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# Mn<sub>2</sub>(CO)<sub>10</sub> and UV light: a promising combination for regioselective alkene hydrosilylation at low temperature

Anthony Vivien,<sup>a</sup> Laurent Veyre,<sup>a</sup> Raphaël Mirgalet,<sup>b</sup> Clément Camp,<sup>a</sup> Chloé Thieuleux\*<sup>a</sup>

The low temperature regioselective hydrosilylation of various alkenes with (1,1,1,3,5,5,5-heptamethyltrisiloxane) MD<sup>H</sup>M is described using Mn<sub>2</sub>(CO)<sub>10</sub> under UV irradiation with Mn loadings as low as 1 mol%, in the absence of additives and with excellent selectivity and yields. The generation of manganese radical allowed to selectively obtain the anti-Markovnikov hydrosilylation products in yields up to 99%.

The catalytic hydrosilylation of alkenes is a major industrial reaction and a very efficient and atom-economical way to obtain organosilane compounds which are widely used in the pharmaceutical industry,<sup>1</sup> organic synthesis<sup>2</sup> and in the materials field.<sup>3</sup> The use of platinum is still widespread for the synthesis of these compounds, so the development of new catalysts remains a major challenge to overcome the high cost and lack of abundance of platinum.

In recent years, attractive molecular non-noble metal complexes have emerged as catalysts to yield selectively the Markovnikov or anti-Markovnikov hydrosilylation or dehydrogenative silylation products of alkenes.<sup>4-8</sup> However, most of these catalysts require several synthesis steps and sophisticated ligands in order to provide good reactivity. Moreover, these complexes remain highly sensitive to air and moisture or require the use of strong reductants or additives for catalyst activation.

Our group has recently shown that non crystalline cobalt nanoparticles, easily synthesized from the commercial precursor Co<sub>2</sub>(CO)<sub>8</sub> at low temperature (60 °C), were extremely active in alkene hydrosilylation with a wide range of olefinic substrates and the industrially relevant tertiary silane 1,1,1,3,5,5,5-heptamethyltrisiloxane, MD<sup>H</sup>M, under mild conditions (30 °C or UV), yielding exclusively the anti-Markovnikov hydrosilylated product.<sup>9</sup> Catalytic tests using the starting Co precursor Co<sub>2</sub>(CO)<sub>8</sub> showed that it could also be used as catalyst but with less selectivity in olefin hydrosilylation reactions as the isomerization of the olefinic reagent occurs. Moreover, when activated by UV light, Co<sub>2</sub>(CO)<sub>8</sub> generated metal aggregates, preventing industrial applications. Nevertheless, these results show that catalytic systems based on commercially available non-noble metal complexes without sophisticated ligands could be of interest in the field of hydrosilylation.

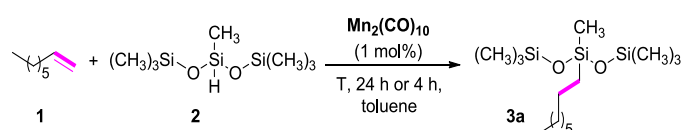
In this context, manganese, which is the third most abundant transition metal in the earth's crust and which is considered as non-toxic,<sup>10</sup> has recently driven major interest to yield molecular complexes used as catalysts in solution, highlighting the potential of manganese in the transformation of various organic substrates.<sup>11-15</sup> Indeed, several significant advances have been made recently in the development of new manganese-based catalysts for hydrosilylation reactions.<sup>16-20</sup> In 2018, Wang's group showed that Mn(CO)<sub>5</sub>Br in presence of triphenylarsine at 150 °C or Mn<sub>2</sub>(CO)<sub>10</sub> with peroxide containing ligands at 120 °C, were able to selectively yield *E* or *Z* alkene products respectively via alkyne hydrosilylation reactions though a radical mechanism.<sup>21</sup> The next year, Zhang and coworkers observed the same type of reactivity using 10 mol% of Mn<sub>2</sub>(CO)<sub>10</sub> under UV light at room temperature in 12 h.<sup>22</sup> Very recently, in the field of alkene hydrosilylation reactions, Xie's group depicted that Mn<sub>2</sub>(CO)<sub>10</sub> with two equivalents of a JackiePhos ligand was able to selectively hydrosilylate alkenes at 120 °C.<sup>23</sup> At the reverse, if one equivalent of *i*PrPNP ligand was introduced, dehydrogenative silylation was selectively observed at 140 °C, again through a radical mechanism.<sup>23</sup> It was proposed that a manganese radical stabilized by the presence of the added ligand was thermally formed upon cleavage of the Mn-Mn bond, such radical being active in hydrosilylation or dehydrogenative silylation reactions.

These pioneer works demonstrate the interest of manganese as alternative to noble metal or other non-noble metal complexes in the field of hydrosilylation. However, it is worth noting that specific ligands were needed and high reaction temperature were used in such major literature precedents.

In this context, we explored the possibility to selectively perform alkene hydrosilylation using simpler catalytic systems based on manganese and smoother reaction conditions and we demonstrate here that Mn<sub>2</sub>(CO)<sub>10</sub> under UV irradiation is able to selectively convert functional alkenes into the desired anti-Markovnikov product at room temperature without additives or external ligands and at low Mn loading (1 mol%).

As initial catalytic tests, octene hydrosilylation with MD<sup>H</sup>M was carried out using a 1:2 molar ratio of alkene:silane. The reaction was set under argon in a 4 mL vial with a concentration of 0.825 M for *n*-octene (74  $\mu$ L, 0.47 mmol) and 1.650 M for MD<sup>H</sup>M (256  $\mu$ L, 0.94 mmol). Then, 100  $\mu$ L of a 47 mM toluene solution of Mn<sub>2</sub>(CO)<sub>10</sub> (i.e. a Mn loading of 1 mol% in the test) was injected and toluene was added to obtain a total volume of 571  $\mu$ L. As shown in Table 1 (entries 1-3), thermal activation (with reaction temperatures from 30 °C to 100 °C) did not yield the hydrosilylation product and no conversion of the reactants was observed. In contrast, exposing Mn<sub>2</sub>(CO)<sub>10</sub> to UV light (300 W,  $\lambda$  = 250-420 nm) allowed to selectively convert octene into the anti-Markovnikov hydrosilylation product with 94% yield after 4 hours (entry 4). It is worth noting that no trace of alkene isomerization nor dehydrogenative silylation products were detected, which are commonly observed side reaction products.<sup>24-26</sup> Increasing the alkene:silane ratio from 1:2 to 1:1 and 2:1 (entries 5 and 6 respectively) led to reasonable decrease of the hydrosilylation yields (from 94% to 78% for the 1:1 ratio and 86% for the 2:1 ratio) and minimal increase of octene isomerization (1% for the 1:1 ratio and 3% for the 2:1 ratio).

**Table 1.** Thermal activation vs UV activation.

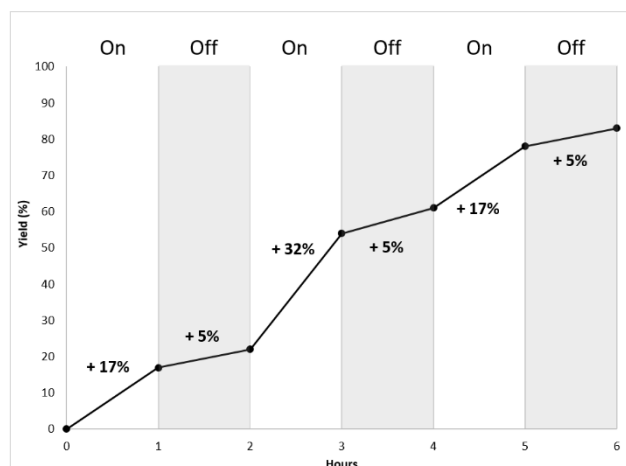


#	Conditions	Conc. 1 (M)	Conc. 2 (M)	yield of 3 (%)	Isom. of 1 (%)
1	30 °C, 24 h	0.825	1.650	n.p	n.p
2	60 °C, 24 h	0.852	1.650	n.p	n.p
3	100 °C, 24 h	0.825	1.650	n.p	n.p
4	UV, 4 h <sup>a</sup>	0.825	1.650	94%	n.p
5	UV, 4 h <sup>a</sup>	1.650	1.650	78%	1%
6	UV, 4 h <sup>a</sup>	3.3	1.650	86%	3%

n.p: no product. Conditions: *n*-octene (74-296  $\mu$ L, 0.47-1.88 mmol), MD<sup>H</sup>M (256  $\mu$ L, 0.94 mmol), mesitylene as GC standard (46  $\mu$ L, 0.335 mmol), Mn<sub>2</sub>(CO)<sub>10</sub> (4.7-9.4  $\mu$ mol, 1 mol %), toluene (21-95  $\mu$ L).<sup>a</sup> UV irradiation does not lead to a significant increase of temperature (<45 °C).

It is worth noting that, in our experimental conditions, UV irradiation did not lead to a significant increase of reaction temperature (measured temperature at the end of the reaction is <45 °C).

To show the importance of UV irradiation for the reaction outcome, an on/off experiment was performed by alternatively exposing the reaction mixture to UV light for one hour and to darkness for the same duration, during 6 hours in total. A clear correlation between the light exposure and the reaction rate was observed (Figure 1). Indeed, 17% yield of hydrosilylation product was detected after one hour of UV irradiation exposure while, in the dark, only 5% of product was generated. This result is even more obvious during the second hour of UV light exposure where an extra increase in yield of more than 32% (cumulative yield of 54%) was observed vs a 5% of yield increase (cumulative yield of 59%) was detected after the second hour in darkness. Again, after a third hour of UV light exposure, an extra increase in yield of 17% (cumulative yield of 78%) was observed vs a 5% of yield increase (cumulative yield of 83%) after a third hour in darkness. This result shows that, in the absence of UV irradiation, the kinetics of the reaction drastically decrease.



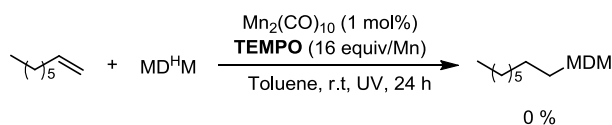
**Figure 1.** UV "on/off" experiment.

To show that the catalytic active species is a radical, we decided to perform a radical trapping experiment using TEMPO to quench the radical formation during the reaction between octene and MD<sup>H</sup>M in the presence of Mn<sub>2</sub>(CO)<sub>10</sub> (Scheme 1a).

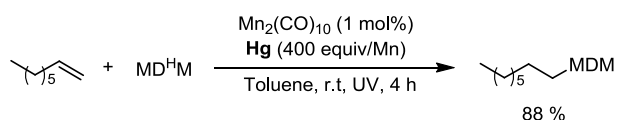
This reaction was performed using the standard conditions as depicted above with alkene:silane ratio of 1:2 and the addition of 16 equiv. of TEMPO with respect to Mn (see SI for details). After 24 hours under UV light, no conversion of the starting materials was detected, showing the pivotal role of the radical for the reaction outcome. In addition, in order to show that the activity did not result from the formation of active manganese particles during the reaction, a mercury test was performed as using 400 equiv. of Hg with respect to Mn (Scheme 1b - see SI for details). It appeared that the presence of Hg has no impact on the reaction, yielding 88% of the anti-Markovnikov hydrosilylation product.

To study the versatility of this catalytic system, we explored the hydrosilylation of various alkenes and the results are summarized in Table 2. In the case of hexene, we quantitatively obtained the anti-Markovnikov hydrosilylation product (>99%) without any trace of hexene isomerization (entry 2). The same result was observed when working with styrene and allylbenzene (yields >99% - entries 3-4). Using 4-phenyl-1-butene, a slightly lower yield of 80% in anti-Markovnikov hydrosilylation product was obtained, still without any trace of isomerization (entries 3-5).

a) Radical trapping experiment



b) Mercury test



**Scheme 1.** Mechanistic studies. GC yields. Conditions: *n*-octene (74 μL, 0.47 mmoles), MD<sup>H</sup>M (256 μL, 0.94 mmoles), mesitylene as GC standard (46 μL, 0.335 mmoles).

Then, we were interested in allyl-ether type substrates known for their difficulty to be selectively hydrosilylated as C=C isomerization and C–O cleavage were frequently observed.<sup>27-28</sup> In the case of phenyl allyl ether, the anti-Markovnikov product **3f** was quantitatively yielded. The reactivity was slightly lower with butyl allyl ether and allyloxytrimethylsilane, yielding 70% and 77% of hydrosilylation product, respectively (entries 7 and 8). Moderate yields were obtained with allylacetate (47% - entry 9). It is important to note that no C=C isomerization nor C–O cleavage products were observed and only the anti-Markovnikov product is obtained. When using tert-

butylacrylate as an illustrative example of electron deficient alkenes, no hydrosilylated product was detected and a complex mixture of unknown products was obtained (entry 10).

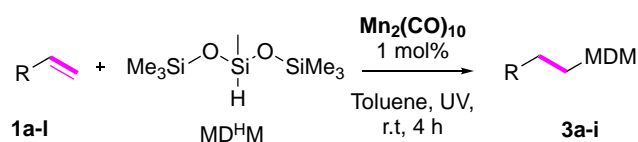
In the case of gem-alkenes and internal alkenes, only starting materials were recovered (entries 11-13). For gem-alkenes, steric hindrance due to the geminal nature of the alkene could explain this lack of reactivity. For internal alkenes, the inability of the catalyst to isomerize the internal double bond prevents the chain-end reactivity to form the anti-Markovnikov product.

Finally, we decided to investigate the capacity of our catalytic system to hydrosilylate 1-octene with other silanes than MD<sup>H</sup>M. Phenylsilane (PhSiH<sub>3</sub>), triethylsilane (Et<sub>3</sub>SiH) and triethoxysilane ((EtO)<sub>3</sub>SiH) were thus tested (see ESI, Table S1). While no reaction occurred with PhSiH<sub>3</sub>, our catalytic system allowed to selectively hydrosilylate 1-octene with Et<sub>3</sub>SiH and (EtO)<sub>3</sub>SiH, leading to the anti-Markovnikov product albeit with lower yields (20% and 46% respectively) along with 10 to 15% of internal octene isomers.

To conclude, we have shown here that it is possible to perform selective anti-Markovnikov hydrosilylation reactions on a variety of terminal alkenes with MD<sup>H</sup>M, starting from the commercially available Mn<sub>2</sub>(CO)<sub>10</sub> precursor by simply using UV light as the activation source. This reaction was performed under mild conditions (RT) with Mn loading as low as 1 mol%, in the absence of additives and with excellent selectivity and yields. This work confirms that manganese is a promising candidate as a non-noble metal catalyst for hydrosilylation reactions and opens the way to other possible reactivities.

**Table 2.** Mn-catalyzed terminal alkenes with

hydrosilylation of various MD<sup>H</sup>M.



Entry	Product	yield(%)
1	 <b>3a</b>	<b>94 (85)</b>
2	 <b>3b</b>	<b>&gt;99 (83)</b>
3	 <b>3c</b>	<b>&gt;99 (84)</b>
4	 <b>3d</b>	<b>&gt;99 (79)</b>
5	 <b>3e</b>	<b>80 (72)</b>
6	 <b>3f</b>	<b>&gt;99 (84)*</b>
7	 <b>3g</b>	<b>70 (59)*</b>
8	 <b>3h</b>	<b>77 (68)</b>
9	 <b>3i</b>	<b>47 (34)*</b>
10	 <b>3j</b>	<b>Complex mixture</b>
11	 <b>3k</b>	<b>n.p</b>
12	 <b>3l</b>	<b>n.p</b>
13	 <b>3m</b>	<b>n.p</b>

Yields are determined by GC and the yield in brackets refers to the isolated yield. n.p: no product. Conditions: alkene (0.47 mmol, 0.825 M, 1 equiv.), MD<sup>H</sup>M (256  $\mu$ L, 0.94 mmol, 1.650 M, 2 equiv.), mesitylene as GC standard (46  $\mu$ L, 0.335 mmol), Mn<sub>2</sub>(CO)<sub>10</sub> (47  $\mu$ mol, 1 mol %), toluene (91–171  $\mu$ L).\*Some minor impurities are present in the final product and visible in the NMR spectra.

## Author Contributions

A.V. performed all the chemical reactions. L.V., C.C. and C.T. supervised the work. A.V., L.V., R. M., C.C. and C.T. participated to the writing and revising of the draft. R. M. and C.T. found the funds and administrated the project. All authors have read and agreed to the published version of the manuscript.

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## Conflicts of interest

There are no conflicts to declare.

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