Manganese-Catalyzed Dehydrogenative Silylation of Alkenes Following Two Parallel Pathways

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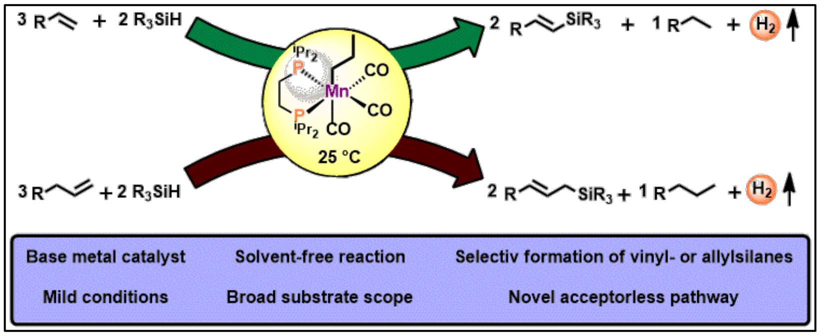
ABSTRACT: We report on an additive-free Mn(I)-catalyzed dehydrogenative silylation of terminal alkenes. The most active pre-catalyst is the bench-stable alkyl bisphosphine Mn(I) complex *fac*-[Mn(dippe)(CO)$_3$(CH$_2$CH$_2$CH$_3$)]. The catalytic process is initiated by migratory insertion of a CO ligand into the Mn-alkyl bond to yield an acyl intermediate which undergoes rapid Si-H bond cleavage of the silane HSiR$_3$ forming the active 16e$^-$ Mn(I) silyl catalyst [Mn(dippe)(CO)$_2$(SiR$_3$)] together with liberated butanal. A broad variety of aromatic and aliphatic alkenes was efficiently and selectively converted into *E*-vinylsilanes and allylsilanes, respectively, at room temperature. Mechanistic insights are provided based on experimental data revealing that two parallel reaction pathways are operative: an acceptorless reaction pathway involving dihydrogen release and a pathway requiring an alkene as sacrificial hydrogen acceptor.



INTRODUCTION

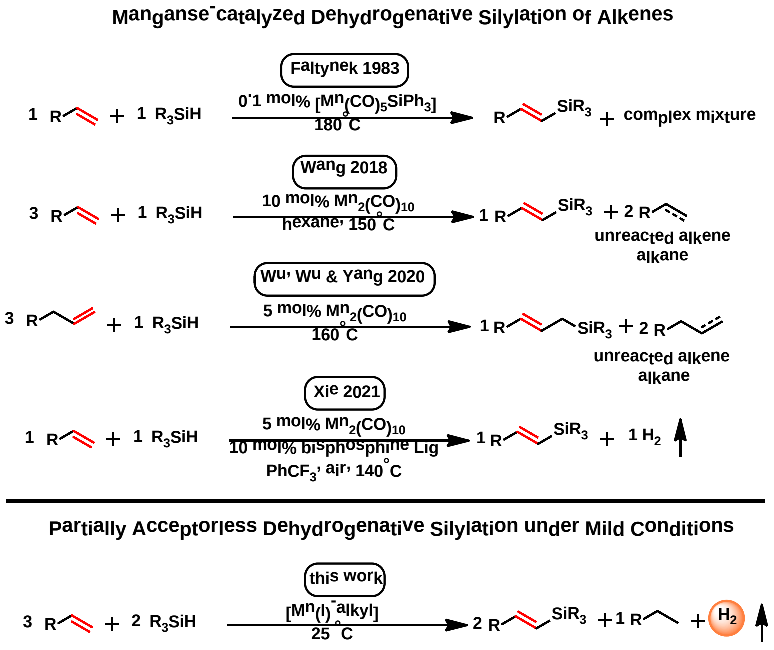
Organosilane-based compounds are widely employed in a broad variety of commercial products such as coating materials, paints or medicinal applicants, which is attributed to high chemical and thermal stability as well as to their low toxicity.[1] Furthermore, they may serve as powerful platform compounds in organic synthesis.[2] Vinyl- and allylsilanes display important substance classes for the synthesis of small molecules and as building blocks in macromolecular chemistry.[3] Unsaturated silanes may serve as substrates in the synthesis of carbonyl moieties, allylic alcohols[4] or as non-toxic reagents in cross-coupling reactions.[5]

Hydrosilylation, catalyzed by transition metals, displays the most common reaction pathway for the synthesis of organosilanes whereas unsaturated silanes may be synthesized by hydrosilylation of alkynes.[6,7] However, selectivity problems such as α- or β-addition to the triple bond or undesired addition of silane to the formed vinyl- or allylsilane often arise. Dehydrogenative silylation (DS) of alkenes displays an interesting alternative to that. Noble metals such as Rh,[8] Ir[9] or Ru[10] are commonly used in DS reactions. Nevertheless, base metals such as Fe[11] or Co[12] were also employed within the last decade. Although being an emerging-field, Manganese-based DS reactions[13] suffer from high catalyst loadings and harsh reaction conditions as depicted in Scheme 1. A drawback of DS in general is attributed to the fact that an excess of alkene or the addition of a sacrificial hydrogen acceptor (SHA) is required to scavenge the formed metal-hydride intermediate due to β-hydride elimination in the product releasing step.

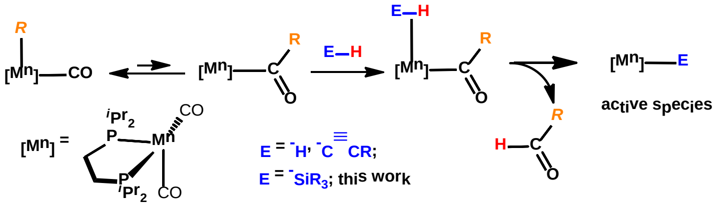
The development of acceptorless dehydrogenative silylation (ADS) protocols releasing hydrogen gas as sole byproduct would be beneficial to increase the atom efficiency. So far, examples of ADS are exceedingly rare. Xu and coworkers reported on an elegant photo-redox induced hydrogen-atom transfer (HAT) cascade in combination with cobalt catalysis for the ADS of alkenes yielding allylsilanes in high selectivity. However, 2 equiv of silane, 5 mol% of the catalyst, 20 mol% of HAT-catalyst, the addition of a photocatalyst and pyridine as base were required for this procedure.[12b] Very recently Xie and coworkers reported on a manganese-based ADS based on an HAT mechanism. A high atom efficiency could be achieved requiring, however, harsh reaction conditions (140 °C), high catalyst loading of [Mn$_2$(CO)$_{10}$] (5 mol%) and the use of the fluorinated solvent trifluoromethylbenzene.[13d]

We recently described the application of a well-defined Mn(I)-alkyl complexes in hydrogenation of nitriles,[14] ketones,[15] CO$_2$[16] and alkenes.[17] We took advantage of the fact that Mn(I)-alkyl carbonyl complexes undergo migratory insertion of the nucleophilic alkyl ligand into the polarized CO moiety, yielding a coordinatively unsaturated acyl complex, which may activate weakly polar E-H bonds (e.g. E = H, C≡C-R, SiR_3) (Scheme 2).[18] We also demonstrated that Mn(I)-alkyl complexes are capable of activating C-H-bonds of terminal alkynes converting aromatic and aliphatic terminal alkynes efficiently and selectively into head-to-head *Z*-1,3-enynes and head-to-tail gem-1,3-enynes.[19] Encouraged by these findings, we wondered if Si-H bonds may also be activated thereby initiating hydrosilylations and/or DS reactions of alkenes.

Scheme 1. Manganese-Catalyzed DS of Alkenes



Scheme 2. Formation of the Active Species *via* Migratory Insertion and Deprotonation of the Entering Ligand



Here, we describe the activity of *fac*-[Mn(dippe)$(CO)_3(CH_2CH_2CH_3)$] (dippe = 1,2-bis(di-*iso*-propylphosphino) (**1**) and *fac*-[Mn(dpre)$(CO)_3(CH_2CH_2CH_3)$] (dpre = 1,2-bis(di-*n*-propylphosphino) (**2**) as pre-catalysts for the DS of alkenes to afford selectively *E*-vinylsilanes. This is a rare example of a base-metal catalyzed DS of alkenes which proceeds at room temperature following two parallel catalytic cycles: an acceptorless reaction pathway involving dihydrogen release and a pathway requiring an alkene as sacrificial hydrogen acceptor.

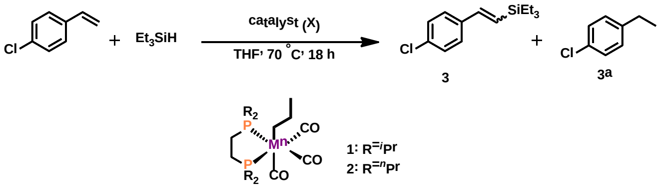
RESULTS AND DISCUSSION

The catalytic performance of alkyl complexes **1** and **2** for the DS of 4-chlorostyrene with $HSiEt_3$ as model substrates was first investigated. Selected optimization experiments are depicted in Table 1. Gratifyingly, high selectivity towards the *E*-isomer could be achieved while the formation of hydrosilylated alkane was not observed. High reactivity at room temperature under solvent free conditions was observed for complex **1**. Complex **2** turned out to be less active. Interestingly, the ratio of silane to alkene could be reduced to 1:1.5, which is uncommon in the field of DS reaction (Table 1, entry 4). Typically, two (or more) equiv of alkene are employed to quench the *in situ* generated hydride-species. An alternative approach in the literature is the utilization of a sacrificial hydrogen acceptor (SHA) such as 3,3-diemethylbuten or cyclooctene.[12a]

By using 3 equiv of 3,3-dimethylbutene as SHA, the ratio of **3**:**3a** was drastically increased to 9:1, but led to a conversion of only 39% to afford **3**, while full conversion of silane was detected. This is attributed to an undesired DS of the SHA (Table 1, entry 5). Increasing the ratio of $HSiEt_3$ to alkene to 3:1 or increasing the ratio of alkene to silane 5:1 only led to negligible changes in the product distribution (Table, 1 entries 6 and 7).

Having established the optimized reaction conditions, scope and limitation of the introduced system was investigated. In order to assure a high conversion of silane, in the following 1.8 equiv of alkene was used. A broad variety of different aromatic substates could be efficiently converted to the desired DS products with excellent selectivity towards the *E*-isomer. Styrene derivatives with electron withdrawing groups (Table 2, **3** and **6**) or electron donating groups (Table 2, **12**, **15** and **18**) gave excellent yields. Functional groups such as halides, ethers or amines were well-tolerated. However, the pyridine-based substrate was not converted indicating an undesirable interaction with the catalyst such as coordination of the pyridine In general, the highest selectivity could be achieved when employing the sterically demanding trisiloxane. Investigation of other tertiary silanes such as trimethoxy- or triisopropylsilane gave no conversion. Presumably, trimethoxysilane is sterically not demanding enough for this transformation, whereas, on the other hand, triisopropyl silane seems to be sterically too hindered. Investigation of substrate scope of aliphatic alkenes resulted in an unexpected reaction pattern. In all investigated cases, exclusively allylsilanes instead of vinylsilanes were obtained. This may be attributed to γ-hydride elimination rather than a β-hydride elimination. Very high selectivity towards *E*-alkenes could be observed in case of allylbenzene (Table 2, **26**-**28**). The usage of vinylcyclohexane resulted in the formation of a trisubstitued alkene (Table 2, **29**-**31**). Moderate *E*-selectivity could be detected for 1-hexene as substrate. It should be noted that no hydrosilylated product could be detected upon substrate scope investigation of aromatic and aliphatic alkenes.

Table 1. Optimization Reactions for DS of 4-Chlorostyrene with $HSiEt_3$[a]



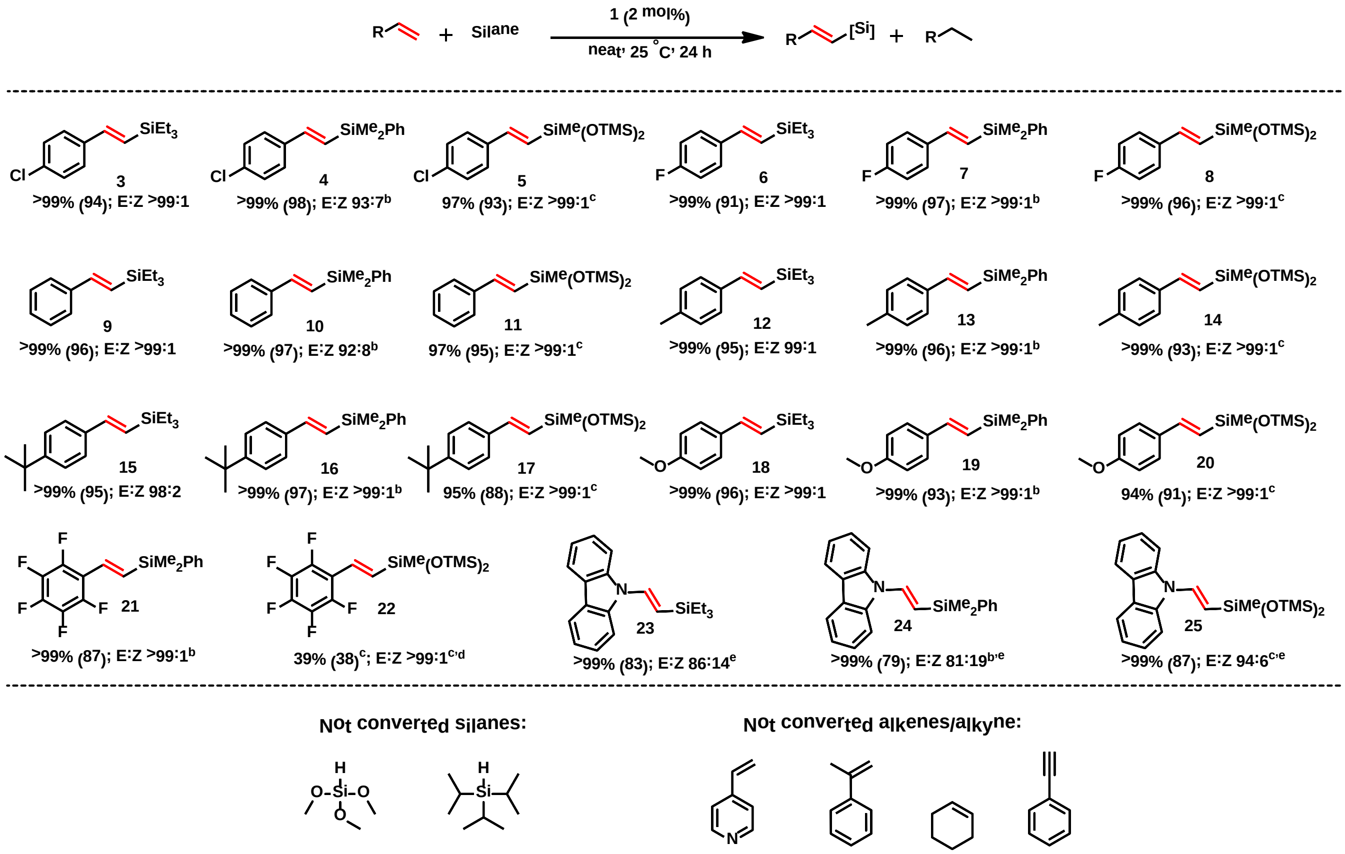
entry	[Mn] (mol%)	conversion (%)	E/Z	3:3a
1	**1** (3)	>99	97:3	2:1
2	**2** (3)	89	94:6	2.1:1
3[b]	**1** (2)	>99	>99:1	2:1
4[b,c]	**1** (2)	>99	>99:1	2:1
5[b,c,d]	**1** (2)	39[d]	>99:1	9:1
6[b,e]	**1** (2)	>99[e]	>99:1	2.2:1
7[b,f]	**1** (2)	>99	>99:1	2:1

[a]Reaction conditions: $HSiEt_3$ (0.56 mmol, 1 equiv.), 4-chlorostyrene (1.12 mmol, 2 equiv.), 0.5 ml anhydrous THF, 70C, 18 h. Conversion of silane, E/Z- and ratio of **3**:**3a** determined by GC/MS. [b]neat, 25°C, 24h. [c]4-Chlorostyrene (0.84 mmol, 1.5 equiv.). [d]3 equiv. 3,3-dimethylbutene used as SHA, conversion to **3** reported. [e]3 equiv $HSiEt_3$, conversion of alkene reported. [f]5 equiv. 4-chlorostyrene

moiety blocking a vacant side during reaction. Moreover, 1,1- or 1,2-disubstitured alkenes or phenylacetylene did not show any reactivity in the investigated transformation. Exploring the reaction scope regarding different silanes revealed high reactivity for $HSiMe_2Ph$ whereas the catalyst loading could be decreased to 0.5 mol%. Thus, excellent yield could be achieved, for pentafluoro styrene as substrate (Table 2, **21**).

Furthermore, excellent yields could be achieved, employing the commercially relevant 1,1,1,3,5,5,5-heptamethyltrisiloxane, although the reaction time had to be increased to achieve high conversions. Slightly lower reactivity towards styrenes, bearing an electron-donating group could be detected in case of trisiloxane (Table 2, **14**, **17** and **20**). In all above-mentioned cases the *E:Z* ratio was 92:8 or higher, whereas a moderate decrease in selectivity could be detected, when vinylcarbazol was used as substrate (Table 2, **23**-**25**).

Table 2. Substrate Scope of DS for Aromatic Alkenes Catalyzed by **1**[a]



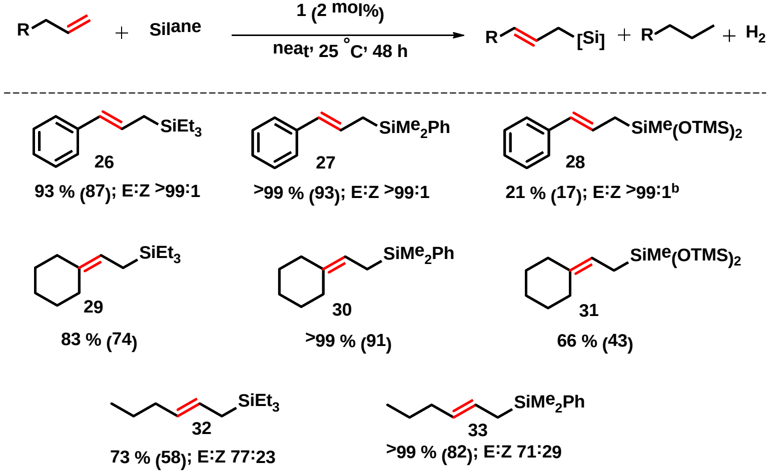
[a]Reaction conditions: silane (0.56 mmol, 1 equiv.), alkene (1.01 mmol, 1.8 equiv.), **1** (2 mol%), neat, 24 h, conversion of silane and *E:Z* ratio determined by GC/MS, isolated yield given in parenthesis [b]0.5 mol%. [c]48 h. [d]Yield determined by ^{1}H NMR analysis using 0.5 equiv. of 1,4-dioxane as standard. [e]0.1 mL THF as solvent.

The homogeneity of the reaction was confirmed by addition of one drop of mercury where no decrease of reactivity and selectivity was observed for the DS of 4-chlorostyrene and $HSiMe_2Ph$. In the presence of 1 equiv of PMe_3 (with respect to substrate), only traces of product formation could be detected, which indicates an inner-sphere mechanism, due to coordination of PMe_3 at a vacant side of the active species. The presence of 1 equiv. 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) did not influence the catalytic reaction, thus, ruling out a radical reaction pathway. This seems to be unique in the field of manganese catalyzed DS reactions of alkenes, since all literature known examples as shown in Scheme 1 appear to proceed *via* radical routes.[13]

A kinetic profile of the reaction $HSiMe_2Ph$ and styrene is depicted in Scheme 3. After an off-set period, the reaction proceeds in an almost linear fashion (Scheme 3a, blue squares). It should be noted that the reactivity of the system is lower by a factor of about 2-3 in THF as solvent when compared to the neat reaction. At low conversion of silane (and alkene respectively) a ratio of **10**:**10a** of 3.7:1 could be detected (Scheme 3a, red triangles). This indicates that in the initial stage of the reaction an acceptorless DS is the dominating reaction pathway. In fact, hydrogen gas could be detected in a head-space analysis of the reaction mixture, which clearly proofs that an acceptorless pathway is involved in the catalytic reaction. As the reaction proceeds the ratio of DS product to alkane decreases.

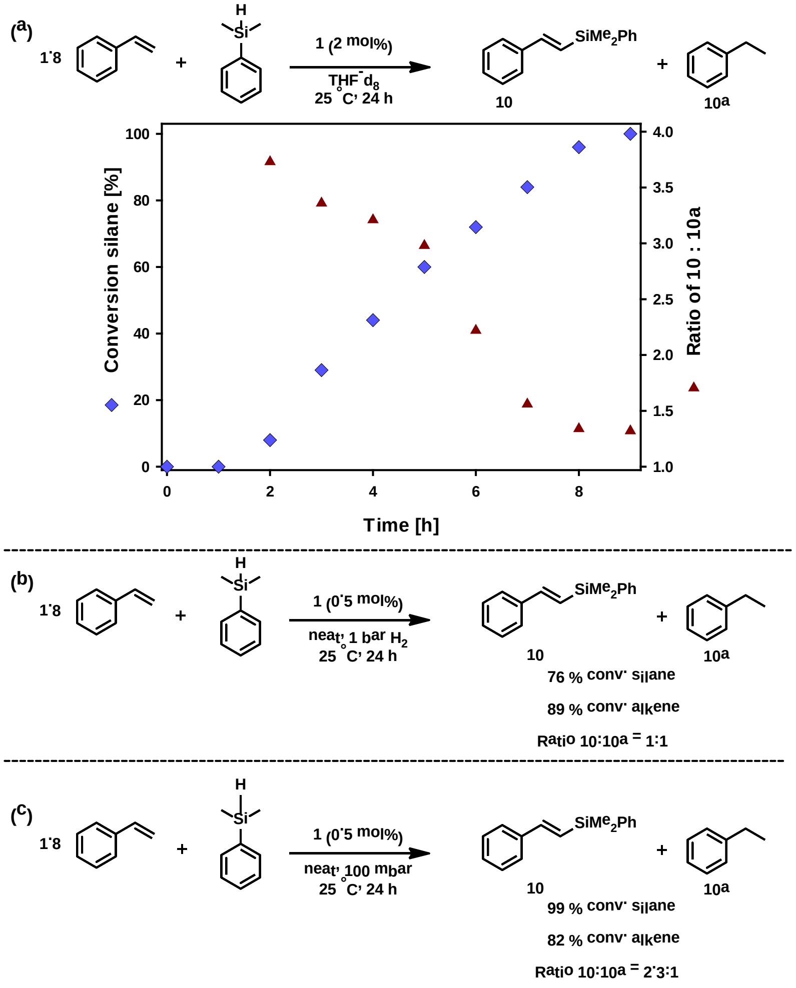
A similar behavior was observed for 4-fluorostyrene, 4-methylstyrene or 4-methoxystyrene. The ratio of **10**:**10a** is dependent on the concentration of hydrogen in the system. Accordingly, when the reaction was carried out under 1 bar hydrogen atmosphere an acceptorless DS took no longer place (Scheme 3b) and the products were formed in an almost 1:1 ratio. If the reaction was carried out under reduced pressure, a ratio of 2.3:1 of **10**:**10a** was observed (Scheme 3c).

Table 3. Substrate Scope of DS for Aliphatic Alkenes Catalyzed by **1**[a]



[a]Reaction conditions: silane (0.56 mmol, 1 equiv.), alkene (1.01 mmol, 1.8 equiv.), **1** (2 mol%), neat, 48 h, conversion of silane and E:Z ratio determined by GC/MS, isolated yield given in parenthesis. [b]Yield determined by ^{1}H NMR analysis using 0.5 equiv. of 1,4-dioxane as standard.

Scheme 3. Kinetic Profile and Mechanistic Experiments

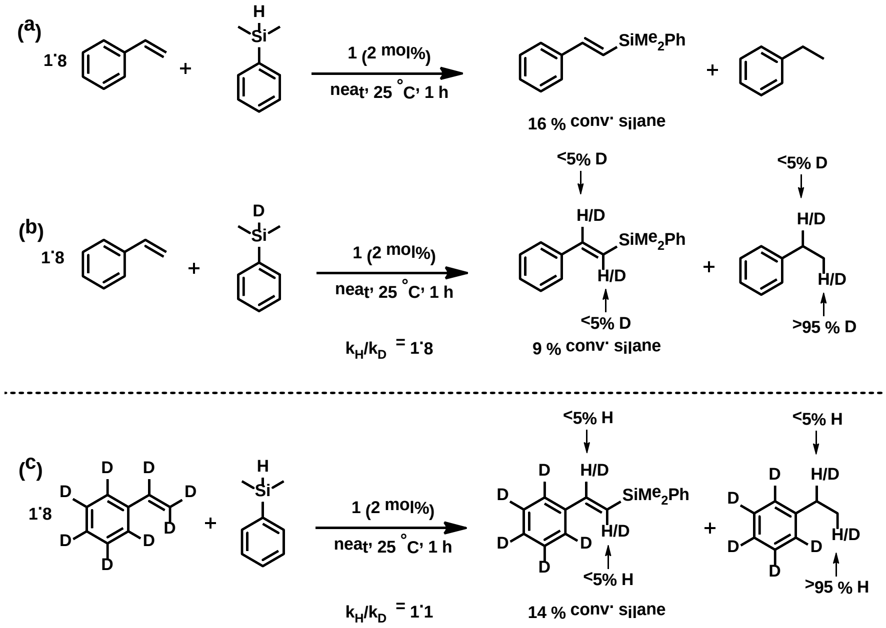


To gain insight in the rate determining step of the catalysis, kinetic isotope experiments were carried out. In two separate experiments, a kinetic isotope effect (KIE) of 1.8 for non-deuterated *vs*. deuterated silane could be detected (Schemes 4a and 4b). This value is slightly lower than for a cobalt-catalyzed DS as reported by Chirik and coworkers.[12a] In an additional experiment, fully deuterated styrene was used as substrate where KIE of merely 1.1 was detected. The rate determining step seems to be the cleavage of the Si-H bond during the activation of the catalyst rather than hydride elimination upon product release. This is also supported by the off-set in the kinetic profile depicted in Scheme 3a.

The incorporation of deuterium (or hydrogen) in products upon full conversion was studied with $DSiMe_2Ph$. Selective incorporation of deuterium in the terminal position of ethylbenzene was observed, whereas negligible deuterium content was found in the DS product or the benzylic position of ethylbenzene (Scheme 4b). If styrene-d_8 was used as substrate in combination with $HSiMe_2Ph$, only traces of hydrogen were found in the DS product and a high level of hydrogen incorporation on the terminal carbon of ethylbenzene was observed (Scheme 4c).

To gain further insight in the reaction mechanism, stochiometric reactions of **1** with silanes were carried out. If **1** was treated with an equimolar amount of $HSiMe_2Ph$ in THF-d_8, a small amount (<3%) of the known tricarbonyl hydride complex $[Mn(dippe)(CO)_3H]$ was generated (Scheme 5).[20] This complex did not show any catalytic activity in the DS reaction of alkenes. Furthermore, a new compound could be detected *via* ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. This species gave rise to a doublet of doublet centered at -10.17 ppm in the ^1H NMR spectrum (calculated value is -9.6 ppm). The chemical shift is in the same region as described by Schubert and coworkers for the manganese complex $[Mn(CpMe)(CO_2)(H\text{-}SiR_2SiR_2H)]$ complex featuring an agostic Si-H bond.[21] The $^{31}P\{^1H\}$ NMR spectrum exhibits two doublets at 121.3 and 108.7 ppm. $^1H/^{31}P$ 2D-NMR analysis revealed that both signals belong to a single species (for details see SI).

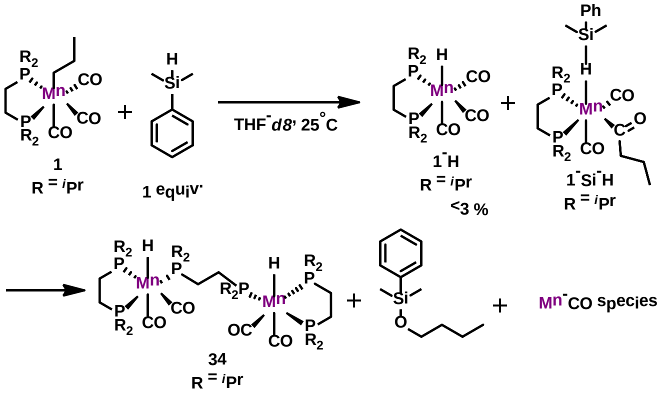
Scheme 4. Determination of KIE and Deuterium Incorporation



It has to be noted that protonation of the alkyl ligand of **1** by the silane, which would lead to liberation of propane and generation of a silyl-complex, was not observed. In fact, such a reaction was described by Chirik and coworkers in the case of a cobalt-catalyzed DS of alkenes.[12a]

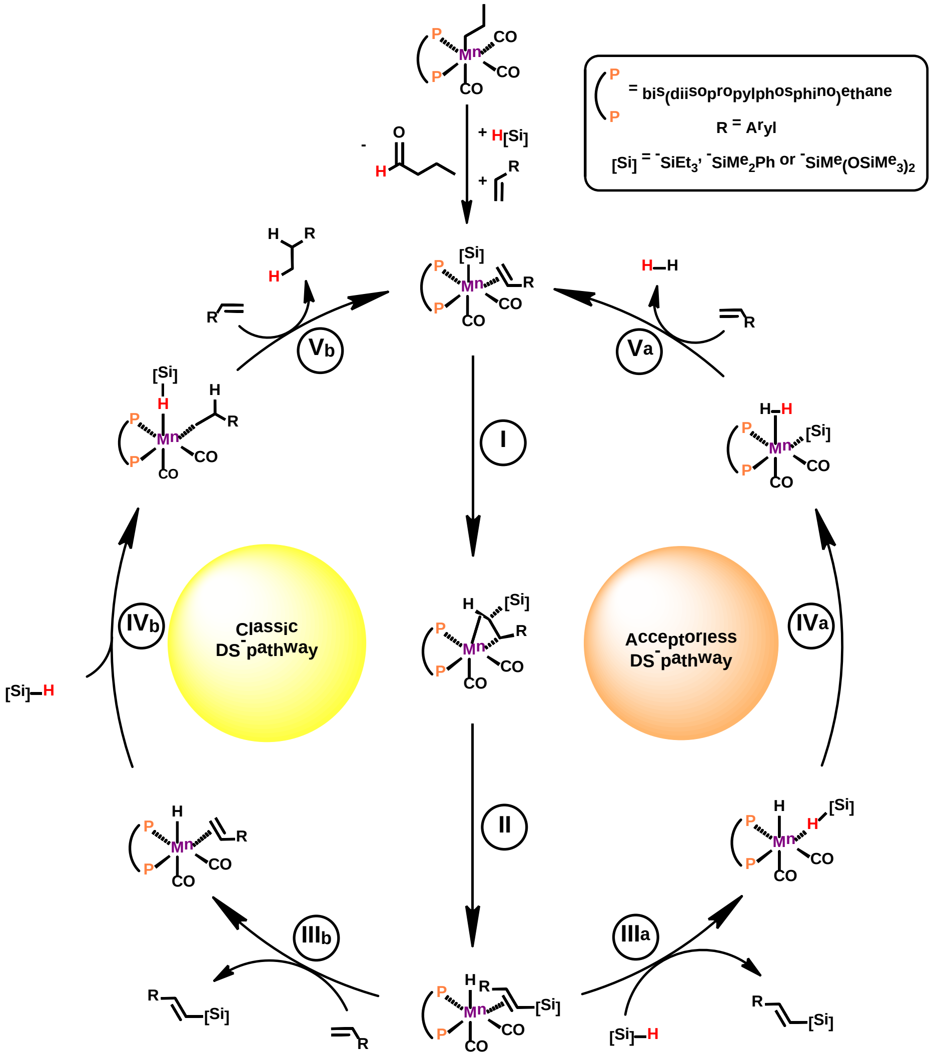
Since manganese(I)-alkyl complexes are known to undergo migratory insertion of the alkyl into the carbonyl ligand,[18] we believe that the resonances of the above described compound may be tentatively assigned to the acyl complex $[Mn(dippe)(CO)_2(\eta^1\text{-}C(O)CH_2CH_2CH_3)(\eta^1\text{-}H\text{-}SiMe_2Ph)]$ (**1-Si-H**). All attempts to isolate this complex failed due to the high reactivity of this species towards the unreacted silane.

Scheme 5. Stochiometric Reaction of **1** with $HSiPhMe_2$



The geometry of complex **1-Si-H** was optimized by means of DFT calculations[22] (Figure S14, SI) and shows a σ-complex with the silane coordinated through the Si–H bond in an apical position position *trans* to a CO ligand. This is reflected in the weakening of that bond in **1-Si-H**, compared with free silane. The Si–H distance rises from 1.50 Å in HSiMe2Ph to 1.54 Å in **1-Si-H**, while the corresponding Wiberg indices (WI)[23] are 0.92 and 0.66, by the same order. Also, Mn–H and Mn–Si correspond to bonding interactions with distances of 1.80 and 3.12 Å, respectively, and Wiberg indices of 0.14 (Mn–H) and 0.07 (Mn–Si).

Scheme 6. Proposed Mechanism for DS Following Two Parallel Pathways



After approximately 50% conversion of silane, decomposition of **1-Si-H** took place affording the dimeric complex **34** which is catalytically inactive. This reaction was accompanied by hydrosilylation of the released *n*-butanal. The molecular structure of this complex was unequivocally established by X-ray crystallography and NMR spectroscopy (see SI). Upon full conversion of the silane, several intractable manganese carbonyl species were formed based on IR spectroscopy. *In situ* NMR analysis during the catalytic reaction also revealed the formation **1-Si-H**. Traces of **34** could be detected after approximately 90% conversion.

Based on the above investigations as well as on recent mechanistic studies of hydrogenation reactions involving alkenes and ketones[14-17] and alkyne dimerizations and cross couplings,[19] a plausible reaction mechanism consistent with the experimental observations is presented in Scheme 6. Pre-catalyst **1** undergoes migratory insertion of the alkyl group into the adjacent CO-ligand which is initiated by silane coordination. Deprotonation of the silane by the strongly basic acyl ligand leads to the formation of the active 16e$^-$ Mn(I) silyl catalyst [Mn(dippe)$(CO)_2(SiR_3)$] which is able to coordinate alkenes. Insertion of the silyl ligand into the C=C bond of the alkene leads to the formation of a silylated alkyl complex which is stabilized by a C-H agostic interaction (**I**). Upon β-hydride elimination a hydride alkene intermediate is formed (**II**). At this stage, the product can either be released upon substitution by another silane paving the way for an acceptorless pathway (**IIIa**) or by substitution by an incoming alkene substrate (**IIIb**) following a classical DS pathway.

Within the acceptorless pathway, the hydride ligand reacts with the coordinated Si-H moiety to afford a silyl complex featuring an η^2-dihydrogen ligand (**IVa**). Substitution of dihydrogen by an alkene substrate and subsequent isomerization reforms the initial catalyst (**Va**). This pathway is favored at low hydrogen pressure (*vide supra*).

In the classic pathway (**IIIb**), alkene insertion into the Mn-H bond takes place which, in the presence of silane, leads to the formation of an alkyl intermediate (**IVb**). Deprotonation of silane and substitution of the formed alkane by the alkene substrate leads to regeneration of the catalyst (**Vb**). This reaction pathway dominates upon reaction progress as higher hydrogen concentrations inhibit the acceptorless pathway. It has to be noted the reaction of alkenes and silanes to give vinylsilanes and dihydrogen is thermodynamically unfavored under standard conditions. In fact, the DFT calculated free energy balance for the formation of product **10** and H_2 from styrene and $HSiMe_2Ph$ is clearly positive: $\Delta G = 6.1$ kcal/mol (Equation S1, SI). However, such conditions are not fulfilled at low hydrogen pressure and accordingly such a reaction becomes feasible.

CONCLUSION

DS of alkenes displays an interesting approach to synthesize unsaturated silanes. However, the atom efficiency is lowered by the fact that an excess of substrate or addition of sacrificial agents is typically required. We have established a solvent free manganese-catalyzed DS procedure of terminal alkenes under mild conditions (room temperature) with no additives needed. The most active pre-catalyst is the bench-stable alkyl bisphosphine Mn(I) complex *fac*-[Mn(dippe)$(CO)_3$ $(CH_2CH_2CH_3)$]. The catalytic process is initiated by migratory insertion of a CO ligand into the Mn-alkyl bond to yield an acyl intermediate which undergoes rapid Si-H bond cleavage of the silane $HSiR_3$ forming the active 16e$^-$ Mn(I) silyl catalyst [Mn(dippe)$(CO)_2(SiR_3)$] together with liberated butanal. The implemented system operates at room temperature without any additives and low catalyst loadings. A broad variety of different styrene derivatives, yielding selectivity *E*-vinylsilanes, and aliphatic systems, giving allylsilanes, were efficiently reacted with different tertiary silanes. Mechanistic studies which include *in situ* NMR measurements, determination of reaction kinetics, analysis of decomposed active species and deuterium labeling experiments provided insights in the reaction mechanism. A proposed reaction mechanism following two parallel pathways is presented proceeding under acceptorless conditions and *via* a pathway requiring an alkene as sacrificial hydrogen acceptor. Thus, in many instances the ratio of vinylsilane or allysilane to alkene approaches a 2:1 rather than a 1:1 ratio as normally observed. In contradiction to other manganese-based procedures, the reaction proceeds *via* an inner-sphere mechanism rather than *via* radical routes.

Supporting Information

Synthetic procedures, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{H\}$ NMR spectra of all compounds and crystallographic data (PDF)
X-ray crystallographic data (CIF)
CCDC 2094811 contains the supplementary crystallographic data for this paper.

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