} & \mbox{Mechanistic studies on dehydrogenative silylation, isolated} \\ \mbox{yields were shown} \end{array}$ 



#### Conclusions

In summary, a general manganese-catalyzed hydrosilylation and the first manganese-catalyzed dehydrogenative silylation of olefins are developed by using mononuclear Mn(CO)<sub>5</sub>Br and dinuclear Mn<sub>2</sub>(CO)<sub>10</sub> respectively. Mechanically, a HAT pathway from key  $\beta$ -silyl-alkyl radical intermediates was deemed operative for the hydrosilylation, while an organometallic  $\beta$ -H elimination pathway might account for the dehydrogenative silylation reaction.<sup>[12]</sup> Further explorations on Mn-catalysis based on radical and/or organometallic processes are underway in our laboratory.

## Experimental

In an oven-dried Schlenk tube, a mixture of the alkene (0.5 mmol), the silane (1 mmol),  $Mn(CO)_5Br$  (0.025 mmol, 5 mol%) and hexane (2.5 mL) was stirred at 60 °C for 4 h under N<sub>2</sub> atmosphere. After completion of the reaction, the mixture was cooled down to room temperature. The solvent was removed under reduced pressure and the hydrosilylation product was isolated by column chromatography on silica gel with EtOAc/PE.

Similarly, in an oven-dried Schlenk tube, a mixture of the alkene (1.5 mmol), the silane (0.5 mmol),  $Mn_2(CO)_{10}$  (0.05 mmol, 10 mol%) and hexane (2.5 mL) was stirred at 150 °C for 12 h under N<sub>2</sub> atmosphere. After completion of the reaction, the mixture was cooled down to room temperature. The solvent was removed under reduced pressure and the dehydrogenative silylation product was isolated by column chromatography on silica gel with EtOAc/PE.

# **Supporting Information**

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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#### **Entry for the Table of Contents**

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Diverse Fates of 6-Silyl Radical under Manganese Catalysis: Hydrosilylation and Dehydrogenative Silylation of Alkenes



When a radical meets manganese: A general hydrosilylation of olefins was enabled by the sole catalysis of Mn(CO)<sub>5</sub>Br, while dehydrogenative silylation of aryl olefins was achieved by using dinuclear  $Mn_2(CO)_{10}$ . Mechanistic studies suggested hydrogen atom tranfer (HAT) and organometallic  $\beta$ -H elimination pathways from the  $\beta$ -silyl radical intermediate operating in the hydrosilylation and dehydrogenative silylation of olefins respectively.