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White-Light initiated $Mn_2(CO)_{10}$/HFIP-Catalyzed *anti*-Markovnikov hydrosilylation of alkenes

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ABSTRACT

This study presents a highly efficient and mild method for radical hydrosilylation of alkenes. The reaction proceeds under white-light, in the presence of $Mn_2(CO)_{10}$ pre-catalyst and HFIP as an additive, at r.t. and under air. Under white-light, [Mn]• is generated, which activates the Si–H-group to form Si• and trigger the autocatalytic process. HFIP acts as a unique activator which enables synthesis of the products with yields close to quantitative and with *anti*-Markovnikov selectivity. The method is applicable to terminal alkenes, including those with O-, N- and halogen-containing functional groups, styrene and allylbenzene derivatives, etc., as well as to a wide range of alkyl-, phenyl-, siloxy- and alkoxy-containing tertiary hydrosilanes. These conditions turned out to be most efficient for hydrosilylation of gaseous reagents such as ethylene and acetylene. In both cases the products showed quantitative yield at 1 atm and at r.t. The method is easily up-scalable in batch- and flow-modes.

1. Introduction

Hydrosilylation of unsaturated hydrocarbons is a key atom-economical method for creating Si–C-bond [1–5]. Organosilicon compounds are broadly applied in different areas from medicine and agriculture to construction and aerospace [6–9].

This process became the first example of the up-scaled application of homogeneous catalysis in industry after Speier [10], and later Karstedt [11], proposed the use of Pt-compounds as hydrosilylation catalysts [1–5,12]: H_2PtCl_6 (Speier's catalyst) and $Pt_2(dvtms)_3$ (where dvtms is divinyltetramethyldisiloxane, i.e. Karstedt's catalyst). However, the difficulty in separating these catalysts leads to contamination of silicone products, environmental pollution, and irreversible "scattering" of platinum [3]. Due to the high cost of platinum, its contribution to silicone products is as high as 30 % [4]. Several main approaches aimed at solving these problems include the development of new selective and active homogeneous catalysts [13–20], application of recyclable heterogeneous [21–27] and heterophase [28–35] (biphase) catalytic systems, transition to cheaper and more accessible earth-abundant metal [3,4,36–38] catalysts.

Fe-, Co-, Ni-, and Mn-catalyzed hydrosilylation significantly improved in the last two decades. Catalysts even superior to homogeneous Pt-catalysts in their activity and selectivity [3,4,36,37] were developed. The use of primary (mono-substituted trihydrosilanes) and secondary silanes (di-substituted dihydrosilanes) showed high selectivity in the hydrosilylation of functionalized unsaturated compounds. Hydrosilylation using industrially more valuable tertiary silanes (trisubstituted hydrosilanes) is developed much less [3,4,36–39]. There are not many easy-to-handle catalysts based on earth-abundant metals, which do not require multistep synthesis techniques, the use of an inert atmosphere, expensive and inaccessible ligands, reducing agents, activators, etc. [3,4,40]. Research aimed at solving these problems is ongoing and significant progress has already been made [3,4,36–45]. However, earth-abundant metal catalysts have not yet found industrial application.

The aim of the present study was to develop a simple and air-stable

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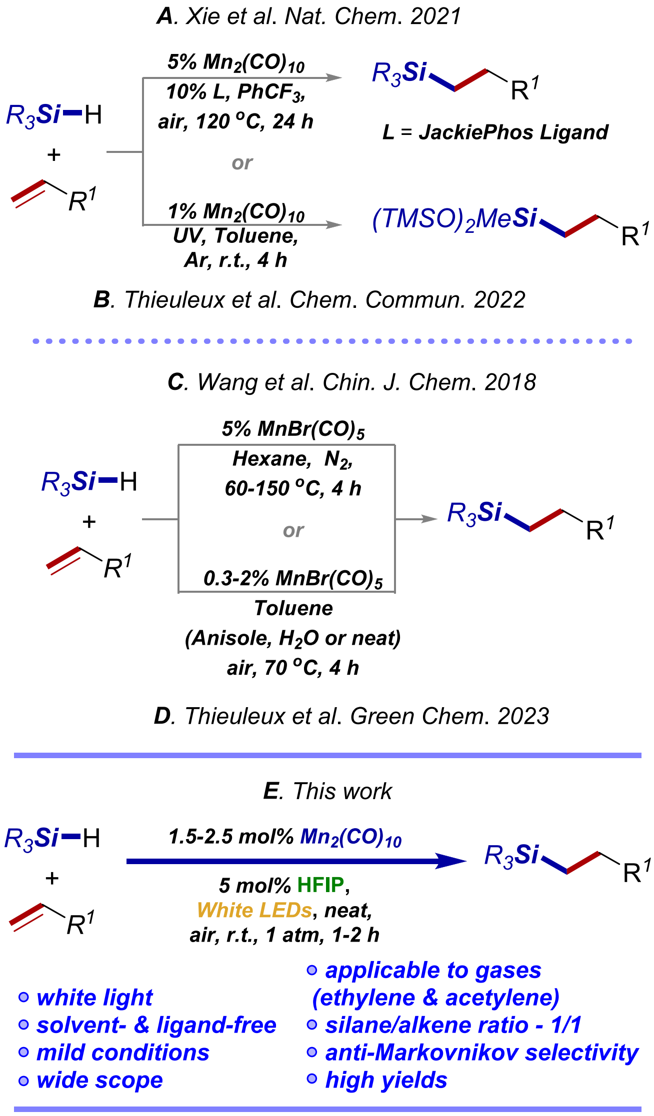


Fig. 1. Previous and this work.

catalytic system based on a commercially available earth-abundant metal pre-catalyst, which performs under mild reaction conditions, does not require the use of a solvent and expensive ligands, and is applicable to tertiary silanes.

Metal carbonyls [46–48] are among the promising metal catalysts. Depending on their type and structure their physicochemical [49] and biochemical [50,51] properties can vary significantly. There are some common characteristics that unite them. Thanks to the M–center being bound to CO and being in a reduced form, metal carbonyls can be used without expensive ligands and external reducing agents. Such complexes are highly soluble even in low-polarity media. It is important in the synthesis of highly hydrophobic organosilicon compounds.

The first reports on the possibility of using metal carbonyls as catalysts for hydrosilylation appeared in the second half of the 20th century [52–55]. A special place among them is occupied by $Mn_2(CO)_{10}$. In recent years, works have been published where $Mn_2(CO)_{10}$ showed itself as an efficient catalyst [56–62], mainly for the hydrosilylation of unsaturated hydrocarbons [63–66]. Thanks to the low energy of Mn–Mn-bond (185 kJ/mol) [67], a reactive Mn-centered radical can participate in atom transfer reactions [57,58,68–72]. For example, Xie et al. [65] developed thermally initiated (at 120 °C) $Mn_2(CO)_{10}$-catalyzed hydrosilylation of alkenes in the presence of JackiePhos ligand in trifluorotoluene solvent (Fig. 1 ***A***). Thieuleux et al. [66] proposed UV-light-promoted $Mn_2(CO)_{10}$-catalyzed hydrosilylation of alkenes with bis(trimethylsiloxy)methylsilane in toluene solvent (Fig. 1 ***B***). $MnBr(CO)_5$ should also be mentioned as an efficient catalyst for hydrosilylation of alkenes in thermally initiated conditions. It was studied by Wang et al. [73] and Thieuleux et al. [45] (Fig. 1 ***C*** & ***D***).

In the present work, a mild white-light initiated $Mn_2(CO)_{10}$/HFIP-catalyzed solvent- and ligand-free selective *anti*-Markovnikov hydrosilylation has been developed (Fig. 1 ***E***). This method is applicable to a range of alkenes, including gaseous reagents such as ethylene and acetylene, as well as to alkyl-, aryl- and siloxy-containing tertiary silanes.

2. Materials and methods

All the starting materials were purchased from Acros, TCI Chemicals and Sigma Aldrich companies and used as supplied.

Batch scaling procedure: A mixture of **1a** (4.5 mmol, 0.5 g, 1 eq) and **2d** (4.5 mmol, 1 g, 1 eq) was added to $Mn_2(CO)_{10}$ (0.113 mmol, 44 mg, 0.025 eq), then HFIP (0.225 mmol, 20 µl, 0.05 eq) was added. The reaction mixture was stirred in culture tube for 24 h under white LEDs irradiation at 30–40 °C. The resulting mixture, consisting of a liquid product and Mn-sediment, was centrifuged (20 min, 4500 rpm); the product **3ad** was decanted from the sediment. The GLC yield was 92 %. To get rid from unreacted reagents, the product was additionally dried (40 °C, 20 mbar). **3ad** was obtained as colorless oil in 90 % yield (1.35 g).

Flow scaling procedure: **1a** (4.5 mmol, 0.5 g, 1 eq), **2d** (4.5 mmol, 1 g, 1 eq), $Mn_2(CO)_{10}$ (0.113 mmol, 44 mg, 0.025 eq) and HFIP (15.21 mmol, 1.6 ml, 3.38 eq) were mixed in opaque bottle. Using syringe pumps, the solution was injected (at 0.002 ml/min) via needle into air stream (0.025 ml/min) in a PTFE tube (length – 3 m, internal diameter – 1 mm), which was rolled into rings. The PTFE tube was irradiated under white LEDs, retention time was 60 min. Resulting biphasic mixture was collected; upper layer is 95 % pure **3ad**, lower phase – Mn-species, dissolved in HFIP. The upper phase was decanted and dried (40 °C, 20 mbar). **3ad** was obtained as colorless oil in 95 % yield (1.42 g).

3. Results and discussion

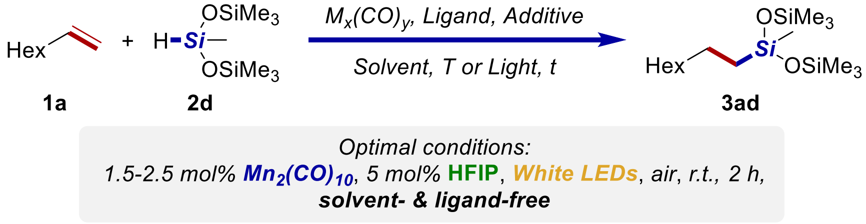
3.1. Reaction Optimization

A hydrosilylation reaction involving 1-octene **1a** (1 eq., 0.45 mmol, 50.1 mg) and bis(trimethylsiloxy)methylsilane **2d** (1 eq., 0.45 mmol, 100 mg) was selected as a model reaction. In the presence of $Mn_2(CO)_{10}$ (5 mol%) at 120 °C for 24 h, without any solvents, ligands, additives or inert atmosphere, the *anti*-Markovnikov addition product **3ad** was obtained in quantitative yield ($\geq$95 %; entry 1, Table 1). Other carbonyl complexes were found to be less active under the same conditions (entries 2–4, Table 1; Tables S1 & S2, Supp. Inf.). Lowering the temperature to 100 °C reduced the yield of **3ad** to 70 % (entry 5, Table 1). The use of additives, ligands or a solvent did not increase the yield of **3ad** (Tables S4 & S5, Supp. Inf.).

To soften the reaction conditions, we switched from the thermally initiated version of the reaction to the photo-initiated one. Under white-light at r.t., $Mn_2(CO)_{10}$ yields 40 % **3ad**; a lower yield was observed with $MnBr(CO)_5$ (31 %), while other carbonyl complexes were shown to be significantly less active (entries 6–8, Table 1; Tables S6 & S7, Supp Inf.). It should be noted, that the yields of **3ad** were significantly lower than in the thermally initiated mode of the reaction, however $Mn_2(CO)_{10}$ in white-light mode was more active than other carbonyl complexes (Table 1; Tables S1, S2, S6 & S7, Supp Inf.).

The study of the effect of additives of different natures on the yield of **3ad** under white-light initiated $Mn_2(CO)_{10}$-catalyzed hydrosilylation conditions gave unexpected results (Table S8, Supp. Inf.). When only 5 mol% of trifluoroethanol (TFE) or hexafluoroisopropanol (HFIP) were added to $Mn_2(CO)_{10}$, the yield of **3ad** was as high as 90 % or $\geq$ 95 %,

Table 1
Optimization of the reaction conditions.



Entry	*T or Light*	*[M]*	*Additives*	*t*	*Yield*
1	120 C°	5 % $Mn_2(CO)_{10}$	–	24 h or 2 h	≥95 %
2	120 C°	10 % $CpMn(CO)_3$	–	24 h	0 %
3	120 C°	10 % $Fe(CO)_5$	–	24 h	22 %
4	120 C°	5 % $Re_2(CO)_{10}$	–	24 h	50 %
5	100 C°	5 % $Mn_2(CO)_{10}$	–	24 h	70 %
6[a]	White-light	5 % $Mn_2(CO)_{10}$	–	24 h	40 %
7[a]	White-light	5 % $MnBr(CO)_5$	–	24 h	31 %
8[a]	White-light	5 % $Re_2(CO)_{10}$	–	24 h	7 %
9[a]	White-light	5 % $Mn_2(CO)_{10}$	5 % TFE	24 h	90 %
10[a]	White-light	5 % $Mn_2(CO)_{10}$	5 % HFIP	24 h or 2 h	≥95 %
11[a]	White-light	5 % $MnBr(CO)_5$	5 % HFIP	24 h	<5%
***12*[a]**	**White-light**	**2.5 % $Mn_2(CO)_{10}$**	**5 % HFIP**	**1–2 h**	**≥95 %**

Reaction conditions: A mixture of **1a** (0.45 mmol, 50.1 mg, 1 eq) and **2d** (0.45 mmol, 100 mg, 1 eq) was added to $M_x(CO)_y$ (0.0113–0.045 mmol, 0.025–0.1 eq), then additive (0.0225 mmol, 0.05 eq; entries 8–10) was added. The reaction mixture was stirred in Schott culture tube for 2–24 h under light-irradiation at r.t. or in darkness at 120 °C. The yield of **3ad** was determined by GLC and ^1H NMR. *Note: (a)* white-light-irradiation does not lead to a significant increase of temperature (30–40 °C).

respectively (entries 9 & 10, Table 1). However, the use of other carbonyl complexes showed either insufficient increase in activity ($Fe(CO)_5$, $Mo(CO)_6$ and $Co_2(CO)_8$) or the same activity ($Re_2(CO)_{10}$), or a dramatic drop of activity ($MnBr(CO)_5$, entry 11, Table 1; Table S9 & S10, Supp. Inf.). The use of aliphatic and aromatic organic alcohols (^{i}PrOH, PhOH, etc.) or F-containing organic compounds ($PhCF_3$, $PhC(O)CF_3$, etc.) does not have such an activating effect (Table S8, Supp. Inf.). There are references in the literature that in $Mn_2(CO)_{10}$-catalyzed radical transformations, the use of HFIP as a solvent significantly increases the reaction efficiency [74,75]. HFIP is characterized by a unique set of physicochemical properties, one of which is its ability to stabilize ionic and radical intermediates formed in various transformations [76–78]. To the best of our knowledge, this is the first example where HFIP works as an effective additive in $Mn_2(CO)_{10}$-catalyzed reactions (at such low loadings – 5 mol%).

Investigation of the effect of loading of $Mn_2(CO)_{10}$ and HFIP, the nature of the solvent and atmosphere, the wavelength of light as well as kinetic studies enabled optimal reaction conditions under which the quantitative yield of product **3ad** is achieved (entry 12, Table 1; Table S9-S15, Supp. Inf.): white-light, 2.5 mol% of $Mn_2(CO)_{10}$, 5 mol% of HFIP, neat, under air at r.t., 1–2 h.

3.2. *Scaling*

We also showed that this reaction can be scaled-up in a batch and flow mode (Sections S4 & S5, Supp. Inf.). Up-scaling the reaction 10-fold in a batch-reactor showed that the white-light initiated $Mn_2(CO)_{10}$/HFIP-catalyzed hydrosilylation is also effective and results in 90 % yield of **3ad** in 3–5 h (Fig. 2 ***A***).

To switch from batch conditions to a flow reactor, several problems needed to be solved, e.g. precipitation of Mn-containing sediment with release of CO. The optimal solution was to increase the HFIP loading (42 or 338 mol%) and carry out the process in biphasic air–liquid mode (Section S5, Supp.Inf.). HFIP prevents sediment from sticking to the walls of a flow reactor, whilst air bubbles withdraw CO from a liquid phase. Additional benefit of using segmented air–liquid flow is the improved mass transfer in both phases thanks to enhanced circulation mixing [79]. Carrying out the reaction in a flow regime with 60–80 min retention time resulted in 95 % yield (Fig. 2 ***B***). Moreover, with increased HFIP loading (168–338 mol%) the system becomes heterophase (biphase) at high conversions whilst initially the mixture is homogeneous (Fig. 2 ***C***). This makes it possible to separate the product from the catalytic system by simple decanting, and the HFIP can be easily separated from the sediment and reused.

3.3. *Insight into the mechanism*

A series of experiments were carried out to investigate the mechanism (Section S6, Supp. Inf.).

We combined *in situ* FTIR spectroscopy which is sensitive to the ligand shell of the catalytic centers and the metal specific Mn K-edge X-ray absorption spectroscopy (XAS) (Fig. 3; Sections S6.8 & S6.9, Supp. Inf.). Under optimal conditions within 1–2 h FTIR and X-Ray spectra showed decreased intensity of $Mn_2(CO)_{10}$ signal up to its complete disappearance (Fig. 3 ***A*** **&** ***B***). It was kinetically coupled to the disappearance of ν(Si–H) and ν(C=C) bands (Fig. 3 ***A***), evidencing almost complete conversion of **1a** and **2d** in 1–2 h (entry 10, Table 1). It is important to note, that HFIP is not coordinated with the Mn-center (Fig. 3 ***A*** **&** ***B***), and the rate of $Mn_2(CO)_{10}$ decomposition to Mn-sediment is the same both in the presence and absence of HFIP (Fig. 3 ***A***).

In the course of the reaction CO is released with initial formation of Mn-clusters and NPs (general formula $Mn_x(CO)_y$) and further formation of the Mn-containing sediment. According to XAS and EDS-SEM, Mn-sediment is not metallic, but is a mixture of Mn-oxides (Fig. 3 ***B***; Sections S6.8 & S6.10, Supp.Inf.).

It was shown that after filtering the Mn-containing precipitate after 10 or 30 min from the start of the reaction, the reaction rate and overall yield of **3ad** did not change (*i.e.* for 2 h the yield of **3ad** was ≥ 95 %; Section S6.1, Supp. Inf.). Addition of mercury at different stages of the reaction also had no effect on the yield of the **3ad** product (Fig. 4 ***A***; Section S6.2, Supp. Inf.). This indicates that the Mn-particles precipitated during the reaction are not catalytically active.

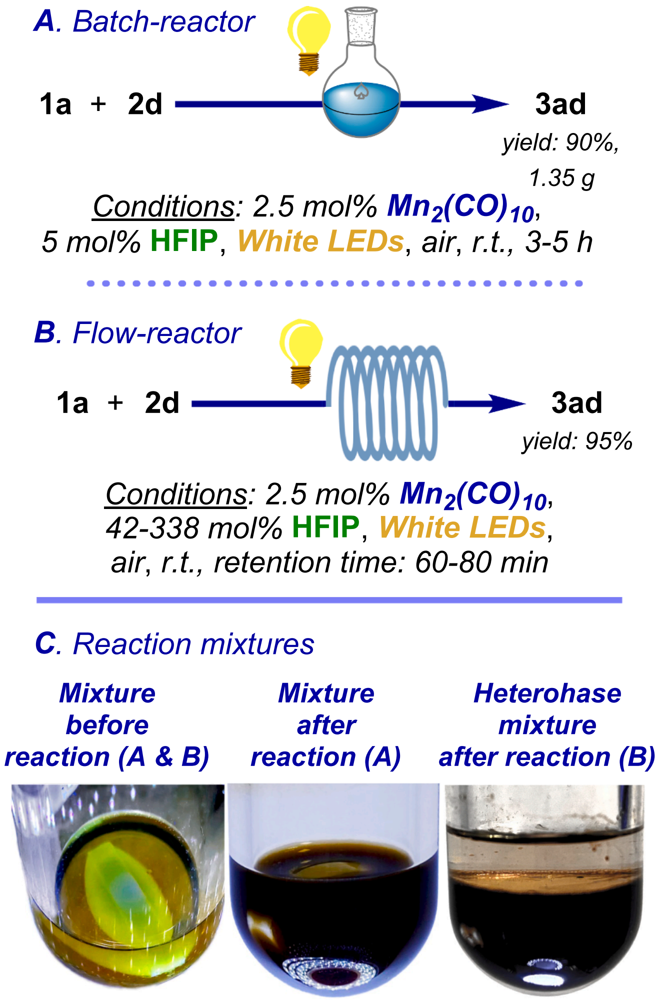


Fig. 2. Reaction scaling. Batch- and flow-reactors.

As we know from the literature, catalytically active [Mn]–H-intermediates can be formed during the reaction [63–65]. In this case, the addition of trityl cation ($Ph_3C^+BF_4^-$) as a hydride abstractor for organometallic compounds should suppress the reaction [80,81]. However, this did not occur under the conditions we used, unlike the conditions of Zhang et al. [64]. A slight drop in the yield of **3ad** to 74 % was observed (Fig. 4 ***A*** Section S6.3, Supp. Inf.). It can be explained by the interaction of $Ph_3C^+BF_4^-$ with hydrosilane **2d**. No formation of the corresponding disilane was observed when triethylsilane (**2a**) or silane **2d** were kept under optimal conditions (Section S6.5, Supp. Inf.). It is additional evidence of the absence of catalytically active [Mn]–H-intermediates.

The addition of TEMPO (or DMPO) as a radical trap prior or after (10 min) the reaction prevents further reaction (Fig. 4 ***A***; Section S6.4 & S6.12, Supp. Inf.). Analysis of the reaction mixture after the addition of TEMPO using HRMS ESI revealed an adduct of TEMPO and a Si-centered radical formed from **2d** – **TEMPO-2d** (Section S6.11, Supp. Inf.). EPR study of the reaction mixture after the addition of DMPO as a spin-trapping reagent [65] also proves a radical reaction mechanism (Section S6.12, Supp. Inf.).

The reaction of 1-octene **1a** (1 eq.) with Et_3SiH **2a** (0.5 eq.) and Et_3SiD **2a**-D (0.5 eq.) gives a mixture of *anti*-Markovnikov addition products **3aa** and **3aa**-D with a ratio of 1.8/1 (**3aa**/**3aa**-D) and a total yield of 80 % (KIE = 1.8, Fig. 4 ***B***; Section S6.6, Supp. Inf.). This confirms the presence of the HAT process [64].

Light on/off experiments showed that the reaction in the dark, although slowing down, continues to proceed (Section S6.7, Supp. Inf.). Within the first 60 min of reaction the yield of **3ad** increased by 10–15 % within every 10 min under light, and by 5 % within every 10 min in the dark (Fig. 4 ***C***). As a result, the quantitative yield of **3ad** in this regime is achieved in 3–4 h. It appeared that white-light initiation of the reaction during the first 5–10 min is sufficient for quantitative conversion of **1a** and **2d** to **3ad** in 5–7 h. It is worth noting that increasing the HFIP loading from 5 % to 20 % in the 5–10 min white-light initiation mode enables quantitative yields as quickly as in 2–3 h.

The experimental data obtained indicate a radical autocatalytic mechanism of the reaction (Fig. 4 ***D***). Affected by white-light $Mn_2(CO)_{10}$ decomposes into $(CO)_5Mn\bullet$, which reacts with [Si]–H and generates [Si]•. The latter gets attached to the double C=C-bond to form a

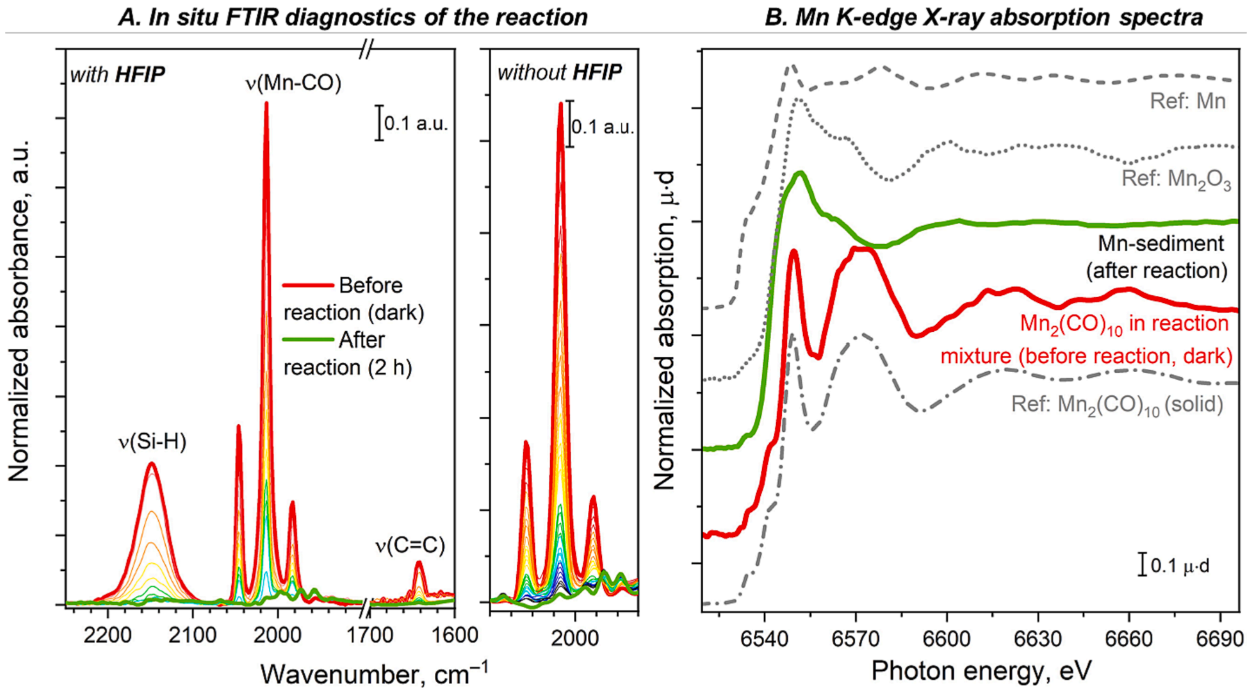


Fig. 3. FTIP and XAS data.

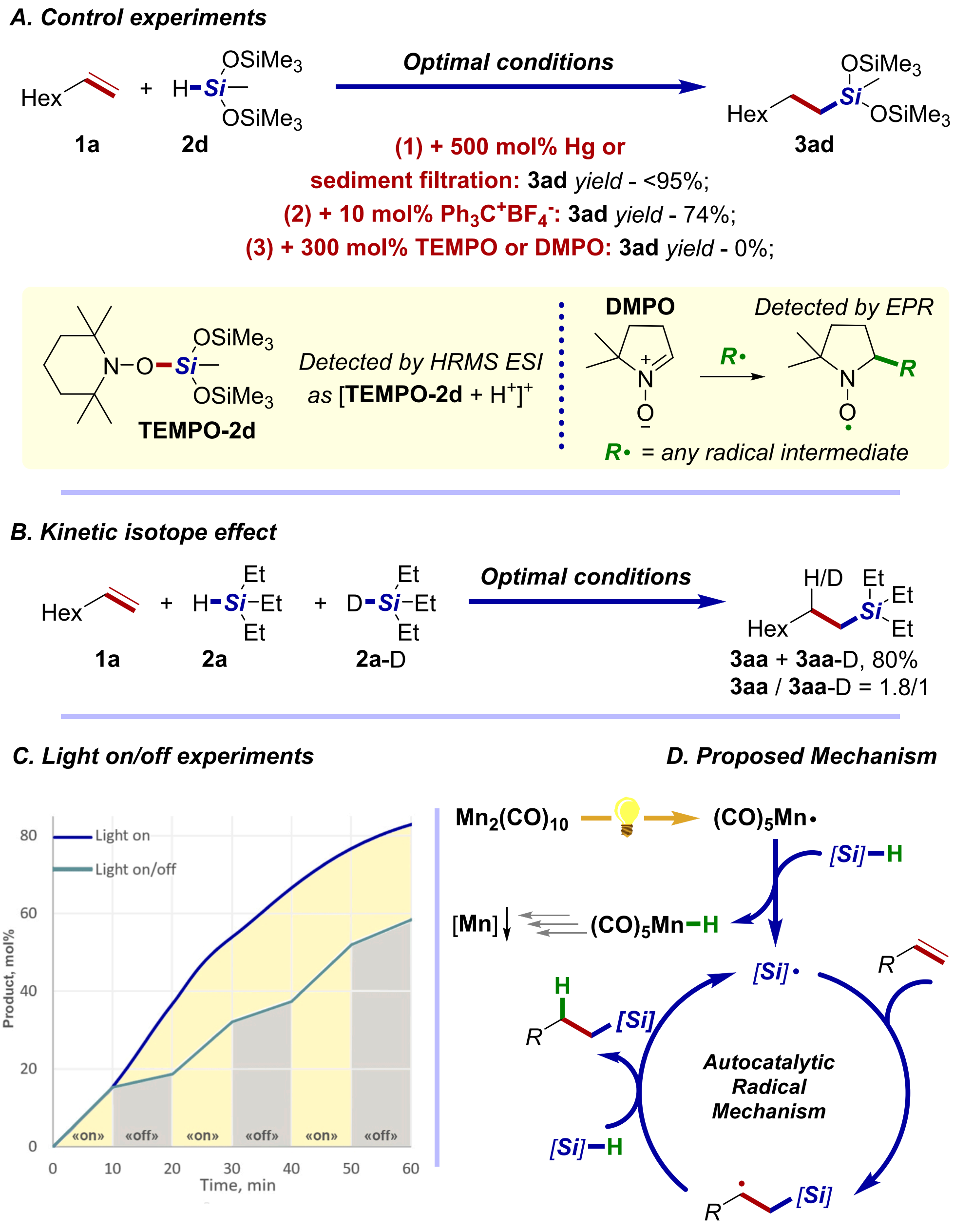


Fig. 4. Mechanistic Experiments.

secondary C-centered radical, the interaction of which with [Si]–H leads to the formation of an *anti*-Markovnikov reaction product and generation of [Si]•, closing the catalytic cycle. Catalytic activity of [Mn]–H-intermediates, described in previous studies [63–65], was not observed under our conditions (Fig. 4 ***A*** & ***D***).

The role of HFIP in this reaction is probably to stabilize the Si- and C-centered radicals [76–78] formed in the autocatalytic radical process (Fig. 4 ***D***).

3.4. Scope

The efficiency of the white-light Initiated $Mn_2(CO)_{10}$/HFIP-catalyzed hydrosilylation of alkenes with tertiary silanes of various nature was studied (Fig. 5; Section S7, Supp. Inf.). The products were studied using 1D and 2D ^1H,^{13}C and ^{29}Si NMR spectroscopy.

At the first stage we studied different hydrosilanes with alkyl-, phenyl-, and siloxy-containing groups **2a-i** in the reaction with 1-octene **1a** (Fig. 5). Selective formation of the *anti*-Markovnikov addition product was observed with all silanes. With triethylsilane **2a**, the yield of the product **3aa** is 80 %, which is significantly higher than with Karstedt's catalyst (25 %; Supp. Inf.) and with thermally initiated $Mn_2(CO)_{10}$/JackiePhos- and $MnBr(CO)_5$-catalyst systems [65]. Hydrosilylation of 1-octene **1a** involving a wide range of mono(siloxy)- and bis (siloxy)-hydrosilanes **2b-g** led to the formation of the products **3a**(**b-g**) in near-quantitative yields (88–97 %). The reaction successfully proceeded with sterically hindered tris(siloxy)silane **2h** (96 %) and bis (siloxy)silane **2i** (79 %) [82]; with the use of Karstedt's catalyst – 13 % (**2h**) and 51 % (**2i**) (Supp. Inf.). Moreover, up to 80 % yield was observed with bis(*tert*-butoxy)methylsilane **2j** (note *c*, Fig. 5). However, this method is not applicable to chlorohydrosilanes and ethoxyhydrosilanes (Section 7, Supp. Inf.).

Applicability of the $Mn_2(CO)_{10}$/HFIP-catalytic system for light initiated hydrosilylation of unsaturated hydrocarbons with diverse structures **1b-q** was studied (Fig. 5).

Styrene derivatives are known as more problematic substrates. They demonstrated good yields but resulted in a mixture of *anti*-Markovnikov

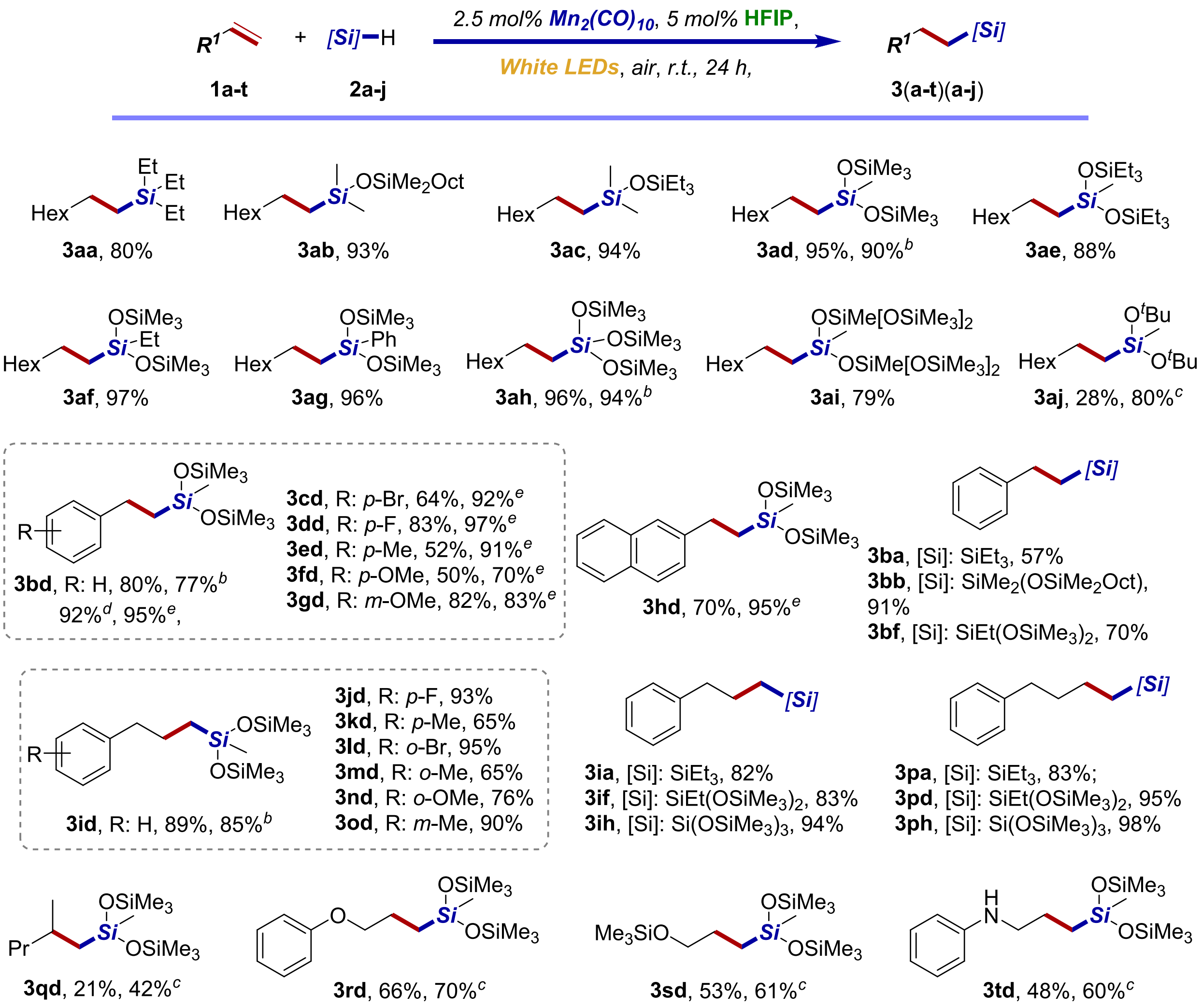


Fig. 5. Scope of White-Light Initiated $Mn_2(CO)_{10}$/HFIP-Catalyzed Hydrosilylation$^{a.}$ Notes: *(a)* **1a-t** (0.45 mmol, 1 eq), **2a-j** (0.45 mmol, 1 eq), $Mn_2(CO)_{10}$ (0.0113 mmol, 0.025 eq), HFIP (0.0225 mmol, 2 μl, 0.05 eq). The yields were determined by ^{1}H NMR (1,2-dimethoxyethane as standard). *(b)* scaling, **1a**,**b**,**i** (4.5 mmol, 1 eq), **2d**,**h** (4.5 mmol, 1 eq), $Mn_2(CO)_{10}$ (0.113 mmol, 0.025 eq), HFIP (0.225 mmol, 20 μl, 0.05 eq), isolated yield. *(c)* HFIP (0.09 mmol, 8 μl, 0.2 eq). *(d)* 3 days. *(e)* **1b-h** (0.45 mmol, 1 eq), **2d** (0.9 mmol, 2 eq).

and minor Markovnikov isomers for Karstedt's catalyst [35] and most other catalysts [1–5,13–38]. However, in radical hydrosilylation using $Mn_2(CO)_{10}$- and $MnBr(CO)_5$-based catalyst systems [65,66] it was possible to obtain *anti*-Markovnikov products with high selectivity. These conditions enabled us to obtain selectively the *anti*-Markovnikov hydrosilylation products (**3**(**b**-**h**)**d**) of a wide range like styrene **1b** and its *p*- and *m*-substituted derivatives with halogen-, alkyl-, and alkoxy groups **1c**-**g** and vinylnaphthalene **1 h** in medium to high yields (50–83 %; Fig. 5). The reactions proceed chemo- and regio-selectively, and the formation of by-products is not observed. Taking hydrosilylation of **1b** as an example shows that by increasing the reaction time from 1 to 3 days, a quantitative conversion of **3bd** (note *d*, Fig. 5) can be achieved. Increasing the yield of products to quantitative values is also possible subject to increased loading of one of the reagents. For example, when the loading of silane **2d** was increased by 2 times, the yields of the products were improved to quantitative yields (note *e*, Fig. 5). The example of hydrosilylation of styrene **1b** also shows applicability of the method to other silanes **2a**,**b**,**f**.

Hydrosilylation of allylbenzene **1i** and its *p*-, *o*-, and *m*-substituted derivatives **1j**-**o** with **2d** hydrosilane leads to selective formation of *anti*-Markovnikov addition products **3**(**i**-**o**)**d** in high yields (65–95 %). Efficiency of this method was shown with other silanes **2a**,**f**,**h** in hydrosilylation of allylbenzene **1i**.

4-Phenyl-1-butene **1p** is selectively hydrosilylated by various silanes (**2a**,**d**,**h**), leading to the formation of *anti*-Markovnikov products in near-quantitative yields. UV-light-initiated $Mn_2(CO)_{10}$- and thermally-initiated $MnBr(CO)_5$-catalyzed hydrosilylation also proceeds selectively but in slightly lower yields [66].

Hydrosilylation of 1,1-dialkyl-substituted alkene **1q** allows to obtain product **3qd** in moderate yields (21 % or 42 %; notes *a* & *c*, Fig. 5), being a challenge when using other catalytic systems based on Mn-complexes [45,66].

Feasibility of using this method for O- and N-containing alkenes was estimated. Hydrosilylation of phenyl- and trimethylsilyl-allyl ethers (**1r**, **s**) leads selectively to *anti*-Markovnikov products **3rd** and **3sd** in good yields (up to 70 %), as in previous research [45,66]. Hydrosilylation of allylphenylamine **1t** gave *anti*-Markovnikov product **3td** in good yield (60 %). At the same time, methyl acrylate hydrosilylation proceeds less efficiently (Figure S7, Supp. Inf).

In addition to **3ad** (Fig. 2 ***A***), the scaling of this method in batch-reactor has been investigated by obtaining **3ah**,**bd**,**id** as an example. These products showed 77–96 % yields in gram amounts (notes *b*, Fig. 5).

The advantages of our method are particularly evident with hydrosilylation of ethylene and acetylene. Work with such gaseous hydrocarbons usually requires gas bubbling, elevated pressures and

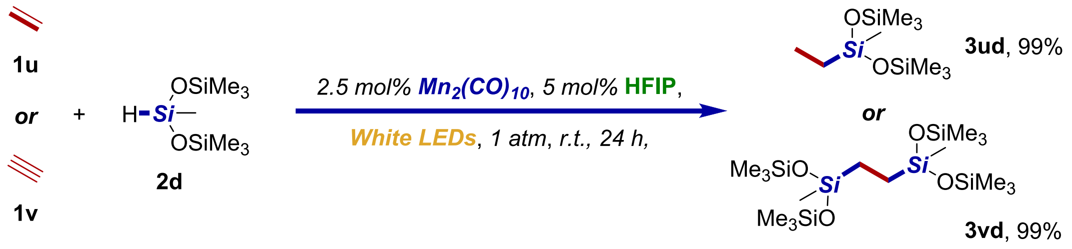


Fig. 6. White-Light Initiated $Mn_2(CO)_{10}$/HFIP-Catalyzed Hydrosilylation of Ethylene and Acetylene. Notes: *(a)* **2d** (0.45 mmol, 100 mg, 1 eq) was added to $Mn_2(CO)_{10}$ (0.0113 mmol, 4.4 mg, 0.025 eq), then HFIP (0.0225 mmol, 2 μl, 0.05 eq) was added. The reaction mixture was stirred under **1u** or **1v** atmosphere (1 atm) in Schott culture tube for 24 h under white-light irradiation at r.t. The yields were determined by ^1H NMR (1,2-dimethoxyethane as standard).

temperatures [83–87]. Previously, hydrosilylation of ethylene was carried out at 130 °C and 2–4 atm using $Mn_2(CO)_{10}$-catalyst and tris(3,5-bis(trifluoromethyl)phenyl)phosphine ligand [65]. However, the use of our method of white-light initiated $Mn_2(CO)_{10}$/HFIP-catalyzed hydrosilylation, enabled us to synthesize **3ud** through hydrosilylation of ethylene **1u** with silane **2d** with the quantitative yield at r.t. and atmospheric pressure (under static **1u** atmosphere, without bubbling) (Fig. 6).

Acetylene **1v** under similar conditions undergoes selective hydrosilylation to form 1,2-bis(silyl)ethane **3vd** in quantitative yield (Fig. 6).

4. Conclusion

Thus, a white-light initiated $Mn_2(CO)_{10}$/HFIP-catalyzed hydrosilylation of alkenes with tertiary hydrosilanes at r.t., under air has been proposed. The method is applicable to terminal alkenes, including those with O-, N- and halogen-containing functional groups, styrene and allylbenzene derivatives, etc. A wide range of alkyl-, phenyl-, siloxy- and alkoxy-containing tertiary hydrosilanes was used. The reaction proceeds in high yields and selectively, with the formation of *anti*-Markovnikov addition products. These conditions turned out to be most efficient for hydrosilylation of gaseous reagents such as ethylene and acetylene. In both cases the products were synthesized with a quantitative yield at 1 atm and r.t.

Additional studies have shown that the reaction proceeds by an autocatalytic mechanism. The reaction is initiated by white-light irradiation. [Mn]• generated activates the Si–H-group to form Si• and trigger the autocatalytic process. HFIP acts as a unique additive activator which enables synthesis of products with yields close to quantitative under mild conditions. It is shown that even with 5–10 min irradiation it is possible to obtain products with quantitative yields.

The method is easily up-scalable in batch- and flow-modes.

CRediT authorship contribution statement

Irina K. Goncharova: Methodology, Validation, Writing – review & editing. **Stepan A. Filatov:** Investigation. **Anton P. Drozdov:** Investigation. **Andrei A. Tereshchenko:** Investigation, Visualization. **Pavel A. Knyazev:** Investigation. **Alexander A. Guda:** Investigation, Validation, Visualization. **Irina P. Beletskaya:** Funding acquisition, Supervision, Writing – review & editing. **Ashot V. Arzumanyan:** Conceptualization, Validation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2023.115269.

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