



HAL
open science

MnBr(CO)₅: a commercially available highly active catalyst for olefin hydrosilylation under ambient air and green conditions

Anthony Vivien, Laurent Veyre, Raphaël Mirgalet, Clément Camp, Chloé Thieuleux

► To cite this version:

Anthony Vivien, Laurent Veyre, Raphaël Mirgalet, Clément Camp, Chloé Thieuleux. MnBr(CO)₅: a commercially available highly active catalyst for olefin hydrosilylation under ambient air and green conditions. *Green Chemistry*, 2023, 25 (19), pp.7721-7728. 10.1039/D3GC02385K . hal-04192149

HAL Id: hal-04192149

<https://cnrs.hal.science/hal-04192149v1>

Submitted on 31 Aug 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

MnBr(CO)₅: a commercially available highly active catalyst for olefin hydrosilylation under ambient air and green conditions

Anthony Vivien,^a Laurent Veyre,^a Raphaël Mirgalet,^b Clément Camp^a and Chloé Thieuleux^{*a}

^a Université de Lyon, Institut de Chimie de Lyon, Laboratory of Catalysis, Polymerization, Processes and Materials, CP2M UMR 5128 CNRS-UCB Lyon 1-CPE Lyon, CPE Lyon 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France. E-mail: chloe.thieuleux@univ-lyon1.fr

^b Elkem Silicones, R&I Chemistry, 9 rue Specia, 69190 Saint Fons, France.

Abstract

The catalytic hydrosilylation of alkenes is a major industrial reaction and a very efficient and atom-economical way to obtain functional organosilane compounds and cross-linked materials. Platinum-based catalysts are currently preferred in the industry despite the low availability and high cost of platinum but considerable efforts are being directed to replace Pt with non-noble metals. In this context, we developed a robust and highly active non-noble metal catalytic system using commercially available MnBr(CO)₅. It was successfully employed in olefin hydrosilylation reactions using various functional olefins and industrially relevant silanes such as 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD^HM) and polymethylhydrosiloxanes (PMHS). This system tolerates unpurified substrates and can be used in green solvents (H₂O, anisole) under ambient air, selectively yielding the anti-Markovnikov hydrosilylated products (yields up to >99%) at 70 °C using 2 mol% of catalyst. MnBr(CO)₅ was also successfully employed for the synthesis of cross-linked materials using dienes, carbonyl and epoxide containing substrates with low Mn loadings (0.3 mol%) at 70 °C under ambient air.

Introduction

Organosilane products are widely used in the pharmaceutical industry,¹ cosmetics,² materials field,^{3,4,5,6} and as release coatings for labels and adhesives.⁷ As a result, the annual market value of silicone materials represented \$3.21bn in 2021 and it is predicted an increase of the silicone market value to \$3.77bn in 2025.⁸ One of the key products on the market, octylsiloxane, yielded from the hydrosilylation reaction between *n*-octene and 1,1,1,3,5,5,5-heptamethyltrisiloxane (MD^HM), is produced approximately on a 6000 ton scale annually and is used to enhance cosmetic formulations and weatherproofing for masonry products, metal oxides and glasses.⁹

Selectivity, activity and stability of the catalysts are very important features for hydrosilylation reactions in industry. Over the past five decades, precious metal catalysts, such as Pt, Rh, Ir and Ru derivatives have been used by the silicone industry to perform catalytic alkene hydrosilylation reactions.¹⁰ In the late 1950s, Speier discovered that hexachloroplatinic acid, [H₂PtCl₆]•H₂O, was a very effective homogeneous catalyst for alkene hydrosilylation.^{11,12} This discovery was key for the development of transition metal catalyzed olefin hydrosilylation reactions and initiated the widespread implementation of platinum catalysis in the silicone industry.¹³ Later, due to long induction periods associated with this catalyst and its poor solubility in polysiloxane mixtures, Karstedt introduced a divinyltetramethylsiloxane-ligated platinum(0) catalyst that exhibited improved activity, selectivity as well as solubility in polysiloxane compositions and is now the most established, and widely used catalyst in the silicone industry.^{7,14}

While, in the production of organofunctional silanes, the catalyst can be recovered in most cases, it should be noted that any hydrosilylation catalyst used in crosslinking reactions leads to the embedment of the valuable metal catalyst in the cross-linked products (such as rubber or coatings). Consequently, high amounts of metal catalyst permanently remain in the silicone polymer products (especially in the production of silicone release coatings). From an industrial point of view, the use of cheap and active first-row metal catalysts for the synthesis of polysiloxane products would thus be highly beneficial. The economic consequences associated with platinum-catalyzed alkene hydrosilylation have long been recognized by the silicone industry.¹⁵ The price volatility associated with the precious metals market, the toxicity of heavy metals and the environmental consequences associated with mining elements of scarce abundance in the Earth's crust are more reasons to look for cheap, environmentally benign and abundant metals.

Consequently, in recent years, a major effort has been dedicated to the development of first-row transition metal catalysts for alkene hydrosilylation.^{16,17,18} Pioneer relevant examples of abundant metal complexes are pyridine(diimine) iron dinitrogen complexes developed by Chirik *et al.* which provide a high activity and exclusive anti-Markovnikov hydrosilylation of commercially important substrates with rates and selectivity exceeding those associated with platinum.^{19,20,21,22,23} However, these catalysts require the preparation of sophisticated ligands and are highly air sensitive: significant obstacles to industrial interest. Recently, our group has shown that non-crystalline cobalt nanoparticles, easily synthesized from the commercial precursor Co₂(CO)₈ at low temperature (60°C), were extremely active in alkene hydrosilylation under inert conditions using purified reagents and distilled solvents. These Co NPs were found to catalyze the addition of the industrially relevant tertiary silane MD^HM on a wide range of olefinic substrates, under mild conditions (30 °C or UV), yielding exclusively the anti-Markovnikov hydrosilylated products.²⁴ Furthermore, we also demonstrated that, in similar reaction conditions, Co₂(CO)₈ was an excellent non-noble metal catalyst for the synthesis of mono- and bi-functionalized PMHS oils in a one-pot reaction, with catalyst loadings as low as 0.1 mol%.²⁵ This complex could also perform the crosslinking of industrially relevant allyl glycidyl ether or 4-vinylcyclohexene oxide as unconventional tethers with PMHS.²⁶ This catalytic system thus offered a unique method for the cross-linking of PMHS with traditional dienes and unconventional organic tethers, such as (un)saturated esters. These results showed that catalytic systems

based on commercially available and structurally simple non-noble metal complexes (without specific ligands) could be of interest in the field of hydrosilylation. However, the air sensitivity of these cobalt catalysts and the need of purified reagents and distilled solvents is still problematic for industrial applications.

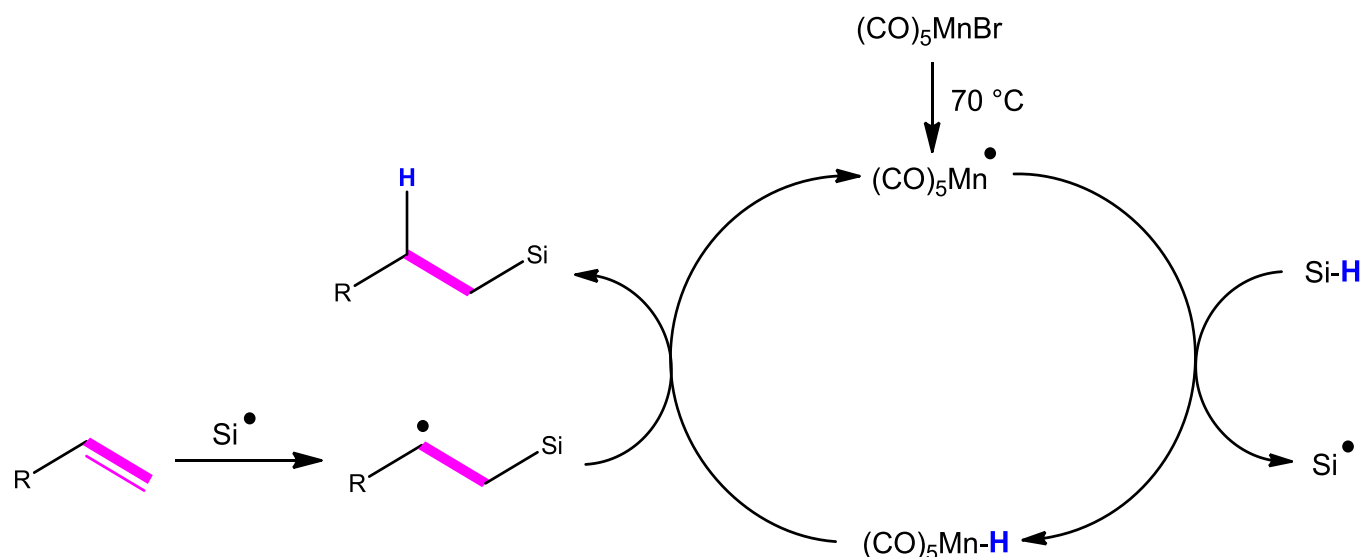
Because of our interest in non-noble metal hydrosilylation catalysts, we focused our attention on manganese, which is the third most abundant transition metal in the earth's crust and which is considered as non-toxic.^{27,28} The potential of manganese in the transformation of various organic substrates^{29,30,31,32,33,34} has recently driven major interest in the field of olefin hydrosilylation.³⁵ Wang *et al.* were able to selectively obtain *Z* or *E* alkenes respectively *via* alkyne hydrosilylation reactions using peroxide containing ligands with $\text{Mn}_2(\text{CO})_{10}$ at 120 °C or triphenylarsine with $\text{MnBr}(\text{CO})_5$ at 150 °C. The group of Zhang also demonstrated in 2019 that $\text{Mn}_2(\text{CO})_{10}$ could perform alkyne hydrosilylation using 10 mol% of catalyst under UV irradiation after 12 hours. Alkene hydrosilylation with the same manganese complex was described by Xie *et al.* using two equivalents of JackiePhos ligand at 120 °C, yielding selectively the hydrosilylated alkane. By replacing the JackiePhos ligand by *i*PrPNP and heating at 140 °C, dehydrogenative hydrosilylation was observed. In all these aforementioned examples, the hydrosilylation reactions were proposed to proceed through a radical mechanism involving the generation of the Mn^\bullet species stabilized by the introduced exogenous ligands. In this context, we showed that $\text{Mn}_2(\text{CO})_{10}$ was able to perform hydrosilylation of various alkenes with MD^HM under mild conditions (room temperature) under UV irradiation without the use of external ligands and using Mn loadings as low as 1 mol%. Under these experimental conditions, the anti-Markovnikov hydrosilylation products were selectively obtained in excellent yields.³⁶ Unfortunately, this catalytic system was found to suffer from rapid deactivation if exposed to air and required the use of quartz glassware for optimal activation under UV irradiation; thermal activation of this catalyst being unsuccessful. In order to overcome these constraints, we explored the reactivity of Mn(I) complexes as alternatives to Mn(0) complexes as Wang and co-workers had shown that $\text{MnBr}(\text{CO})_5$ was able to perform anti-Markovnikov hydrosilylation of alkenes without ligand or additives.³⁷ This pioneer work was however limited to the hydrosilylation of styrene derivatives with activated silanes, namely HSiMe_2Bn , under N_2 atmosphere with 5 mol% of catalyst in distilled hexane at quite high temperatures (up to 150 °C).

Results and discussion

In this context, as initial catalytic tests, we studied the reaction between *n*-octene and MD^HM using standard literature conditions, i.e. a 1 : 2 molar ratio of alkene : silane, using two different Mn(0) and Mn(I) complexes, namely $\text{Mn}_2(\text{CO})_{10}$ or $\text{MnBr}(\text{CO})_5$.³⁶ The reaction was set under argon in a 4 mL vial with concentrations of 0.825 M for *n*-octene (74 μL , 0.47 mmoles) and 1.650 M for MD^HM (256 μL , 0.94 mmoles). Alkenes and MD^HM were purified and stored under inert atmosphere in a glovebox prior to use (see ESI). Then, a solution of the Mn catalyst (2 mol%) in distilled toluene was added to obtain a total volume of 571 μL . Importantly, an ICP-MS analysis was performed on the commercial $\text{MnBr}(\text{CO})_5$ complex to evaluate the presence of platinum traces in such compound. Only few ppb of Pt were found, ruling out the potential role of Pt to catalyze the hydrosilylation reaction (see ESI).

As shown in Table 1, thermal activation (with reaction temperatures from 50 °C to 100 °C) did not yield the hydrosilylation product with $\text{Mn}_2(\text{CO})_{10}$ as catalyst and no conversion of the reactants was observed (entries 1-2). In contrast, exposing $\text{Mn}_2(\text{CO})_{10}$ to UV light (300 W, $\lambda = 250\text{-}420$ nm) allowed octene to be selectively converted into the anti-Markovnikov hydrosilylation product with 94% yield after 4 hours (entry 3). The activity of the Mn(I) catalyst under UV irradiation was lower than that observed with the Mn(0) complex, leading to the anti-Markovnikov product in 67% yield (entry 6) along with 6% of *n*-octene internal isomers (mainly 2-octene). Surprisingly, under thermal activation, good to excellent yields were obtained at 50 °C and 70 °C in 4 hours, yielding the hydrosilylated product in 62% and 99% yields respectively, without any traces of *n*-octene isomerization products (entries 4-5). Based on these promising results, the exact same reaction was repeated under ambient air using non-purified reagents (used as received from commercial providers) and non-distilled toluene as solvent. Under these experimental conditions, 99% of the anti-Markovnikov product was selectively obtained, showing the robustness of the catalytic system (entry 7).

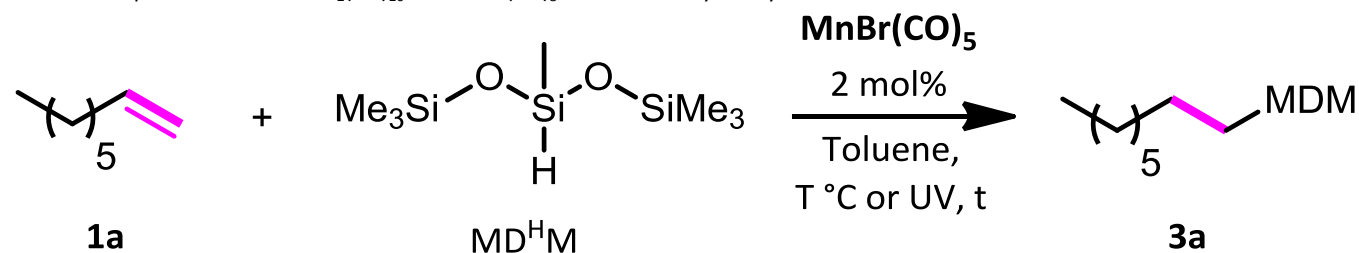
In order to increase the atom economy efficiency of the reaction, we performed the reaction with a *n*-octene : MD^HM ratio of 1 : 1, using 0.94 mmoles of both substrates. Under these specific conditions, we obtained the desired product with an excellent yield of 96% and only traces of alkene isomerisation was detected (< 1%, Table 1 - entry 8). In the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO), the catalyst activity was quenched and only traces of the hydrosilylated products were observed (entry 9), which is compatible with a radical mechanism, as shown in Scheme 1.



Scheme 1 Proposed mechanism for manganese-catalyzed alkene hydrosilylation.

In this putative mechanism, a thermal cleavage of the Mn-Br bond led to the active specie $(\text{CO})_5\text{Mn}^\bullet$. Then, a hydrogen atom transfer (HAT) reaction from the silane to the reactive $(\text{CO})_5\text{Mn}^\bullet$ intermediate, generating a silyl radical and $(\text{CO})_5\text{Mn-H}$ was postulated. Finally, the addition of this silyl radical to the alkene reagent led to the formation of an alkyl radical species which underwent a HAT with $(\text{CO})_5\text{Mn-H}$, giving the final product and regenerating $(\text{CO})_5\text{Mn}^\bullet$.

Table 1 Comparison between $\text{Mn}_2(\text{CO})_{10}$ and $\text{MnBr}(\text{CO})_5$ for *n*-octene hydrosilylation

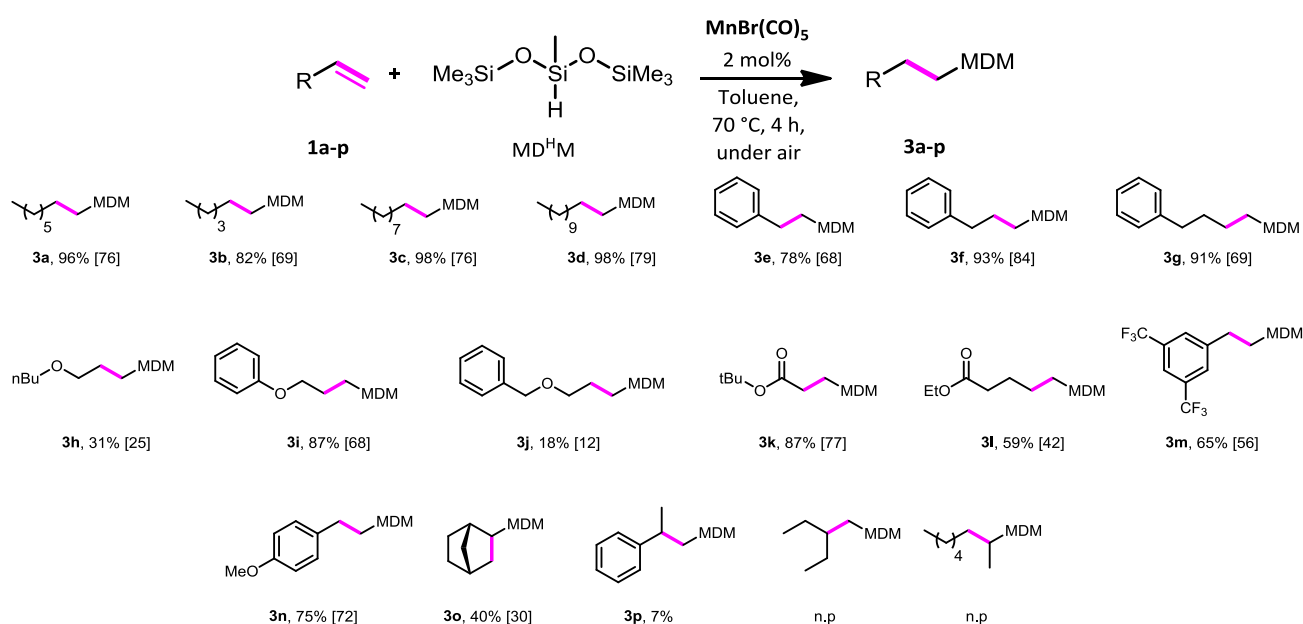


#	[Mn]	Conditions	Yield (%)	Isom. of 1 (%)
1	$\text{Mn}_2(\text{CO})_{10}$	50 °C, 24 h	n.p.	n.p.
2	$\text{Mn}_2(\text{CO})_{10}$	100 °C, 24 h	n.p.	n.p.
3 ^a	$\text{Mn}_2(\text{CO})_{10}$	UV, 4 h	94	n.p.
4	$\text{MnBr}(\text{CO})_5$	50 °C, 4 h	62	n.p.
5	$\text{MnBr}(\text{CO})_5$	70 °C, 4 h	99	n.p.
6 ^a	$\text{MnBr}(\text{CO})_5$	UV, 24 h	67	6
7 ^b	$\text{MnBr}(\text{CO})_5$	70 °C, 4 h	99	n.p.
8 ^c	$\text{MnBr}(\text{CO})_5$	70 °C, 4 h	96	< 1
9 ^d	$\text{MnBr}(\text{CO})_5$	70 °C, 24 h	< 1	n.p.

n.p.: no product. Conditions: *n*-octene (74 μL , 0.47 mmol), $\text{MD}^{\text{H}}\text{M}$ (256 μL , 0.94 mmol), mesitylene as GC standard (46 μL , 0.335 mmol), [Mn] (9.4 μmol , 2 mol%), toluene (195 μL). ^a UV irradiation did not lead to a significant increase of temperature (<45 °C). ^b The reaction was performed under ambient air without any purification of substrates nor toluene. ^c The reaction was performed under air without any purification of substrates nor toluene with a 1:1 ratio of *n*-octene (0.94 mmol) and $\text{MD}^{\text{H}}\text{M}$ (0.94 mmol). ^d The reaction was carried out in the presence of TEMPO (16 equiv./catalyst).

To study the versatility of this catalytic system, we explored the hydrosilylation reaction using various alkenes. This scope of alkenes was performed using a 1 : 1 molar ratio of alkene : MD^HM and all reactions were carried out under ambient air using non-purified substrates and non-distilled toluene. The results are summarized in Figure 1. Concerning aliphatic alkenes, the anti-Markovnikov product was quantitatively obtained with *n*-octene (**1a**), *n*-hexene (**1b**) *n*-decene (**1c**) and *n*-dodecene (**1d**) without any traces of alkene isomerization. Good to excellent results were also observed with styrene (**1e**), allylbenzene (**1f**) and 4-phenyl-1-butene (**1g**) with yields of 78%, 93% and 91% respectively. The presence of an ether group was found to give the hydrosilylated products in lower yields as shown with *n*-butyl allyl ether (**1h**) and benzyl allyl ether (**1j**), yielding 80% and 62% of products **3h** and **3j**, respectively. For the phenyl allyl ether (**1i**), the yield in product **3i** was higher (87%). This catalytic system was also found to tolerate the presence of ester groups: with *tert*-butyl acrylate (**1k**) and ethyl-4-pentenoate (**1l**), the anti-Markovnikov products **3k** and **3l** were obtained with 87% and 59% yields, respectively. Again, only anti-Markovnikov products were obtained and no traces of C=C nor C-O cleavage were observed. Regarding styrene derivatives possessing electron-withdrawing or electron-donating groups, the catalytic system performed well, yielding 65% of **3m** and 75% of **3n**. With norbornene (**1o**), a moderated hydrosilylation yield (40%) was observed with 100% stereoselectivity for the *exo*-isomer product **3o**. As already observed previously with Mn₂(CO)₁₀,³⁶ no reactivity was obtained with other internal alkenes or gem-alkenes and only starting materials were recovered. Steric hindrance and the inability of the catalyst to isomerize the internal double bond, in these cases, most likely prevent the chain-end reactivity to form the anti-Markovnikov product. However, one exception was observed with methylstyrene for which 7% of the hydrosilylated product **3p** was obtained.

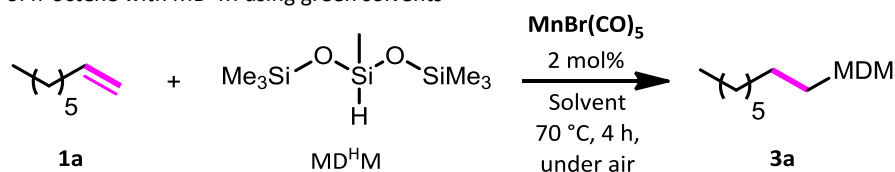
Figure 1 Mn-catalyzed hydrosilylation of various terminal alkenes with MD^HM under ambient air.



Yields are determined by GC and the yield in brackets refers to the isolated yield. n.p.: no product. Conditions: alkene (0.94 mmol, 1.650 M, 1 equiv.), MD^HM (256 μ L, 0.94 mmol, 1.650 M, 1 equiv.), mesitylene as GC standard (46 μ L, 0.335 mmol), MnBr(CO)₅ (18.8 μ mol, 2 mol%), toluene (added to complete a total volume of 571 μ L), 70 °C, 4 hours, under ambient air.

In order to work in more sustainable conditions, we investigated the possibility to replace toluene by greener solvents and we targeted some of the most environmentally friendly solvents: anisole, ethyl acetate and even water.^{38,39}

As shown in Table 2, hydrosilylation of *n*-octene with MD^HM proceeded very well in anisole, a solvent ranked as “recommended” in the commonly used solvents listed in industry,³⁸ yielding 95% of the anti-Markovnikov product **3a** (Entry 1). With ethyl acetate, another recommended green solvent, a moderate yield was obtained (50%) and 2% of 2-trans-octene was observed (Entry 2). Note that the reaction also proceeded very well without solvents, yielding 96% of **3a** (Entry 4). Surprisingly, when working in distilled water, 85% of hydrosilylated product was obtained with traces of alkene isomerization. Indeed, in our experimental conditions, the Si-H bond of MD^HM did not undergo hydrolysis very rapidly, allowing the hydrosilylation reaction to proceed in water.

Table 2 Hydrosilylation of *n*-octene with MD^HM using green solvents

Entries	Solvent	Yield (%)	Isom. of 1a (%)
1	Anisole	95	n.p
2	Ethyl acetate	50	2
3	Water	85	<1
4	None	96	<1

n.p.: no product. Conditions: *n*-octene (148 μL , 0.94 mmol), MD^HM (256 μL , 0.94 mmol), mesitylene as GC standard (46 μL , 0.335 mmol), MnBr(CO)₅ (18.8 μmol , 2 mol%), solvent (195 μL), 70 $^\circ\text{C}$, 4 hours, under air.

These promising results prompted us to explore the scope of the reaction in anisole, water and under neat conditions. Various alkenes and silanes were thus evaluated under the same conditions as before (non-purified substrates and solvents, a 1 : 1 molar ratio of alkene : silane and under ambient air). The results are summarized in Figure 2.

Concerning anisole, the results were found similar to those obtained with toluene with good to excellent yields in hydrosilylated products **3a** (95%), **3b** (70%), **3c** (98%) and **3d** (95%) when using aliphatic substrates (*n*-octene (**1a**), *n*-hexene (**1b**), *n*-decene (**1c**) and *n*-dodecene (**1d**)). Same observation was made with the aromatic containing alkenes **1e**, **1f**, **1g**, **1m** and **1n** with 76%, 94%, 87%, 61%, and 62% yields in hydrosilylated products **3e**, **3f**, **3g**, **3m** and **1n**, respectively. As with toluene, when olefinic substrates containing ether groups were used, low yields of hydrosilylated products starting from *n*-butyl allyl ether (**3h**, 22%) and benzyl allyl ether (**3j**, 21%) and a slightly higher product yield from phenyl allyl ether (**3j**, 66%) were observed. For alkene reagents exhibiting ester groups, a lower product yield was obtained from tert-butyl acrylate (**3k**, 60% vs 87% in toluene) but no significant changes were observed with ethyl-4-pentenoate (**3l**, 52%). Finally, the hydrosilylation of norbornene yielded the desired hydrosilylated product **3o** in 22% yield (without side reactions).

Concerning the use of water as solvent, lower yields were obtained, except for *n*-decene and 3,5 bis(trifluoromethyl)styrene, with product yields close to those obtained in toluene and anisole (**3c**, 90%) and **3m** (62%) respectively) for the same reaction time. Slightly lower product yields were obtained from *n*-octene (**3a**, 85%) and benzyl allyl ether (**3j**, 18%). Concerning the other substrates, much lower yields were obtained: from styrene, allyl benzene and homo allylic benzene, the hydrosilylated products (**3e**, **3f** and **3g**) were respectively obtained in 47%, 54% and 40% vs 76%, 94% and 87% in anisole. Same results were observed with *n*-hexene and *n*-dodecene, yielding products **3b** and **3d** in 45% (vs 70% in anisole) and 60% (vs 95% in anisole) respectively. For the olefinic substrates containing an ester group, the hydrosilylated products (**3k** and **3l**) were recovered with 30% and 6% yields (vs 62% and 52% in anisole). The poor solubility of these compounds in water was found responsible for the lower reaction efficiency as no side product was detected (no or only traces of hydrolysis for MD^HM). Surprisingly, better yields of hydrosilylated products **3h** (53%) and **3o** (57%) were observed from *n*-butyl allyl ether and norbornene respectively.

When working in neat conditions, very good to excellent results were obtained both for aliphatic, aromatic and ester compounds, with product yields from 69% (**3n**) to 99% (**3d**). The substrates exhibiting an ether group provided moderated to good yields with 39%, 79% and 32% for products **3h**, **3i**, and **3j**. For norbornene, 35% of the desired product **3o** was obtained. In the case of methylstyrene, whatever the solvent, the product **3p** yield remained low, ranging from 4% in water to 16% without solvent. To assess the greenness of these reactions, E-factors were calculated with anisole as solvent. In many cases E-factor were below 5, which is within the acceptable E factor range of 1-5 for bulk chemicals production in industry.⁴⁰ Exceptions were observed with products **3h**, **3j**, **3o** and **3p** due to the low products yields, with E-factors of 5.3, 5.33, 8 and 15 respectively.

To further explore the versatility of this catalytic system, we performed the hydrosilylation of 6 representative alkenes with 5 different activated or non-activated silanes (quoted silanes **4** to **8**) using anisole as solvent under ambient air at 70 °C (Figure 3). Using phenyldimethylsilane (silane **4**) and benzyldimethylsilane (silane **5**), very similar results were obtained for the hydrosilylation of styrene (**1e**), *n*-butyl allyl ether (**1h**), *tert*-butyl acrylate (**1k**) and 3,5 bis(trifluoromethyl)styrene (**1m**) with products yields from 68% for to 90%. Using *n*-octene and 4-methoxystyrene, different results were obtained with product yields of 43% for **4a** vs 70% for **5a** and 94% for **4n** vs 75% for **5n**. With triethylsilane (silane **6**), the anti-Markovnikov product was obtained with moderate to excellent yields from 56% (**6n**) to 94% (**6k**). Lower activity was observed for triethoxysilane (silane **7**) with product yields from 10% (**7m**) to 33% (**7k**). The reaction of **6** with 4-methoxystyrene was unsuccessful, leading to a complex mixture with many unidentified products. Finally, working with Ph₂SiH₂ (silane **7**) allowed the selective formation of the anti-Markovnikov hydrosilylation with good yields for products **8e**, **8m** and **8n**, i.e. 80%, 76% and 72% respectively. Moderate product yields were observed with *n*-butyl allyl ether (**8h**, 44%) and *n*-octene (**8a**, 43%). The use of *tert*-butyl acrylate led to the degradation of the starting substrate.

With all these results in hands, we finally investigated the use of MnBr(CO)₅ for the synthesis of functionalized PMHS oils and cross-linked gels as such products represent a very important class of materials that are used as adhesives binders, ceramic and dielectric coatings, encapsulates, membranes, sealants and a lot more.³ We thus investigated the reaction between PMHS and several commercially available dienes: divinyltetramethyldisiloxane (DVTMS) and diethyl diallymalonate (DEDAM). The Si-H containing polysiloxane (1.0 equiv. of Si-H) and 0.5 equiv. of the diene (i.e. 1.0 equiv. of C=C) were mixed in a vial with 0.3 mol% of MnBr(CO)₅ in neat conditions under ambient air and the resulting solution was heated at 70 °C. Gelation was observed with both substrates, in 2 hours for DVTMS and 20 minutes for DEDAM (Table 3 - entries 1-2). The crosslinking reaction occurred *via* the hydrosilylation of both double bonds as already observed by our group when Co₂(CO)₈ was used as catalyst.²⁵

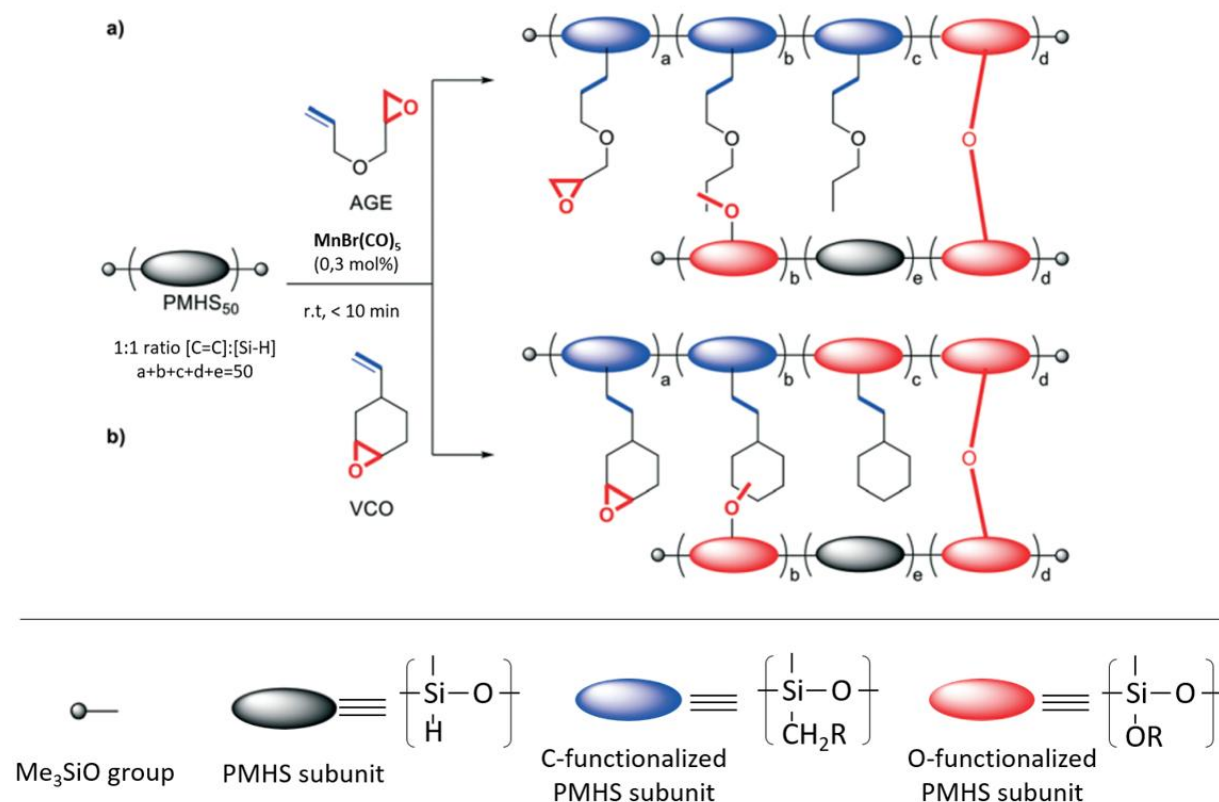
Table 3 Cross-linking of PMHS with various alkenes under air.

Entries	Label	Alkenes	Gelation time
1	4a	DVTMS	2 h
2	4b	DEDAM	20 min
3	4c	Allyl acetate	10 h
4	4d	Vinyl acetate	4 h
5	4e	Methyl methacrylate	15 min
6	4f	Allyl methacrylate	2.5 h
7	4g	Hex-5-en-2-one	3 h

Conditions: alkene (2.4 mmol, 1.0 equiv.), PMHS (2.4 mmol, 1.0 equiv. [Si-H] functionalities), MnBr(CO)₅ (0.3 mol% compared to Si-H functionalities), 70 °C, under air. The samples were further post-cured at 60 °C for 24 h.

We further focused our attention to the use of other unsaturated C=O containing compounds for the cross-linking of PMHS. Working with unsaturated acetates led to the formation of gels after 10 hours for allyl acetate and 4 hours for the vinylic homologue (Table 3 - entries 3-4). The reaction was faster with methacrylate compounds, leading to the cross-linked product after 15 minutes for methyl methacrylate and 2.5 hours for allyl methacrylate (Table 3 - entries 5-6). With hex-5-ene-2-one, a less reactive carbonyl compound, the gel was obtained after 3 hours. These results indicated that the cross-linking reaction was not limited to esters groups but also proceeded well with acetates, acrylates and ketones.²⁹ Si NMR studies showed that Si-O-Si bonds were formed during the reaction (see ESI) and then led to the formation of the cross-linked polysiloxane gels. While platinum is known to catalyze the reaction between PMHS and unsaturated carbonyl reagents, leading to the classical double bond hydrosilylation without gelation resulting from the ester group reduction,^{41,42} this unconventional result was also obtained when working with Co₂(CO)₈ as catalyst under inert conditions.²⁵ Finally, we performed the reaction between industrially relevant allyl glycidyl ether (AGE) and PMHS (internal Si-H content ~45.5 wt%) using 0.3 mol% of Mn(I) complex in neat conditions under air. The reaction led to the formation of a gel in less than 10 minutes at room temperature (scheme 2a). We also tested 4-vinylcyclohexene oxide (VCO) as the olefinic reagent under the same reaction conditions (Scheme 2b) and a gel was obtained in less than 10 minutes. This gelation was related to the epoxide ring opening, leading to the formation of Si-O-C bonds that underwent further reduction and led to the formation of Si-O-Si bridges along with alkyl pendant groups (see the ²⁹Si solid-state spectra of the resulting gel in ESI).

In order to assess the reproducibility of such reactions, the cross-linking experiments were carried out using Allyl methacrylate, DEDAM and AGE as olefinic partners and a second source of PMHS (purchased from another supplier). The reactions proceeded in the same way as those using our initial batch of PMHS.



Scheme 2 Cross-linking of PMHS with AGE and VCO. Reaction conditions: alkene (3.75 mmol, 1 equiv.), PMHS (3.75 mmol, 1 equiv. [Si-H] functionalities), and MnBr(CO)₅ (0.3 mol% compared to [Si-H]), r.t., under ambient air. The samples were further post-cured at 60 °C for 24 h.

Conclusions

We have shown here that MnBr(CO)₅ is a very promising catalyst for the production of functional silanes and cross-linked materials through olefin hydrosilylation. It was found to be highly efficient for the selective production the anti-Markovnikov hydrosilylated products from various molecular functional alkenes and silanes but also with PMHS polymers. We also showed here that this specific complex was able to catalyse hydrosilylation reactions in very simple and green reaction conditions: low reaction temperature (RT to 70 °C), under ambient air atmosphere, using non-purified substrates and green non-distilled solvents (see ESI). This is in sharp contrast with results obtained using other non-noble metal catalysts which are highly sensitive and require purified olefins, distilled and degassed solvents and inert atmosphere to exhibit catalytic performances. These results thus pave the way to replacement of platinum catalysts in the silicone industry and to the development of greener and more economically viable processes.

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. obtained the funds and administrated the project. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was performed, in collaboration with Elkem Silicones, in the frame of the F.U.I. project "DISCOVER" (F.U.I. standing for "Fonds unique interministériel") and we gratefully thank the Region Auvergne-Rhône-Alpes, the European Union through the "Fonds Européens de Développement Régional" (FEDER) for funding.

Notes and references

- ¹ A. K. Franz and S. O. Wilson, *J. Med. Chem.*, 2013, **56**, 388.
- ² V. B. Pukhnarevitch, E. Lukevics, L. I. Kopylova and M. Voronkov, Perspectives of Hydrosilylation, Institute for Organic Synthesis, Riga, Latvia, 1992.
- ³ B. Marciniac, H. Maciejewski, C. Pietraszuk and P. Pawluc, Hydrosilylation: A Comprehensive Review on Recent Advances, Springer Science & Business Media, 2009.
- ⁴ C. Sanchez, P. Belleville, M. Popall and L. Nicole, *Chem. Soc. Rev.*, 2011, **40**, 696.
- ⁵ C. Herzig, US Patent 6, 265, **497**, 2001.
- ⁶ G. Friedman, P. Sperry and J. Brossas US Patent 5, 166, **298**, 1992.
- ⁷ L. N. Lewis, J. Stein, Y. Gao, R. E. Colborn and G. Hutchins, *Platin. Met. Rev.*, 1997, **41**, 66.
- ⁸ B. Rupasinghe and J. C. Furgal, *Polym. Int.*, 2022, **71**, 521.
- ⁹ B. Marciniac, H. Maciejewski, C. Pietraszok and P. Pawluc, in Advances in Silicone Science, ed. J. Matisons, vol 1, Springer, 2009.
- ¹⁰ D. Troegel and J. Stohrer, *Coord. Chem. Rev.*, 2011, **255**, 1440.
- ¹¹ J. L. Speier, J. A. Webster and G. H. Barnes, *J. Am. Chem. Soc.*, 1957, **79**, 974.
- ¹² J. L. Speier and D. E. Hook, Dow Corning Corp., US2823218 A, 1958.
- ¹³ Y. Nakajima and S. Shimada, *RSC Adv.* 2015, **5**, 20603.
- ¹⁴ B. D. Karstedt, General Electric Company, US3775452 A, 1973.
- ¹⁵ R. J. Hofmann, M. Vlatković and F. Wiesbrock, *Polymers*, 2017, **9**, 534.
- ¹⁶ J. Sun and L. Deng, *ACS Catal.*, 2016, **6**, 290.
- ¹⁷ X. Du, and Z. Huang, *ACS Catal.*, 2017, **7**, 1227.
- ¹⁸ J. Chen, J. Guo and Z. Lu, *Chin. J. Chem.*, 2018, **36**, 1075.
- ¹⁹ S. C. Bart, E. Lobkovsky and P. J. Chirik, *J. Am. Chem. Soc.*, 2004, **126**, 13794.
- ²⁰ C. C. H. Atienza, A. M. Tondreau, K. J. Weller, K. M. Lewis, R. W. Cruse, S. A. Nye, J. L. Boyer, J. G. P. Delis and P. J. Chirik, *ACS Catal.*, 2012, **2**, 2169.
- ²¹ I. Pappas, S. Treacy and P. J. Chirik, *ACS Catal.*, 2016, **6**, 4105.
- ²² C. H. Schuster, T. Diaio, I. Pappas and P. J. Chirik, *ACS Catal.*, 2016, **6**, 2632.
- ²³ J. V. Obligacion and P. J. Chirik, *Nat. Rev. Chem.*, 2018, **2**, 15.
- ²⁴ M. Jakoobi, V. Dardun, L. Veyre, V. Meille, C. Camp and C. Thieuleux, *J. Org. Chem.*, 2020, **85**, 11732.
- ²⁵ M. Jakoobi, V. Dardun, C. Camp and C. Thieuleux, *Catal. Sci. Technol.*, 2021, **11**, 3176.
- ²⁶ M. Jakoobi, A. Vivien, C. Camp and C. Thieuleux, *Catal. Sci. Technol.*, 2021, **11**, 4714.
- ²⁷ S. H. Gilani, and Y. J. Alibhai, *J. Toxicol. Environ. Health*, 1990, **30**, 23.
- ²⁸ Guideline on the Specification Limits for Residues of Metal Catalysts or Metal Reagents, Committee for Medicinal Products for Human Use, 2008, pp. 5–6.
- ²⁹ J. R. Carney, B. R. Dillon, S. P. Thomas, *Eur. J. Org. Chem.*, 2016, 3912.
- ³⁰ A. Bruneau-Voisine, D. Wang, V. Dorcet, T. Roisnel, C. Darcel, J-B. Sortais, *Org. Lett.*, 2017, **19**, 3656.
- ³¹ P. Schlichter, C. Werlé, *Synthesis*, 2021, **53**, A.
- ³² A. Kaithal, L-L. Gracia, C. Camp, E. A. Quadrelli, W. Leitner *J. Am. Chem. Soc.* 2019, **44**, 17487.
- ³³ R. Jamatia, A. Mondal, D. Srimani, *Adv. Synth. Catal.* 2021, **363**, 1
- ³⁴ D. A. Valyaev, G. Lavigne, N. Lugan, *Coord. Chem. Rev.* 2016, **308**, 191.
- ³⁵ (a) J. R. Carney, B. R. Dillon, L. Campbell and S. P. Thomas *Angew. Chem. Int. Ed.*, 2018, **57**, 10620; (b) C. Obradors, R. M. Martinez, and R. A. Shenvi, *J. Am. Chem. Soc.*, 2016, **138**, 4962; (c) T. K. Mukhopadhyay, F. Marco, L. T. Groya and R. J. Trovitch, *Chem. Sci.*, 2018, **9**, 7673; (d) J. Dong, Xi-A. Yuan, Z. Yan, L. Mu, J. Ma, C. Zhu and J. Xie, *Nature Chem.*, 2020, **13**, 182; (e) X. Yanga and C. Wang, *Chem. Asian J.*, 2018, **13**, 2307.
- ³⁶ A. Vivien, L. Veyre, R. Mirgalet, C. Camp and C. Thieuleux, *Chem. Commun.*, 2022, **58**, 4091.
- ³⁷ X. Yanga, and C. Wang, *Chin. J. Chem.*, 2018, **36**, 1047.
- ³⁸ C. M. Alder, J. D. Hayler, R. K. Henderson, A. M. Redman, L. Shukla, L. E. Shuster and H. F. Sneddon, *Green Chem.*, 2016, **18**, 3879.
- ³⁹ D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehadad and P. J. Dunn, *Green Chem.*, 2016, **18**, 288.
- ⁴⁰ R. A. Sheldon, *Green Chem.*, 2017, **19**, 18.
- ⁴¹ X. Coqueret, A. Hajaiej, A. Lablache-Combiere, C. Loucheux, R. Mercier, L. Pouliquen and L. Randrianarisoa-Ramanantsoa, *Pure Appl. Chem.*, 1990, **62**, 1603.
- ⁴² X. Yang and C. Yao, *J. Appl. Polym. Sci.*, 2007, **106**, 3600.