Showcasing research from Professor Emslie’s laboratory, Department of Chemistry, McMaster University, Hamilton, Ontario, Canada.

Interconversion and reactivity of manganese silyl, silylene, and silene complexes

This work involves the reaction of a monosubstituted manganese silylene complex (L,H,Mn=SiHR) with ethylene to afford the first transition metal silene complex with an SiH substituent (L,H,Mn(RHSi=CHMe)), unprecedented isomerization to a silylene isomer (L,H,Mn=SiEtR), and further reaction with ethylene to afford a new silene complex (L,H,Mn(REtSi=CHMe)). Reaction mechanisms were elucidated through reactions with C2,D4, and we report the involvement of the aforementioned silene complexes in catalytic ethylene hydrosilylation. The image shows Mn atoms traversing 4 mountain peaks representing the stepwise silylene $\rightarrow$ silene $\rightarrow$ silylene $\rightarrow$ silene transformations in the research.

As featured in:

Interconversion and reactivity of manganese silyl, silylene, and silene complexes

Jeffrey S. Price and David J. H. Emslie

Manganese disilyl hydride complexes [(dmpe)₂MnH(SiH₂R)₂] (4₈H: R = Ph, 4Bu: R = "Bu) reacted with ethylene to form silene hydride complexes [(dmpe)₂MnH(RH₂=C=CHMe)] (6₈H: R = Ph, 6BuH: R = "Bu). Compounds 6₈H reacted with a second equivalent of ethylene to generate [(dmpe)₂MnH(RE₃=S=C=CHMe)] (6₈H; R = Ph, 6₈BuH: R = "Bu), resulting from apparent ethylene insertion into the silene Si–H bond. Furthermore, in the absence of ethylene, silene complex 6₈BuH slowly isomerized to the silylene hydride complex [(dmpe)₂MnH(=SiEt₂Bu)] (3₈BuH). Reactions of 4₈H with ethylene likely proceed via low-coordinate silyl ([(dmpe)₂Mn(SiH₂R)] (2₈H: R = Ph, 2₈Bu: R = "Bu)) or silene hydride ([(dmpe)₂MnH(=SiH₃R)] (3₈H; R = Ph, 3₈BuH: R = "Bu)) intermediates accessed from 4₈H by H₂SiR elimination. DFT calculations and high temperature NMR spectra support the accessibility of these intermediates, and reactions of 4₈H with isonitriles or N-heterocyclic carbenes yielded the silyl isonitrile complexes [(dmpe)₂Mn(SiH₂R)(CNR₂)] (7a–d: R = Ph or "Bu; R' = α-xylyl or "Bu), and NHC-stabilized silene hydride complexes [(dmpe)₂MnH(=SiHR(NHC)] (8a–d: R = Ph or "Bu; NHC = 1,3-disopropylimidazolin-2-ylidene or 1,3,4,5-tetramethyl-4-imidazolin-2-ylidene), respectively, all of which were crystallographically characterized. Silyl, silylene and silene complexes in this work were accessed via reactions of [(dmpe)₂MnH(C₆H₄)] (1) with hydrosilanes, in some cases followed by ethylene. Therefore, ethylene (C₆H₄H₂ and C₆D₆) hydrosilylation was investigated using [(dmpe)₂MnH(C₆H₄)] (1) as a pre-catalyst, resulting in stepwise conversion of primary to secondary to tertiary hydrosilanes. Various catalytically active manganese-containing species were observed during catalysis, including silylene and silene complexes, and a catalytic cycle is proposed.

Introduction

Silylenes (SiR₂)² and silenes (R₂=C=SiR₂),³–⁴ heavy analogues of carbenes and alkenes, are highly reactive species, and in the absence of extremely bulky or π-donor substituents,³ transition metal coordination is required for stabilization.³⁻⁴⁻⁸ However, complexes bearing unstabilized silylene ligands are involved in various catalytic processes involving silanes, including dehydrosilylation, substituent redistribution, hydrosilylation, and the Direct process for silane chlorination.⁷ Similarly, silene complexes have in several instances been hypothesized to play an important role in catalysis, typically on the basis of indirect observations. For example, they are thought to be active species in polycarbosilane synthesis from dichloromethylsilanes and sodium in the presence of [CP₂ZrCl₂],⁹ dehydrogenative coupling of HSiMe₃ by [[(Me₂P)₃RuH₂(SiMe₃)]],¹⁰ transfer dehydrogenative coupling of HSiEt₃, catalysed by [(p-cymene)RuH₂( SiEt₃)] or [Cp⁴Rh₂H₂(SiEt₃)]¹¹ and trialkylsilane (e.g. HSiMe₃) perdeuteration catalysed by [[(Me₂P)₃OsH(SiMe₃)]],¹² or [(C₆Me₆) RuH₂(SiMe₃)] in C₆D₆. Furthermore, silene complexes were recently proposed as off-cycle species in sila-heterocycle synthesis by intramolecular silylation of primary C–H bonds,¹⁴ and free silenes play a key role in hot wire CVD of SiC using alkylsilanes.¹⁵

Early examples of isolable transition metal complexes bearing a terminal silylene ligand featured Lewis base coordination to silicon,¹⁶ and base-free terminal silylene complexes were not isolated until 1990.¹⁷ Since then, a range of such complexes have been reported; almost exclusively mid- and late-transition metal complexes,¹⁸ which are electrophilic at silicon. By contrast, silylene complexes with an SiH substituent remain relatively rare; the first example, [(Et₃P)₃IrH₂(=SiH(C₆H₃-Mes₂-2,6)][B(C₆F₅)₃]₃, was reported in 2002,¹⁹ and in the same year, Tilley et al. suggested [(PhB(CH₂PPh₂)₃]IrH₂(=SiH(Trip))] as an intermediate in the synthesis of [(PhB(CH₂PPh₂)₃]IrH₂(=Si(C₆H₄)₃(Trip))].²⁰ Two years later, the Tobita²¹ and Tilley²² groups independently reported the first structurally characterized examples,
[[(C₂H₅Me)₂Et][O(OC)₂WH(=SiH[C(SiMe₃)$_3$])]] and [Cp*(dmpe)MoH(=SiHPh)], respectively. Base-free L₂M=SiHR complexes have only been isolated for groups 6, 8 and 9,19-28 and group 7 examples are notably absent. Extensive studies by the Tilley and Tobita groups have demonstrated that hydrogen substituents on the sp² Si centers permit these silylene complexes to demonstrate unusual reactivity, including alkene insertion into the silylene Si–H bond in cationic complexes, and conversion to silylene (M=SiR) complexes.26,23,25

A small number of transition metal silene complexes have also been isolated, with 2nd and 3rd row transition metal examples (bearing sterically and electronically unstabilized silene ligands)37 limited to complexes of Ir, Ru, and W (Fig. 1).26-30 Furthermore, outside of our recent report of manganese silene complexes (vide infra), first row transition metal complexes bearing unstabilized silene ligands have not been isolated.

We recently communicated the synthesis (Scheme 1) of the first unsubstituted terminal silylene complexes of a group 7 metal, [[(dmpe)₂MnH(=SiR)] (3²⁻: R = Ph, 3¹¹⁻: R = Et), by the reaction of [[(dmpe)₂MnH(C₂H₄)] (1)³¹ with secondary hydrosilanes (H₂SiR₂).22 In the solid state, the silylene and hydride ligands are cis (diphenyl analogue 3²⁻) or trans (diethyl analogue 3¹¹⁻) disposed, in the former case with an Si–H interligand interaction. Silylene hydride complexes with interligand Si–H interactions were first reported in 2004 by the Tobita³¹ ([[C₅Me₅Me][O(OC)₂WH(=SiH[C(SiMe₃)$_3$])]) and Tilley²² ([[Cp*(dmpe)MoH(=SiEt₂)])³³ groups, and since that time, W, Fe, Ru, and Ni examples have been reported.²⁵-²⁶,³¹ Uniquely, the cis and trans isomers of 3²⁻ exist in equilibrium with one another in solution (Scheme 1).

In contrast to the reactions of 1 with secondary hydrosilanes, reactions with primary hydrosilanes (H₂SiR) yielded disilyl hydride complexes [[(dmpe)₂MnH(SiH₂R₂)] (4²⁻: R = Ph, 4¹¹⁻: R = 4Bu; Scheme 1).³⁵ The syntheses of both silylene hydride complexes 3²⁻ and disilyl hydride complexes 4²⁻ from 1 were proposed to proceed via a 5-coordinate silyl intermediate [(dmpe)₂Mn(SiHRR)] (2²⁻: R = R’ = Ph; 2¹¹⁻: R = R’ = Et; 2²⁺: R = Ph, R’ = H; 2³⁻: R = 4Bu, R’ = H), which undergoes z-hydride elimination to generate 3²⁻, or oxidative addition of a second equivalent of hydrosilane to afford 4²⁻ (Scheme 1).

Reactions of the silylene hydride complexes with ethylene generated the silene hydride complexes cis-[[(dmpe)₂MnH(R₂Si=CHMe)] (R = Ph (5²⁺) or Et (6¹¹⁻), Scheme 1). This type of silylene to silene transformation is unprecedented, although Tilley et al. have reported conversion of [Cp*(Me₂P)Ir(Me)(=SiMe₂)]⁺ to the silene hydride isomer,

\[
\text{[Cp*(Me₂P)IrH(Me₂Si=CH₂)]}²⁺
\]

The intermediacy of a trimethylsilyl iridium complex in this reaction was supported by trapping reactions with CO and ethylene. Additionally, the iridium silene hydride cation reacted with pyridine to afford [Cp*(Me₂P)Ir(Me)(=SiMe₂(py))], highlighting the reversibility of the silylene–silene transformation (Scheme 2).

Furthermore, many of the known silene complexes were synthesized by installation of a CH₂SiR₂H (R = Me or Ph) or SiR₂Me group, followed by β-hydride elimination.¹⁴,²⁶,²⁹ These classes of reaction are combined in Scheme 2, highlighting the potential to interconvert between silylene, silyl, silene, and alkyl (CH₂SiR₂H) complexes.

Both silylene hydride complexes 3²⁻ and disilyl hydride complexes 4²⁻ have been shown to react with H₂ (Scheme 1) to

![Fig. 1 Second and third row transition metal complexes bearing sterically and electronically unstabilized silene ligands.](image)

![Scheme 1 Reactions of [(dmpe)₂MnH(C₂H₄)] (1) with primary and secondary hydrosilanes to generate silylene-hydride (3⁻) and disilyl hydride (4⁻) complexes respectively, reactions of the latter two complexes with H₂ to generate isostructural silyl dihydride complexes (3²⁻ or 5⁻ respectively), and reaction of silylene hydride complexes 3²⁻ with ethylene to generate silyl hydride complexes (6²⁻). Only one isomer is shown for 2, 5, and A.](image)

![Scheme 2 Reported reactions capable of converting between silylene, silyl, silene and alkyl isomers.](image)
generate silyl dihydride complexes \([\text{[dmpe]}_2\text{MnH}_2(\text{SiHRR'}\text{])}]\) \(5^{\text{Ph2}}\); \(R' = \text{Ph}; 5^{\text{Et2}}\); \(R' = \text{Et}; 5^{\text{B}u}\); \(R = \text{Ph}, R' = \text{H}; 5^{\text{Bu}}\); \(R = \text{Bu}, R' = \text{H})\), suggesting the accessibility of a common low-coordinate silyl intermediate, \([\text{[dmpe]}_2\text{Mn(\text{SiHRR'})}]\) \(2\).\(^2\)\(^{3,4}\)
Therefore, disilyl hydride complexes \(4^R\) could potentially react as sources of manganese silylene hydride complexes with an SiH substituent, and exposure of \(4^R\) to ethylene may provide a route to silene complexes bearing an SiH substituent.

Herein, we report the reactions of disilyl hydride complexes \(4^R\) with ethylene to generate the first examples of silene complexes with a hydrogen substituent on silicon. Their unique reactivity is also described, including (a) silene hydride to silylene hydride isomerization, and (b) reaction with a second equivalent of ethylene to convert the SiH substituent to an SiEt group. The reactions of \(4^R\) with ethylene likely proceed via a low-coordinate silyl or silylene hydride intermediate, and DFT calculations, high temperature NMR spectroscopy, and trapping studies are described, providing insight into the accessibility of these intermediates.

All of the silyl, silylene and silene complexes in this work are accessed via reactions of \([\text{[dmpe]}_2\text{MnH}(\text{C}_2\text{H}_4\text{])}]\) \(1\) with hydrosilanes, in some cases followed by ethylene. Therefore, ethylene \((\text{C}_2\text{H}_4\text{ and C}_2\text{D}_4\text{)}\) hydrosilylation was investigated using \([\text{[dmpe]}_2\text{MnH}(\text{C}_2\text{H}_4\text{])}]\) \(1\) in combination with primary and secondary hydrosilanes, and a catalytic cycle is proposed (based on the metal species and hydrosilane products observed throughout the course of the reactions). Alkene hydrosilylation is an industrially important transition metal-catalysed process for allylsilane production,\(^{-3,9}\) and the most common olefin hydrosilylation catalyst used in industry is Karstedt’s catalyst, \(\text{[Pt}(\text{O(SiMe}_2\text{)(CH} = \text{CH}_2\text{))}_3\text{]}\).\(^3\)\(^4\) However, the development of catalytic systems based on first row transition metals such as manganese is of interest due to high abundance, low cost, reduced toxicity, and improved environmental compatibility.\(^10\) In this regard, manganese mediated hydrosilylation of polar unsaturated bonds has been well studied,\(^{11,12}\) but only a handful of manganese complexes have been reported for alkene hydrosilylation.\(^12,13\)

The typical mechanism for alkene hydrosilylation (Chalk–Harrod mechanism) involves oxidative addition of a hydrosilane to generate a silyl hydride complex, followed by alkene coordination, C–H bond-forming 1,2-insertion, and finally Si–C bond-forming reductive elimination. However, in some cases alkene coordination is followed by C–Si bond-forming 1,2-insertion and then C–H bond-forming reductive elimination (modified Chalk–Harrod mechanism). Furthermore, catalytic cycles which proceed via a monosilyl complex rather than a silyl hydride complex have been reported, including hydrosilylation reactions utilizing a cationic palladium(II) or cobalt(III) alkyl pre-catalyst.\(^10,14\)

**Results and discussion**

**Reactions of disilyl hydride complexes \(4^R\) with ethylene**

The disilyl hydride complexes \([\text{[dmpe]}_2\text{MnH}(\text{SiHR}_2\text{])}]\) \(4^4\text{Ph}: R = \text{Ph}, 4^\text{Bu}: R = \text{Bu}\) reacted with ethylene at room temperature to afford the silene hydride complexes \([\text{[dmpe]}_2\text{MnH}(\text{RHSi} = \text{CHMe})\text{]})\) \((6^{\text{PhH}}: R = \text{Ph}, 6^{\text{BuH}}: R = \text{Bu})\). This reaction mirrors the reactions of silylene hydride complexes \(3^{R2}\) with ethylene (vide supra; Scheme 1).\(^15\) Moreover, complexes \(6^R\text{Et}\) reacted with a second equivalent of ethylene to form silene hydride complexes with two hydrocarbyl groups on Si. \([\text{[dmpe]}_2\text{MnH}(\text{REtSi} = \text{CHMe})\text{]})\) \(6^{\text{PhH},\text{Et}}\), \(R = \text{Ph}, 6^{\text{BuH},\text{Et}}: R = \text{Bu}\); the products of apparent ethylene insertion into the Si–H bond (Scheme 3 and Fig. 2). This silene SiH to SiEt conversion reaction is unprecedented. Complexes \(6^\text{Et}\text{BuH}\) also reacted further with ethylene to generate \([\text{[dmpe]}_2\text{MnH}(\text{C}_2\text{H}_4\text{])}]\) \((1,15\text{) potentially by substitution of the silene ligand which undergoes subsequent decomposition to unidentified products.**

A range of byproducts were observed in the syntheses of silene hydride complexes, including primary, secondary, and tertiary hydrosilanes \(\{\text{H}(3-n)\text{SiEt}_nR \quad (n = 0, 1, 2; R = \text{Ph}, \text{3Bu})\}\),\(^45\) the latter two are formed by stepwise manganese-catalysed hydrosilylation reactions between the primary hydrosilane byproduct and excess ethylene (vide infra). For \(R = \text{Bu}\), silene SiH to SiEt conversion did not proceed until all of the primary hydrosilane byproduct had been consumed, so conversion of \(4^\text{Bu}\) to \(6^{\text{BuH}}\), and then to \(6^{\text{BuH},\text{Et}}\), proceeded in a stepwise fashion. By contrast, for \(R = \text{Ph}\), silene SiH to SiEt conversion commenced as soon as \(6^{\text{PhH}}\) was available (Fig. 2).

Compounds \(6^{\text{BuH}}\) and \(6^{\text{PhH}}\) were isolated as a red oil and a brown solid, respectively, in \(>95\%\) purity. By contrast, \(6^{\text{PhH}}\) and \(6^{\text{BuH}}\) were characterized in situ by NMR spectroscopy (Table 1). Compounds \(6^{\text{PhH}}\) and \(6^{\text{BuH}}\) were not isolated due to the formation of mixtures of products (e.g. \(6^{\text{PhH}}\) accompanied by \(6^{\text{BuH}}\) and 1)), combined with instability in solution over a period of days at room temperature.

In solution (in the absence of ethylene or free hydrosilanes), SiH-containing silene hydride complex \(6^{\text{BuH}}\) underwent isomerization to the silylene hydride complex trans-\([\text{[dmpe]}_2\text{MnH}(\text{==SiEtBu})\text{]})\) \((\text{trans-3}^{\text{BuH},\text{Et}}\text{)}\), Scheme 4), with \(20\%\) conversion after 2 days at room temperature in \(\text{C}_6\text{D}_6\).\(^46\) NMR spectra of \(\text{trans-3}^{\text{BuH},\text{Et}}\text{)}\) feature an MnH \(\text{^1}H\) NMR peak at
manganese hydride complex (with a quintet $^1$H NMR peak at $-9.06$ ppm; $^2$J$_{H,P} = 47$ Hz) and the silene hydride complex [(dmpe)$_2$MnH($^6$BuEtSi=CHMe)] ($^6$BuEt). Isomerization of a silene hydride complex to a silylene hydride complex is, to our knowledge, unprecedented. However, this isomerization is related to Tilley and Bergman’s report of an equilibrium between the silylene alkyl complex [CP*(Me$_6$P)Ir(Me)(=SiMe$_3$)] and the silene hydride isomer, [CP*(Me$_6$P)IrH(Me$_2$Si=CH$_3$)], which relies upon reversible α- and β-H elimination from a trimethylsilyl intermediate.$^{26}$

For silene hydride complexes $^6$H,Et (those with a hydride substituent on Si), two sets of NMR signals were observed due to a pair of isomers present in solution with a 1 : 1 ($^6$H,Et, $^6$Bu$^-$ ratio, whereas only a single set of NMR signals (indicative of a single isomer) was observed for $^6$Bu,Et (silene hydride complexes with two hydrocarbyl substituents on Si). NMR spectra of the silene hydride complexes feature (for each isomer) four $^3$P NMR signals, a single $^2$Si NMR environment (at $-17.4$ to 0.7 ppm), a low frequency $^1$C NMR signal for the Si=CH$_2$ environment (at $-19.3$ to $-21.7$ ppm), and a silene $^1$H$_{C,H}$ coupling constant ($137$–$139$ Hz) intermediate between those typical for sp$^3$ and sp$^2$ hybridized carbon atoms; Table 1. Additionally, the Mn$^{\text{H}}$ signal was located at $-14.5$ to $-15.3$ ppm in the $^1$H NMR spectra of $^6$H,Et and $^6$Bu,Et, and the Si=CH$_2$ signals were observed at $3.7$ to $4.5$ ppm, $-0.2$ to 0.2 ppm, and $1.7$ to $1.9$ ppm, respectively. These data are very similar to those for [(dmpe)$_2$MnH($^6$BuSi=CHMe)] ($^6$Bu$^-$, R = Ph, $^6$Bu$^+$, R = Et); pertinent NMR data is included in Table 1, which have been

Table 1. Selected $^1$H, $^{13}$C, $^{29}$Si and $^{31}$P NMR chemical shifts (ppm) and coupling constants (Hz) for silene hydride complexes [(dmpe)$_2$MnH($^6$Bu$^-$Si=CHMe)] ($^6$Bu$^-$, R = R$^\prime$ = Ph, $^6$Bu$^+$, R = R$^\prime$ = Et, $^6$Ph$^-$, R = Ph, R$^\prime$ = H; $^6$Bu$^+$, R = Ph, R$^\prime$ = Et; $^6$BuEt, R = $^6$Bu, R$^\prime$ = Et), in C$_6$D$_6$ ($^6$Bu$^-$ and $^6$Ph$^+$, Et$^-$) or $^6$Bu$^+$-toluene ($^6$Bu$^+$ and $^6$Ph$^+$, Et$^-$). Unless otherwise noted, values are from NMR spectra at 298 K. For $^6$H,Et NMR environments are reported for both observed isomers. Chemical shifts for $^6$Ph$^+$ and $^6$Bu$^+$ are from our prior communication$^{23}$

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$^a$ Due to the minor isomer of $^6$Bu$^-$, $^b$ Due to the major isomer of $^6$Bu$^-$, $^c$ Both isomers have identical chemical shifts. $^d$ Measured at 213 K [because this environment was not located by $^{29}$Si($^1$H) or 2D $^1$H–$^{29}$Si (HSQC or HMBC) NMR spectroscopy at 298 K]. $^e$ Coupling between the Si=CH$_2$ and Si=CHCH$_3$ environments. $f$ $^1$J$_{C,H}$ could only be resolved for one isomer.
spectroscopically, and (for 6Ph) crystallographically, characterized. To the best of our knowledge, 6Ph,H are the first spectroscopically observed examples of transition metal silene complexes with a hydrogen substituent on silicon.

Despite numerous attempts, we were unable to obtain X-ray quality crystals of 6Ph,H or 6Ph,Et. Therefore, we turned to DFT calculations in order to gain further insight into the structures of these complexes (ADF, gas-phase, all-electron, PBE, D3-BJ, T2P, ZORA). For all four complexes, energy minima were located for four cis silene hydride isomers with $E$ or $Z$ silene stereochromesty, and differing in the orientation of the silene methyl substituent (RR'Si=CHMe) relative to the two dppe ligands, as shown in Fig. 3 (see Fig. 4 for the lowest energy isomer of 6Bu,H). In all cases, isomers (i) and (ii) are within a few kJ mol$^{-1}$ of one another, and are 13–22 kJ mol$^{-1}$ lower in energy than isomers iii and iv, consistent with observation of just 2 isomers in the solution NMR spectra of 6Ph,H. By contrast, the apparent formation of a single isomer of compounds 6Ph,Et suggests that these reactions proceed under kinetic control.

In the calculated structures of silene hydride isomers (i) and (ii) (for bond metrics, see Table S4†), the Si–C bond distances of 1.80–1.81 Å fall within the range for previously reported transition metal silene complexes (1.78(2)–1.838(11) Å), and correspond to Mayer bond orders ranging from 0.96 to 1.10 (cf. 0.70–0.91 for Si–C single bonds in the same complexes). Also, as in previously reported $6^\text{H}_2$, significant interligand interactions exist between silicon and the hydride. Computationally, this is illustrated by short Si–H$_\text{Mn}$ distances (1.64–1.66 Å), with substantial Mayer bond orders (0.45–0.49), and is also reflected by a large negative $^{29}$Si–H$_\text{Mn}$ coupling constant of $-80$ Hz (measured using $^{29}$Si-edited 2D $^1$H–$^1$H COSY NMR spectroscopy) for the major isomer of 6Bu,H. (cf. $-30$ to $-31$ Hz for 4$^\text{Ph}$ and $>0$ in classical silene hydride complexes). Short Mn–Si distances (2.35–2.42 Å) with Mayer bond orders of 0.49–0.53, and Mn–H distances of 1.64–1.66 Å with Mayer bond orders of 0.52–0.56, combined with the short Si=C distance (vide supra) support the identification 6Ph,H and 6Ph,Et as cis silene hydride complexes, as opposed to 5-coordinate alkyl complexes with a strong β-Si–H–Mn interaction.

**DFT calculations on low-coordinate silyl and silylene hydride intermediates derived from 4$^\text{Ph}$**

The reactions of the disilyl hydride complexes [[dmpe]$_2$MnH(SiH$_R$)$_n$]$_2$ (4$^{	ext{Ph}}$: R = Ph, 4$^\text{Bu}$: R = $^8$Bu) with C$_2$H$_4$ (vide supra) likely proceed via either (a) 5-coordinate mono-silyl intermediates, [[dmpe]$_2$MnH(SiH$_R$)$_n$]$_2$ (4$^\text{Ph}$: R = Ph, 4$^\text{Bu}$: R = $^8$Bu), or (b) silylene hydride intermediates, [[dmpe]$_2$MnH$_2$]$_2$ (4$^\text{Ph}$: R = Ph, 3$^8$Bu,H: R = $^8$Bu), formed by sequential hydrosilane reductive elimination and $\alpha$-hydride elimination from disilyl hydride complexes 4$^\text{Ph}$ (Scheme 6; vide infra). Therefore, DFT calculations (ADF, gas-phase, all-electron, PBE, D3-BJ, T2P, ZORA) were carried out to assess the thermodynamic accessibility of such intermediates (Fig. 5 and Table 2).

In the case of low-coordinate silyl species, energy minima were located for structures in which the silyl group is either cis (cis-2$^\text{Ph}$) or trans (trans-2$^\text{Ph}$) to the vacant coordination site generated by hydrosilane reductive elimination. At 298 K, $\Delta$G for the formation of these monosilyl compounds and free hydrosilane from 4$^\text{Ph}$ is very similar (63–71 kJ mol$^{-1}$).

In the global minima for the cis isomers (rotamer 1 of cis-2$^\text{Ph}$), the hydrocarbyl substituent on silicon engages in a $\gamma$-agostic interaction with manganese (via an ortho-$CH$ bond in cis-2$^\text{Ph}$ or a CH$_2$CH$_2$CH$_2$CH$_3$ bond in cis-2$^{8}$Bu, with Mn–H$_n$ distances of 1.91–1.93 Å. The Mn–H$_n$–C$_g$ angles in this rotamer of cis-2$^\text{Ph}$ are 115.9° and 131.4°, respectively, and the presence of a $\gamma$-agostic interaction is further supported by Mayer bond orders of 0.22–0.24 between Mn and H$_n$, and 0.13–0.15 between Mn and C$_g$.

For the phenyl analogue 2$^\text{Ph}$, a higher-energy cis isomer was also located, corresponding to a rotamer where one of the two hydrogen substituents on silicon is now oriented in the direction of the vacant coordination site (rotamer 2 of cis-2$^\text{Ph}$; Fig. 5 and Table 2). Relative to rotamer 1, this structure features an acute Mn–Si–H$_{Si}$ angle of 101° (cf. 119°), an Mn–H$_n$–Mn bond order of 0.06 (cf. $<0.05$), a marginally elongated Si–H$_{Si}$ distance of 1.53 Å (cf. 1.51 Å), and a marginally lower Si–H$_n$–Mn bond order of 0.80 (cf. 0.85), together suggestive of a weak $\alpha$-Si–H–Mn interaction. Rotamer 2 of 2$^\text{Ph}$ is presumably involved in silylene hydride formation via $\alpha$-hydride elimination, and indeed, all...
isomer of [(dmpe)₂MnH(SiH₂R)] with a disphenoidal dmpe arrangement and a hydrocarbyl substituent on silicon oriented towards the vacant coordination site (rotamer 1 of cis-2R: R = Ph (cis-2Ph), cis-4Bu (cis-2Bu)), (ii) an isomer of [(dmpe)₂Mn(SiH₂R)] with a disphenoidal dmpe arrangement and an SiH₂ substituent oriented towards the vacant coordination site (rotamer 2 of cis-2R: R = Ph (cis-2Ph), a minimum was not located for R = 4Bu), (iv) an isomer of [(dmpe)₂MnH(═SiHR)] with interacting cis-disposed silylene and hydride ligands (cis-2PhH: R = Ph, cis-2BuH: R = 4Bu), and (v) trans-[(dmpe)₂MnH(═SiHR)] (trans-5PhH: R = Ph, trans-3BuH: R = 4Bu). Geometry optimized cores of the phenyl analogues of reactive intermediates are depicted below each energy level, showing Mn in red, Si in pink, C in dark grey, and H in light grey, accompanied by stick bonds to the phosphorus donor atoms.

Fig. 5 DFT calculated Gibbs free energies at 298.15 K (ΔG₂₉₈₁₅ K kcal mol⁻¹) to access reactive intermediates (and the H₃SiR byproduct) from disilyl hydride complexes [dmpe]₂MnH(SiH₂R)₂ (4Ph: R = Ph, blue dotted lines; 4Bu: R = 4Bu, red dashed lines). Calculated intermediates (left to right) are: (i) an isomer of [(dmpe)₂MnH(SiH₂R)] with an equatorial dmpe arrangement (trans-2Ph: R = Ph, trans-2Bu: R = 4Bu), (ii) an isomer of [(dmpe)₂Mn(SiH₂R)] with a disphenoidal dmpe arrangement and a hydrocarbyl substituent on silicon oriented towards the vacant coordination site (rotamer 1 of cis-2R: R = Ph (cis-2Ph), cis-4Bu (cis-2Bu)), (iii) an isomer of [(dmpe)₂Mn(SiH₂R)] with a disphenoidal dmpe arrangement and an SiH₂ substituent oriented towards the vacant coordination site (rotamer 2 of cis-2R: R = Ph (cis-2Ph), a minimum was not located for R = 4Bu), (iv) an isomer of [(dmpe)₂MnH(═SiHR)] with interacting cis-disposed silylene and hydride ligands (cis-2PhH: R = Ph, cis-2BuH: R = 4Bu), and (v) trans-[(dmpe)₂MnH(═SiHR)] (trans-5PhH: R = Ph, trans-3BuH: R = 4Bu). Geometry optimized cores of the phenyl analogues of reactive intermediates are depicted below each energy level, showing Mn in red, Si in pink, C in dark grey, and H in light grey, accompanied by stick bonds to the phosphorus donor atoms.

Table 2 Thermodynamic parameters calculated by DFT for the formation of intermediates in Fig. 5 from disilyl hydride complexes [dmpe]₂MnH(SiH₂R)₂ (4Ph: R = Ph, 4Bu: R = 4Bu); ΔE; ΔH; ΔS (320 K) values to access (3R-H). Hydride isomer. These isomers are isostructural to the X-ray crystal structures of cis-[(dmpe)₂MnH(═SiPh₂)] (3PhH) and trans-[(dmpe)₂MnH(═SiPh₂)] (3BuH), respectively. Calculated ΔG values to access (3R-H) from 4Ph range from 41 kJ mol⁻¹ (trans isomers) to 47–60 kJ mol⁻¹ (cis isomers) at 298.15 K, decreasing to 33–34 kJ mol⁻¹ (trans isomers) and 39–52 kJ mol⁻¹ (cis isomers) at 335 K, highlighting their thermodynamic accessibility.

High temperature NMR spectra of 4R in situ generation of trans-silylene hydride (trans-3R-H) species

At 335 K, ¹H NMR spectra of the disilyl hydride complexes [(dmpe)₂MnH(SiH₂R)₂] (4Ph: R = Ph, 4Bu: R = 4Bu) revealed the formation of a small amount of a new manganese complex and free hydroisilane (H₃SiR; R = Ph or 4Bu). This process is reversible, and clean spectra of 4R were observed upon cooling back to room temperature. The new manganese complex
exhibits a high frequency (9.83 or 9.53 ppm) and a low frequency (−9.01 or −9.60 ppm) 1H NMR signal. The former is in the range observed for the terminal =SiHR (R = hydrocarbyl substituent) environment in diamagnetic silylene complexes of Mo, W, Fe, Ru, Os, and Ir (6.34–12.1 ppm),19,20,22–26 while the latter is consistent with a metal hydride environment. The low frequency hydride signal is a quintet (2JH,H = 54 or 51 Hz) consistent with a hydride ligand apical to a plane of four equivalent phosphine donors. Taken together, these data suggest that the new complex observed at elevated temperature is trans-[(dmpe)2MnH=SiHR] (trans-3Ph; R = Ph, trans-3Bu; R = Bu) the most thermodynamically accessible silyl or silylene species in Fig. 5.

Characterization of trans-3Bu (R = Ph or 3Bu) by 29Si NMR spectroscopy was not successful since the new species were formed at very low concentrations (~4% and ~2% relative to 4Ph or 4Bu, respectively). However, EXSY NMR spectroscopy at 335 K indicates exchange between the two diastereotopic SiH protons in 4Ph or 4Bu, the free hydrosilane SiH peak, the high frequency trans-3Bu silylene SiH environment, and the MnH signals from both 4Ph and trans-3Bu (shown in Fig. 6 for R = 3Bu).54 This is consistent with an equilibrium in which 4Bu eliminates free H3SiR to form trans-3Bu (vide infra).

Trapping experiments with isonitriles and N-heterocyclic carbenes

To provide experimental corroboration for the accessibility of 5-coordinate silyl [(dmpe)2Mn(SiH2R)] (trans-2Bu; R = Ph, 2Bu, R = Bu) and silylene hydride [(dmpe)2MnH=SiHR] (3Ph; R = Ph, 3Bu, R = Bu) species from 4Ph, reactions with neutral donor ligands were carried out, with a view towards coordination to manganese in 2Ph or silicon in 3Ph (Scheme 5).

![Image of chemical structures](https://example.com/image.png)

**Scheme 5** Trapping of putative silyl (2Ph) and silylene hydride (3Ph) intermediates: synthesis of silyl isonitrile complexes [(dmpe)2MnSiHR(CNR)] (R' = o-xylyl, R = Ph, R' = o-xylyl; 6b: R = 3Bu, R' = o-xylyl; 6c: R = Ph, R' = 3Bu; 6d: R = 3Bu), and NHC-stabilized silylene hydride complexes [(dmpe)2MnH=SiHR(NHC)] (8a: NHC = tBuNHC, R = Ph, 8b: NHC = tBuNHC, R = 3Bu, 8c: NHC = tBuNHC, R = Ph, 8d: NHC = tBuNHC, R = 3Bu).

Addition of o-xylylN≡C or tBuN≡C to solutions of 4Ph resulted in hydrosilane elimination, and isolation of yellow or orange silyl isonitrile complexes [(dmpe)2MnSiHR(CNR)] (R' = o-xylyl, R = Ph (7a) or 3Bu (7b); R' = tBu, R = Ph (7c) or tBu (7d)), effectively trapping silyl complexes 2Ph (Scheme 5). In solution, all four reactions initially led to mixtures of two complexes identified by NMR spectroscopy as cis (85–97%) and trans (3–15%) isomers of 7a–d. Slow isomerization was observed between the cis and trans isomers of 7a–d in solution, and unexpectedly, these isomerization reactions proceeded in the direction of the trans isomers at elevated temperature (resulting in an increase in the proportion of trans isomer to 44–74% after heating solutions containing exclusively the cis isomer at 65–80°C for 4–21 days), and in the opposite direction upon leaving the same solutions at room temperature for 3 weeks (e.g. leaving cis/ trans mixtures of 7a,b containing 44–48% trans isomer at room temperature resulting in solutions containing 99% cis isomer after 3 weeks).
X-ray quality crystals were obtained for the four silyl isonitrile complexes 7a–d, in each case as the cis isomer (Fig. 7). All four structures are octahedral with Mn-Si distances of 2.3552(5) Å and Mn-C distances of 1.805(4)–1.847(3) Å. The isonitrile ligands show elongated C-N-C distances of 1.176(4)–1.225(9) Å and non-linear C-N-C angles of 159.2(8)–167.5(1)°, indicative of appreciable π-backbonding.

In contrast to reactions with isonitriles, reactions of disilyl hydride complexes 4® with 1,3-diisopropylimidazolidin-2-ylidene (iPrNHC) or 1,3,4,5-tetramethyl-1-imidazolidin-2-ylidene (MeNHC) afforded the base-stabilized silylene hydride complexes [[dmpe]2MnH(=SiHR(NHC))]; [NHC = iPrNHC, R = Ph (8a) or 4®Bu (8b); NHC = MeNHC, R = Ph (8c) or 4®Bu (8d)], trapping the proposed silylene hydride species 3®R-H (Scheme 5). Compounds 8b–d were isolated as analytically pure red powders, whereas 8a evaporated purification.

A variety of NHC-stabilized silylene complexes have been reported for V, Cr, W, Fe, Co, Rh, and Ni, and relative to base-free silylene complexes, they feature longer metal–silicon bond distances, pyramidalization at silicon, and lower frequency 29Si NMR chemical shifts (typically 25–100 ppm,® compared with >200 ppm for base-stabilized silylene complexes)®.

Room temperature NMR spectra of iPrNHC adducts 8a,b revealed two sets of broad NMR signals in the process of coalescence/decaushe, due to a pair of rapidly interconverting isomers. Cooling the solutions afforded two sets of well resolved NMR signals corresponding to compounds with a disphenoidal arrangement of the phosphorus donor atoms, each with a single SiH signal (5.1 to 6.4 ppm), a single MnH resonance (–12.3 to –12.6 ppm), a single 29Si NMR environment (22.2 to 29.6 ppm), and four unique 31P NMR environments (65.6–81.9 ppm). These data are indicative of NHC-coordinated cis silylene hydride complexes existing as a pair of interconverting diastereomers (due to chirality at Si and Mn).

In contrast, NMR spectra of the iPrNHC silylene hydride complexes (8c,d) revealed the same two rapidly interconverting cis diastereomers plus a third isomer which afforded a sharp set of 1H and 31P NMR signals at room temperature. This third isomer corresponds to an NHC-coordinated trans silylene hydride complex, as evidenced by a single MnH (–14.9 or –15.0 ppm) signal with a quintet coupling pattern (J_H,Mn = 48–49 Hz) and two sharp signals in the 31P{1H} NMR spectra (78.7–80.6 ppm) due to diastereotopic phosphorus atoms. The 1H NMR SiH and 29Si NMR chemical shifts in these trans isomers (4.9–5.8 ppm and 22.4 ppm, respectively)® are similar to those in the cis isomers.

At 335 K, the two cis diastereomers of 8a–d gave rise to a single set of averaged signals, with the MnH peak at –12.5 to –12.7 ppm (quintets for cis-8a,c,d with J_H,Mn = 32–34 Hz, while the NMR signal for 8b remained a broad singlet in the process of coalescence), accompanied by (in solutions of 8c,d only) a set of sharp signals for the trans isomer. For 8c,d, EXSY NMR spectroscopy at 335 K showed cross peaks between the MnH and SiH and 31P NMR signals due to both the cis and trans isomers (i.e. chemical exchange between all four environments). This equilibrium between cis- and trans-8c,d mirrors that previously reported between the cis and trans isomers of base-free [[dmpe]2MnH(=SiPr2)] (3®PH)®.

Possible mechanisms for ambient temperature exchange between the cis diastereomers of 8a–d are (a) phosphine donor dissociation, isomerization of the 5-coordinate product, and phosphine re-coordination, or (b) NHC dissociation to generate cis-[[dmpe]2MnH(=SiHR)] (cis-3®PH); R = Ph, cis-3®Bu®H; R = 4®Bu®, followed by re-coordination to the opposite face of the silylene ligand. The latter mechanism would imply that 8a–d, like disilyl hydride complexes 4®, could react as sources of either base-free silylene hydride complexes 3®R-H, or 5-coordinate silyl complexes 2®. The accessibility of this pathway is implied by the reactions of 8d with 1BuNC® and 8b with ethylene, which afforded [[dmpe]2Mn(=SiH2®Bu)(CN®Bu)] (7d) and [[dmpe]2MnH(=BuSi=CHMe)] (6®Bu®,® respectively; these are the same complexes formed in reactions of these reagents with 4®Bu®. Furthermore, the accessibility of 2® provides a mechanism for the observed exchange between the SiH and MnH environments in the EXSY NMR spectra of 8c,d at 335 K (vide supra).

X-ray quality crystals were obtained for complexes 8a–d by recrystallization from concentrated hexanes solutions (8a,b), toluene layered with pentane (8c), or a dilute hexanes solution (8d) at –30 °C. The solid state structures of 8a–c (Fig. 8; top row and bottom left) feature a cis arrangement of the hydride and base-stabilized silylene ligands, corresponding to one of the two cis diastereomers observed in solution.® By contrast, 8d crystallized as the trans isomer (Fig. 8; bottom right). In all four structures (complementary DFT calculations modelled 8b,d with an 4®Bu group in place of the Et group; [[dmpe]2MnH (=SiHe(NHC))], where NHC = iPrNHC (8®b) or MeNHC (8®d)),...
NHC coordination to silicon resulted in elongated Mn–Si distances (2.255(1)–2.299(1) Å; calc 2.26–2.30 Å for both isomers of 8a,b,c,d), and correspondingly weaker Mayer bond orders of 1.03–1.08 (Table S6†), relative to base-free silylene complexes 3{H} [2.16–2.20 Å and 1.17–1.57, respectively]. Unlike base-free analogues (vide supra), cis-8a–d display only negligible interligand Si–H interactions (with Mayer bond orders ≤0.13). Additionally, substantial pyramidalization at silicon was observed for both isomers of 8a–d, where the sum of the angles around silicon (for non-NHC substituents) ranged from 322(3) to 342(2)° (calc 336.1–341.5°; Table S6† cf. >356° in 3{H}). Nevertheless, the Mn–Si distances are significantly shorter than those in related silyl complexes 7a–d (the Mn–Si distances in 7a–d range from 2.3552(5)–2.3618(5) Å [calc 2.35–2.36 Å (cis) and 2.41–2.42 Å (trans), with Mayer bond orders of 0.89–0.93]), indicative of residual Mn–Si multiple bond character in 8a–d.

**Pathways for reactions of 4{R} with ethylene**

Previously, we reported the reactions of the silylene hydride complexes, [(dmpe)2MnH(=SiR2)] (3{H}; R = Ph, 3{Et}; R = Et), with ethylene to form the silene hydride complexes [(dmpe)2MnH(=SiH2Bu)(NHC)] (3b–d), which can provide access to 6{Bu,H} by sequential β-hydride elimination (to form E{H}), 1,2-insertion to generate secondary alkyl complex F{R}, and a second β-hydride elimination involving the hydrogen substituent on silicon. Consistent with this mechanism, the reactions of [(dmpe)2MnH(=SiH2Bu)] (4{Bu}) or [(dmpe)2Mn(=SiH2Bu)(NHC)] (8b) with d4-ethylene yielded [(dmpe)2MnH(=BuH)(CDDC3)] as the only observed isotope of 6{Bu,H}.

After conversion of 4{R} to 6{H}, reaction with a second equivalent of ethylene resulted in conversion of a silene SiH group in 6{H} to an SiEt group, yielding 6{Et,H} (vide supra). This reactivity likely involves the experimentally observed isomerization of 6{H} to silenes 3{Et} (vide supra), presumably via a low-coordinate silyl intermediate (2{Et} in Scheme 7) formed from 6{H} by C–H bond-forming 1,2-insertion. Conversion to 6{Et} can then take place via previously discussed pathways (Scheme 6) involving reactions of the silylene or low-coordinate silyl species with ethylene to afford intermediates B{Et} and C{Et}, respectively (B{Et} and C{Et} are analogues of B{H} and C{H} in Scheme 6, but with an ethyl group in place of one hydrogen atom on silicon).

Deuterium labelling studies were employed to provide experimental support for these mechanistic proposals. Specifically, [(dmpe)2MnH(=BuH)(CDDC3)] (d4-6{Bu,H}) isomerized to exclusively form trans-[(dmpe)2MnH(=SiH2Bu(CHDC3))] (trans-
unassigned Si reactions with H₃SiR, the headspace was re-filled with ethylene after 1 week) at 60 °C in C₆D₆ under ethylene (1.7 atm initial pressure) led to catalytic incorporation of one or two equivalents of ethylene into the Si–H bond of the free hydrosilanes, leading to a mixture of new hydrosilanes (Table 3). The major products in reactions of secondary hydrosilanes were tertiary hydrosilanes (HSiEtPh or HSiEt₃), while reactions involving primary hydrosilanes first formed secondary hydrosilanes (H₃SiEt³Bu or H₂-SiEtPh), followed by reaction with an additional equivalent of ethylene to generate the tertiary hydrosilane (HSiEtPh or HSiEt₃Bu) as the major product. Hydroisilylation reactions with H₃SiEtBu, H₂SiPh₂, and H₂SiEt₃ produced fewer byproducts than those with H₂SiPh (as noted in Table 3). Additionally, hydroisilylation with H₂SiEt₃ progressed much more rapidly than that with H₂SiPh₂. By contrast, no reactivity was observed when 1 was exposed to ethylene and the tertiary hydrosilanes HSIEt₃Bu or HSIEt₃B; various other hydroisilylation catalysts exhibit higher activities than 1, especially precious metal catalysts, but the ability of 1 to selectively form tertiary but not quaternary hydrosilanes from ethylene is uncommon.

Organic byproducts were observed during conversion of secondary to tertiary silanes, but not conversion of primary to secondary silanes. The major byproduct was a hydrosilane with a vinyl group (VI) in place of an ethyl substituent (HSIEtViR, R = Et or Bu or HSiViR, R = Et or Ph), accompanied by one or more unidentified SiH-containing silanes (Table 3). Vinyl silanes are commonly observed byproducts in olefin (e.g. H₂C=CHR) hydrosilylation, formed by β-hydride elimination from an M(CH₃CHRSiR₃) intermediate in the catalytic cycle, and were an impetus for the initial proposal of a modified Chalk–Harrod catalytic cycle involving C–Si rather than C–H bond-forming 1,2-insertion from an alkene-coordinated silyl hydride intermediate.

During catalysis using primary and secondary hydrosilanes, a variety of manganese-containing complexes were observed by NMR spectroscopy, including disilyl hydride complexes (for reactions involving primarily hydrosilanes only), silylene hydride complexes (for reactions involving secondary silanes only), silylene hydride complexes, silene hydride complexes, and ethylene hydride complex 1. Furthermore, all of these classes of complex are catalytically active. For example, [[(dmpe)₂MnH₂(SiH₂Bu)] (6Bu)] and [(dmpe)₂MnH(SEt₂)] (6EE₂) were catalysts for ethylene hydrosilylation using secondary hydrosilanes, and [(dmpe)₂MnH(SiH₂Bu₂)] (4Bu) and [(dmpe)₂MnH₃(SiH₂Bu)] (5Bu) were active for ethylene hydrosilylation by H₂SiBu. Reactions involving 6EE₂, 3EE₂, and 4Bu rapidly generated distributions of Mn-containing species and hydrosilane products which are very similar to those formed when [(dmpe)₂MnH(C₂H₄)] (1) was used as the pre-catalyst. By contrast, when 5Bu was
employed, hydrosilylation proceeded at a slower rate, and even after 24 hours the dominant manganese-containing species was \( \text{SiBu} \).

In order to monitor ethylene hydrogysilation reactions under conditions where ethylene concentration does not vary significantly during the course of the reaction, multiple aliquots from a stock solution of 1 and \( \text{H}_2\text{SiBu} \) in \( \text{C}_6\text{D}_6 \) were placed under a large excess of ethylene in a sealed 50 mL flask (initial pressure 1.7 atm, \( n_{\text{C}_2\text{H}_4} \approx 40 \times n_{\text{SiBu}} \)) and heated at 60 °C for various time periods prior to analysis by NMR spectroscopy (Fig. 9). Key observations were: (a) nearly complete conversion of the primary hydrosilane to secondary hydrosilane \( \text{H}_2\text{SiBu} \) was observed before any formation of the tertiary silane \( \text{HSiEt}_2\text{Bu} \) product or vinyl silane \( \text{HSiEtViBu} \) byproduct, (b) during hydrosilylation by the primary hydrosilane \( \text{H}_2\text{SiBu} \), the dominant metal-containing species was the \( \text{SiH} \)-containing silene hydride \( \text{[(dmpe)MnH(BuHSi=CHMe)] (6Bu,H*SiBu)} \), with small amounts of the disilyl hydride \( \text{[(dmpe)MnH(SiH}_2\text{Bu)}_2] (4Bu,SiBu)} \), (c) after 13 hours, almost all \( \text{H}_2\text{SiBu} \) had been consumed, (d) from 13 to 18 hours, conversion of \( \text{H}_2\text{SiBu} \) to \( \text{HSiBu} \) proceeded rapidly with concurrent formation of the vinylsilane byproduct \( \text{HSiEtViBu} \) (see below for experiments to determine the manganese species present between 13 and 18 hours), (e) after 18 hours, 1 was the dominant manganese species in solution (accompanied by small amounts of the silene hydride \( \text{[(dmpe)MnH(BuEtSi=CEtMe)] (6Bu,Bu)} \) and the silyl dihydride \( \text{[(dmpe)MnH(SiHEtBu)] (3Bu,Bu)} \), and conversion of \( \text{H}_2\text{SiBu} \) to \( \text{HSiEtBu} \) now proceeded more slowly, and (f) after 12 days, >99.5% of the \( \text{H}_2\text{SiEtBu} \) intermediate had been consumed yielding 81% \( \text{HSiEt}_2\text{Bu} \), 16% \( \text{HSiEtViBu} \), and 3% of an unidentified \( \text{SiH} \)-containing byproduct (assuming that this species contains one \( \text{SiH} \) proton), which is non-volatile at room temperature (5 mTorr); at this point, the only Mn-containing species in the reaction mixture was \( \text{[(dmpe)MnH(C_6H_6)] (1)} \). Relative amounts of the different hydrosilane and MnH-containing species in solution during ethylene hydrogysilation by \( \text{H}_2\text{SiBu} \) are plotted as a function of time in Fig. 9.

Between 13 and 18 hours in Fig. 9, conversion of \( \text{H}_2\text{SiEtBu} \) to \( \text{HSiEt}_2\text{Bu} \) proceedeed rapidly (to more than 50% conversion), and then slowed down dramatically, as the resting state of the catalyst switched to \( \text{[(dmpe)MnH(C_6H_6)] (1)} \). However, during secondary to tertiary hydrosilane conversion, \( \text{[(dmpe)MnH(BuHSi=CHMe)] (6Bu,H*SiBu)} \) cannot be regenerated, indicating that a different manganese species may have spiked in concentration between the 13 and 18 hour data points (this species is presumably responsible for continued rapid \( \text{H}_2\text{SiBu} \) to \( \text{HSiEt}_2\text{Bu} \) conversion observed during this time period). Consequently, the reaction in Fig. 9 was repeated and stopped after most but not all of the primary hydrosilane had been consumed (the resulting mixture of hydrosilanes and Mn-containing species in \( \text{C}_6\text{D}_6 \) was similar to that observed at 13 h in Fig. 9; i.e. mostly secondary hydrosilane \( \text{H}_2\text{SiEtBu} \) and \( \text{[(dmpe)MnH(BuHSi=CHMe)] (6Bu,H*SiBu)} \), with a small amount of the primary hydrosilane, \( \text{H}_2\text{SiBu} \)). This mixture was then sealed under a near-stoichiometric (relative to the hydrosilane)
amount of ethylene in an NMR tube, and monitored by NMR spectroscopy at 56 °C in 5 minute intervals (Fig. 10).

In Fig. 10, consumption of remaining primary hydrosilane was complete after 10 minutes, followed by rapid secondary to tertiary hydrosilane conversion and a spike in the concentration of a new silene hydride complex, [(dmpe)₂MnH(C₂H₄)] (6Bu,H), while the concentrations of 6Bu,H (the resting state of the catalyst during primary to secondary hydrosilane conversion) and [(dmpe)₂MnH(C₂H₄)] (1) (the Mn-containing species dominant after the 18 h mark) diminished and increased, respectively. Furthermore, a small amount (~12%) of the silyl dihydride complex [(dmpe)₂MnH₂(SiH₂Bu)] (5Bu,Et) grew in over this time period, and vinylsilane (HSiEt₂Bu) production was observed to accompany the formation of 1 and 5Bu,Et. The slowdown in the rate of catalysis between 13 and 18 hours in Fig. 9 can therefore be attributed to a change in the resting state of the catalyst, from more active silene hydride complexes 6Bu,H and 6Bu,Et, to 1 and 5Bu,Et, both of which are formed via vinylsilane elimination (vide infra), and re-enter the catalytic cycle slowly (5Bu,Et is particularly slow to enter the cycle; vide supra).

A catalytic cycle (Scheme 8) can be envisaged based on the reaction pathways already proposed for (a) reaction of ethylene with disilyld hydride complexes 4F (formed in reactions of 1 with primary hydrosilanes) to afford silene hydride complexes 6R,H and (b) reaction of ethylene with silylene hydride complexes 3R₂ (formed in reactions of 1 with secondary hydrosilanes)³⁵ to afford silene hydride complexes 6R₂. These reactions are identified with blue reaction arrows in Scheme 8. In the presence of free hydrosilane substrate, the catalytic cycle can be completed (green reaction arrows) by reaction of hydrosilanes with primary alkyl intermediate D (pathway ‘a’ in Scheme 8) or secondary alkyl intermediate F (pathway ‘b’ in Scheme 8); via oxidative addition followed by reductive elimination, or σ-bond metathesis.⁶⁷

Alternatively, for conversion of primary to secondary hydrosilanes, the catalytic cycle in Scheme 8 can be completed by C–H bond-forming 1,2-insertion from intermediate 6R,H (pathway ‘c’, green reaction arrow) to generate silyl and silylene hydride species 2R,Et and 3R₂. Isomerization of 6Bu,H to 3Bu,Et has been observed in the absence of ethylene and hydrosilanes (Scheme 4), and this pathway is also thought to be involved in the reactions of [(dmpe)₂MnH(RHSi==CHMe)] (6R,H) with ethylene to afford [(dmpe)₂MnH(REtSi==CHMe)] (6Et) in which an SiH group is converted to an SiEt group (Scheme 7). If pathway ‘c’ is involved in the catalysis, the resulting [Mn]SiH3Et (2Et) complex must react with free H₂SiR to form [Mn]SiH₂R (2Et) and eliminate H₂SiR (likely via an unobserved disilyl hydride intermediate analogous to 4F), given that the observed reactivity converts primary hydrosilanes to free secondary hydrosilanes prior to the formation of significant amounts of tertiary hydrosilane products. The accessibility of this reaction pathway is highlighted by the reaction of [(dmpe)₂MnH(==SiR₂)] (R = Ph (3Ph₂) or Et (3Et₂)) with excess H₂SiBu at 20 °C to afford [(dmpe)₂MnH(SiH₂Bu)] (4F) and free H₂SiPh₂ or H₂SiEt₂, respectively. This reaction was complete in several hours (for 3Et₂) or minutes (for 3Ph₂).

Unidentified SiH-containing byproducts (formed in larger amounts in reactions with H₂SiPh₂ and H₂SiPh (after conversion to H₂SiEtPh); Table 3) may arise from reactions of D (or less likely F) with hydrosilanes resulting in C–Si rather than C–H bond-formation to eliminate a disilylated organic product and generate manganese hydride intermediate [(dmpe)₂MnH] (A), which can re-enter the proposed catalytic cycle (vide infra) as shown in Scheme 8. This reactivity bears resemblance to that of ‘(dmpe)₂MnEt’ (an isomer of 1)³⁵ with H₂SiPh₂ to afford a 1 : 1 mixture of [(dmpe)₂MnH(==SiPh₂)] (3Ph₂) and ethanol, the products of C–H bond-forming oxidative addition/reductive elimination (or σ-bond metathesis) followed by ζ-hydride elimination, and (b) [(dmpe)₂MnH₂(SiPh₂Bu)] (5Ph₂) and Ph₂SiEt, the products of C–Si bond-forming oxidative addition/reductive elimination (or σ-bond metathesis) to form [(dmpe)₂MnH] (A), followed by oxidative addition of a second equivalent of H₂SiPh₂.³²

Pathways ‘a’, ‘b’ and ‘c’ described above (green reaction arrows in Scheme 8) generate the observed disilyld hydride (4F), silylene hydride (3) and silylene hydride (6) complexes. However, they do not explain the formation of vinyl silane byproducts. These byproducts can be accessed by vinylsilane dissociation from intermediate E,⁶⁴ forming low-coordinate hydride species A, which can react with either of the available organic
substrates: ethylene to form 1, or hydroxilanes to form silyl dihydride complexes (5); Scheme 8. While 1 reacts with primary or secondary hydroxilanes (but not tertiary hydroxilanes) to generate ethane and low-coordinate silyl species 2, complex 5 can slowly rejoin the catalytic cycle by H₂ elimination to afford 2. Support for this H₂ elimination process was obtained experimentally at elevated temperatures. For example, heating a solution of \([\text{dpme}_2\text{MnH}_2(\text{SiH}_2\text{Ph})]\) \(5^{\text{Ph}}\) under \(D_2\) at 70–80 °C overnight resulted in >90% deuterium incorporation into the MnH environments, exclusively. Furthermore, reactions of \(5^{\text{Bu}}\) with \(\text{BuNC}\), and \([\text{dpme}_2\text{MnD}_2(\text{SiH}_2\text{Ph})]\) \(d_5-5^{\text{Ph}}\) with o-xlylNC, afforded \([\text{dpme}_2\text{MnH}(\text{SiH}_2\text{Bu})(\text{CNBu})]\) \(7d\) and \([\text{dpme}_2\text{Mn}(\text{SiH}_2\text{Ph})(\text{CNXyl})]\) \(7a\), respectively, after 1 h at 75 °C.

In an attempt to determine whether pathway ‘a’ (via primary alkyl intermediate \(D_1\)), ‘b’ (via secondary alkyl intermediate \(F_1\)), or ‘c’ (via a silene hydride complex with an SiH substituent; \(6^{\text{R,H}}\)) in Scheme 8 is operative, catalysis was carried out using \(d_5-\)ethene; pathway ‘a’ would generate \(\text{CD}_2\text{CD}_2\text{H}\) groups, whereas pathways ‘b’ and ‘c’ would generate \(\text{CHDCHD}_3\) groups.\(^6\) Hydrolysis of \(C_2D_4\) by the secondary hydroxilane H₂SiEt₂ yielded \(d_5-H\text{SiEt}_3\), primarily as HSiEt₂(\(\text{CD}_3\text{CD}_3\text{H}\)) \(97\%\), with a minor amount of HSiEt₂(\(\text{CDHCD}_3\)) \(3\%\), as determined by \(^1H\), \(^2H\), and \(^13C\{^1H\}\) NMR analysis (Fig. S471†), indicating that pathway ‘a’ in Scheme 8 is dominant. By contrast, \(C_2D_4\) hydrosilylation by H₂Si²Bu under identical conditions yielded a solution containing \(20\%\) HSi²Bu(\(\text{CD}_3\text{CD}_3\text{H}\)), and \(80\%\) HSi²Bu(\(\text{CDHCD}_3\)). Given that H₂SiEt₂ has been shown to react almost exclusively via pathway ‘a’ (affording a \(\text{CD}_3\text{CD}_3\text{H}\) substituent on silicon), and H₂Si²BuEt can be expected to react analogously, this product distribution indicates that H₂Si²Bu is converted to H₂Si³BuEt primarily via pathway ‘b’ and/or ‘c’ (\(~77\%)\), with a lesser contribution from pathway ‘a’ (\(~23\%)\).

DFT calculations indicate that alkyl intermediates \(D\) and \(F\) are very similar in energy (within 5 kJ mol\(^{-1}\)). Therefore, the preferential reactivity of secondary silanes towards less hindered \(D\) (pathway ‘a’) may be sterically driven. By contrast, for conversion of primary to secondary hydroxilanes, where pathway ‘b’ and/or ‘c’ is dominant, it is not obvious why pathway ‘b’ would be preferred over pathway ‘a’. Pathway ‘c’ is therefore a viable alternative, especially given that ‘c’ has been demonstrated \(\text{(vide supra)}\) in room temperature stoichiometric reactions involving silenes with a hydrogen substituent on silicon \(\langle 6^{\text{R,H}}\rangle\). Furthermore, it is notable that silenes \(\langle 6^{\text{R,H}}\rangle\) are the dominant metal-containing species during the first phase of catalysis (conversion of primary to secondary hydroxilanes).

**Summary and conclusions**

The disilyl hydride manganese complexes, \([\text{dpme}_2\text{MnH}(\text{SiH}_2\text{R})_{\text{R}_2}]\) \(R = \text{Ph or } ^8\text{Bu}\), reversibly dissociate H₂SiR to access low-coordinate silyl \(\langle [\text{dpme}_2\text{Mn}(\text{SiH}_2\text{R})]\rangle\) and silylene hydride \(\langle [\text{dpme}_2\text{MnH}(\text{=SiHR})]\rangle\) complexes. The trans isomers of the silylene hydride complexes were observed in small amounts (<5% relative to the disilyl hydride) by NMR spectroscopy at 333 K, and are the first spectroscopically observed examples of group 7 L₂M=SiHR compounds. DFT calculations support the thermodynamic accessibility of cis- and trans-isomers of these low coordinate silyl and silylene species, and both sets of intermediates were trapped by coordination of isonitriles (to manganese) or N-heterocyclic carbenes (to silicon).

The reactivity of \([\text{dpme}_2\text{MnH}(\text{SiH}_2\text{R})_{\text{R}_2}]\) \(R = \text{Ph or } ^8\text{Bu}\) with ethylene was investigated, affording silane hydride complexes \([\text{dpme}_2\text{MnH}^{\text{RHSi} = \text{CHMe}}]\). This reaction represents a unique method to access silene complexes (analogous to reactions of ethylene with \([\text{dpme}_2\text{MnH}(\text{=SiR}_2)]\) compounds in our previous
and the resulting silene complexes are the first transition metal examples with a SiH substituent. As such, they displayed unusual reactivity: for example, [(dmpe)2MnH(CHMe)] slowly converted to a more stable silylene hydride isomer, [(dmpe)2MnH(=SiEtR)]; the first example of isomerisation of a silene hydride complex to a silylene hydride complex. Furthermore, [(dmpe)2MnH(=SiEtMe)] reacted with a second equivalent of ethylene to convert the SiH substituent to a SiEt substituent, which is an unprecedented transformation for a silene ligand.

All of the silyl, silene and silane complexes in this work were accessed via reactions of [(dmpe)2MnH(C2H4)] (1) with hydrosilanes and/or ethylene. Therefore, ethylene hydrosilylation was investigated using 1 as a pre-catalyst, resulting in stepwise conversion of primary to secondary to tertiary hydrosilanes. Manganese complexes observed during catalysis include (a) disilyl hydride complexes, (b) silylene hydride complexes, (c) silene hydride complexes, (d) silyl dihydride complexes, and (e) the ethylene hydride pre-catalyst. All of these species are catalytically active (although the silyl dihydride complexes are significantly less active than the others), and a catalytic cycle is proposed on the basis of these observations, the aforementioned stoichiometric reactions, and hydrosilylation of d<sub>5</sub>-ethylene. This catalytic cycle is unusual due to the involvement of silylene hydride and silene hydride complexes, potentially as on-cycle species.

Conflicts of interest
There are no conflicts to declare.

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Notes and references


33 A variety of other Mo silylene hydride complexes have been reported to feature Si-H interligand interactions, but for these complexes an X-ray crystal structure was not obtained, or the bridging hydride was not located from the difference map.


44 In the reaction of $^4$H with ethylene, no tertiary hydrosilane was observed. However, small amounts of a vinyl hydrosilane were observed.

45 DFT calculations indicated that isomerization of SiH-containing silene hydride complexes $^6$H to silylene hydride complexes trans-[[dimpe],MnH(=SiEtR)] ($^6$H$^\text{SiH}$) was not observed.
3$^{3}\text{E}$$^\text{L}$ is thermodynamically favourable for $R = \text{Ph}$ and $^{6}\text{Bu}$$^\text{H}$; minima for the latter complexes were located 20–34 kJ mol$^{-1}$ lower in energy than the lowest energy silene hydride isomer. In addition, cis silylene hydride isomers were determined to be 1 (3$^{3}\text{E}$$^\text{L}$) and 9 (3$^{3}\text{Bu,}\text{H}$) kJ mol$^{-1}$ less stable than the respective trans isomers.

47 NMR data for trans-$[\text{dmpe}]_2\text{MnH}([\text{SiEt}_3])$ (trans-$3\text{E}$$^\text{L}$) includes an MnH$^\text{1}$H NMR peak at −10.46 ppm (quintet with $J_{\text{H}^\text{H},\text{H}^\text{P}}$ of 51 Hz), a single sharp singlet in the $^{29}\text{Si}$NMR spectrum at 80.95 ppm, and a $^{29}\text{Si}$NMR chemical shift of 365 ppm; see ref. 32.


49 Not including enantiomers where the stereochemistry at manganese is switched from $\Delta$ to $\Delta$.

50 The dominant isomer for $6\text{Bu,}\text{H}$ was assigned as isomer i given that the SiH$^\text{1}$H NMR signal for this isomer exhibits a large (18 Hz) $J_{\text{H}^\text{H},\text{H}^\text{P}}$ coupling to one of the phosphorus donor atoms, and in the calculated structures of isomers (i) and (ii) for a model of $6\text{Bu,}\text{H}$ where the $^{6}\text{Bu}$ group was replaced with an Et group), only isomer (i) exhibited a $^{3}\text{J}^\text{H,31P}$ coupling of comparable magnitude (23 Hz). As well, isomer i of $6\text{Bu,}\text{H}$ is slightly (4 kJ mol$^{-1}$) lower in energy than isomer (ii).


52 By comparison, terminal Si–H distances and Mayer bond orders in $6\text{H}$ are 1.50–1.51 \AA and 0.82–0.86, respectively.


54 In the case of $4\text{Ph}$, an additional low frequency $^1\text{H}$ NMR signal (a broad singlet with <2% intensity relative to the MnH$^\text{2}$ peak of $4\text{Ph}$) was observed at −12.1 ppm (335 K), which could potentially be from the MnH$^\text{2}$ environment of cis-$[\text{dmpe}]_2\text{MnH}([\text{SiPh}_3])$ (cis-$3\text{Ph,H}$). However, EXSY NMR spectroscopy did not show chemical exchange between this peak and those from $4\text{Ph}$ or trans-$3\text{Ph,H}$ (potentially due to broadness and low intensity of the signal). A further low frequency $^1\text{H}$ NMR signal (also a broad singlet, but present in the room temperature and high temperature NMR spectra in similar intensities; ~1.5% relative to the MnH$^\text{2}$ region of $4\text{Ph}$) was observed at −13.8 ppm, which could potentially be from another isomer of $4\text{Ph}$; this environment was observed by EXSY NMR spectroscopy to be in chemical exchange with the SiH$^\text{2}$ and MnH$^\text{2}$ environments of both $4\text{Ph}$ and trans-$3\text{Ph,H}$.


56 A handful of NHC-stabilized silylene complexes have also been reported with $^{29}\text{Si}$ chemical shifts lower than 25 ppm (see ref. 55e–h), and this has been rationalized by adoption of a zwitserionic bonding motif which results in limited π-backdonation to the Si center from the metal (see ref. 55h).

57 We could not determine the $^{29}\text{Si}$NMR chemical shift of trans-$8\text{c}$ due to the low proportion of trans isomer in solution (cis : trans ratio of 14 : 1).

58 The lability of NHCs in $8\text{a–d}$ was also illustrated by initial generation of mixtures of reagents and products upon addition of free NHCs to $4\text{Ph}$; complete conversion to $8\text{a–d}$ required removal of the free hydrosilane byproducts. For $8\text{b–d}$, this was achieved by periodically removing all solvent and hydrosilane byproducts in vacuo. By contrast, for $8\text{a}$ this was achieved by the reaction of the H$_3$SiPh byproduct with excess $^{10}\text{NHC}$ to form 1-phenyl-2,5-diisopropyl-3,4-dehydro-2,5-diazasilinane; this reaction has previously been reported at 100 °C, and in our hands 98% conversion was observed after 24 h at 55 °C (consistent with the reaction conditions involved in the synthesis of $8\text{a}$). D. Schmidt, J. Berthel, S. Pietesch and U. Radius, Angew. Chem., Int. Ed., 2012, 51, 8881–8885.

59 Unlike the reaction of $4\text{Bu}$ with ethylene, the reaction of $8\text{b}$ with ethylene does not generate H$_3$Si$^\text{Bu}$ as a byproduct.
and under these conditions, complex $6\text{Bu}_2\text{H}$ reacted readily with a further equivalent of ethylene, so that both $6\text{Bu}_2\text{H}$ and $6\text{Bu}_{\text{Et}}$ were formed concurrently.

60 In the structures of cis-$8a,b$, the dmpe ligands are disordered, and modelling this disorder allowed the structures of both diastereomers observed in solution to be elucidated.

61 $7b,d$ were computationally modelled with Et groups in place of $n\text{Bu}$ groups; $[(\text{dmpe})_2\text{Mn}([\text{SiH}_2\text{Et}])\text{(CNR)}]$ ($7b^*: R = o\text{-xylyl}$, $7d^*: R = t\text{Bu}$).

62 Alternative pathways requiring initial dissociation of a phosphine donor in $6\text{R}_2\text{H}$ followed by ethylene coordination (with subsequent oxidative coupling or 1,2-insertion reactivity) cannot be ruled out.

63 Silylene complexes were only observed during catalysis when most of the ethylene had been consumed.


67 Energy minima for alkyl intermediates D and F were found to lie 46–67 kJ mol$^{-1}$ higher in energy than the respective silene hydride resting states, indicating their thermodynamic accessibility from complexes observed by solution NMR spectroscopy.

68 In hydrosilylation reactions with $d_4$-ethylene, the vinyl byproducts contain fully deuterated vinyl groups, in keeping with the proposed pathway for their formation.

69 Hydrosilylation reactions involving $\text{C}_2\text{D}_4$ (with either $\text{H}_3\text{Si}^\text{Bu}$ or $\text{H}_2\text{SiEt}_3$) proceeded to completion (i.e. complete consumption of the secondary hydrosilane reagent/intermediate) after 4 days at 60 °C, while analogous reactions using a higher pressure of $\text{C}_2\text{H}_4$ still contained 6–7% of the secondary hydrosilane ($\text{H}_2\text{SiEt}^\text{Bu}$ intermediate or $\text{H}_2\text{SiEt}_3$ reagent), suggestive of an inverse kinetic isotope effect.