Manganese Silylene Hydride Complexes: Synthesis and Reactivity with Ethylene to afford Silene Hydride Complexes

Jeffrey S. Price, David J. H. Emslie,* and James F. Britten

Dedicated to Professor Neil G. Connelly on the occasion of his 72nd birthday

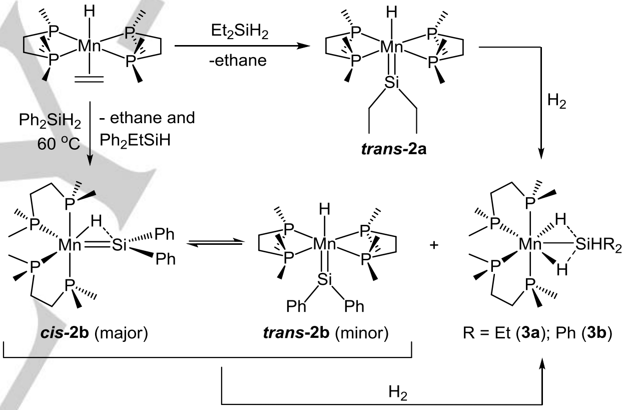
Abstract: Reaction of the ethylene hydride complex *trans*-[(dmpe)$_2$MnH(C$_2$H$_4$)] (**1**) with Et$_2$SiH$_2$ at 20 °C afforded the silylene hydride [(dmpe)$_2$MnH(=SiEt$_2$)] (**2a**) as the *trans* isomer. By contrast, reaction of **1** with Ph$_2$SiH$_2$ at 60 °C afforded [(dmpe)$_2$MnH(=SiPh$_2$)] (**2b**) as a mixture of the *cis* (major) and *trans* (minor) isomers, featuring a Mn–H–Si interaction in the former. The reaction to form **2b** also yielded [(dmpe)$_2$MnH$_2$(SiHPh$_2$)] (**3b**); [(dmpe)$_2$MnH$_2$(SiHR$_2$)] {R = Et (**3a**) and Ph (**3b**)} were accessed cleanly by reaction of **2a** and **2b** with H$_2$, and the analogous reactions with D$_2$ exclusively afforded [(dmpe)$_2$MnD$_2$(SiHR$_2$)]. Both **2a** and **2b** engaged in unique reactivity with ethylene, generating the silene hydride complexes *cis*-[(dmpe)$_2$MnH(R$_2$Si=CHMe)] {R = Et (**4a**) and Ph (**4b**)}. Compounds *trans*-**2a**, *cis*-**2b**, **3b** and **4b** were crystallographically characterized, and bonding in **2a**, **2b**, **4a**, and **4b** was probed computationally.

The first compound containing a transition metal–silicon bond, [CpFe(CO)$_2$(SiMe$_3$)], was reported by Wilkinson in 1956,[1] and over the past 60 years the area has undergone remarkable development, including the stabilization of reactive species such as silylenes (SiR$_2$) and silenes (R$_2$Si=CR$_2$) by metal coordination.

Silylene ligands can be divided into two categories: electronically/sterically stabilized silylenes, such as N-heterocyclic silylenes,[2] and reactive silylenes with fleeting existences in the absence of metal coordination.[3] Complexes of silylenes in the latter category have been postulated as intermediates in catalytic processes involving silanes (e.g. dehydrocoupling, substituent redistribution, hydrosilylation, and the Direct process for silane chlorination),[4] and a range of terminal silylene complexes have been isolated for transition metals in groups 8-10.[5] These complexes are electrophilic at silicon, and in many cases were prepared by abstraction of a hydride or halide from an α-hydrosilyl or α-halosilyl precursor, or α-hydride elimination from an α-hydrosilyl complex.[6] For mid-and early-transition metals, electrophilic group 6 (Mo and W) silylene complexes have been isolated,[7-9] nucleophilic group 4 (Ti and Hf) silylene complexes were recently reported,[10-11] and group 5 (V) silylene complexes have been proposed on the basis of EPR or elemental analysis.[12]

In the case of silene complexes, only a handful have been isolated, with examples bearing sterically/electronically-unstabilized silene ligands[13] confined to complexes of Ir,[14-15] Ru,[16-21] and W.[22] These complexes were generated via one of three methods: (i) β-X (X = H or Cl) elimination from silicon in an M–CH$_2$SiXR$_2$ (M = Ru or Ir) fragment,[15-18] (ii) β-H elimination from carbon in an M-SiMe$_2$R (M = Ru or Ir) fragment,[14, 19-21] and (iii) reductive dechlorination of [Cp$_2$WCl(CH$_2$SiClMe$_2$)].[22] In contrast, first row transition metal complexes bearing unstabilized silene ligands have not been isolated. For example, [CpFeH(CO)(CH$_2$SiMe$_2$)] was generated by low temperature photolysis of [CpFe(CO)$_2$(CH$_2$SiMe$_2$H)], but converted to [CpFe(SiMe$_3$)(CO)$_2$] above 225 K.[23]

Herein we present an unprecedented transformation of a silylene into a silene ligand, as well as the first examples of isolable group 7 complexes bearing an unstabilized terminal silylene ligand, and first row transition metal complexes bearing an unstabilized silene ligand.



Scheme 1. Reactions of [(dmpe)$_2$MnH(C$_2$H$_4$)] with R$_2$SiH$_2$ to form *trans*-**2a** (R = Et) or a mixture of ***cis*-2b**, ***trans*-2b** and **3b** (R = Ph), and subsequent reactions of the silylene hydride complexes (***trans*-2a** or ***cis*-** and ***trans*-2b**) with H$_2$ to form **3a** (R = Et) and **3b** (R = Ph), respectively.

Girolami and Wilkinson's [(dmpe)$_2$MnH(C$_2$H$_4$)] (**1**) complex[24] reacted with Et$_2$SiH$_2$ (4.5 equiv.) at room temperature to form [(dmpe)$_2$MnH(=SiEt$_2$)] (**2a**) with release of ethane (Scheme 1). Compound **2a** gave rise to one ^{31}P resonance, a hydride ^{1}H NMR signal at –10.46 ppm, and a ^{29}Si resonance at 365.3 ppm, characteristic of a C_{2v} symmetric *trans* silylene hydride complex (note: 1-2% of an unidentified product was always observed in ^{1}H NMR spectra of **2a**, and may be the *cis* isomer). An X-ray crystal structure of **2a** (Figure 1; 4 independent molecules in the unit cell) confirmed this assignment, revealing an octahedral geometry at manganese, trigonal planar geometry at silicon [Σ(C–Si–X) = 360.0(1)°; X = C or Mn], and a Mn–H distance of 1.60(3)-1.62(3) Å. The Mn–Si distance in **2a** is 2.1880(12)-2.1948(12), which compares well with the Fe–Si distance of 2.154(1) in [CpFe(SiMe$_3$)(CO)(=SiMes$_2$)],[25] taking into consideration the larger ionic radius of Mn(I) vs Fe(II), and is much shorter than the Mn–Si distances of 2.2789(9)-2.3571(7) Å in the base-stabilized *N*-heterocyclic silylene complexes

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[(CO)$_4$Mn{SiR((*t*BuN)$_2$CPh))}$_2$]$^+$ (R=Cl, NPh$_2$),[26-27] and 2.402(2)-2.434(3) Å in the bridging silylene complexes [{CpMnH(CO)$_2$}$_2$(μ-SiH$_2$)][28] and [{Mn(CO)$_4$}$_2${μ-SiPh$_2$}$_2$].[29]

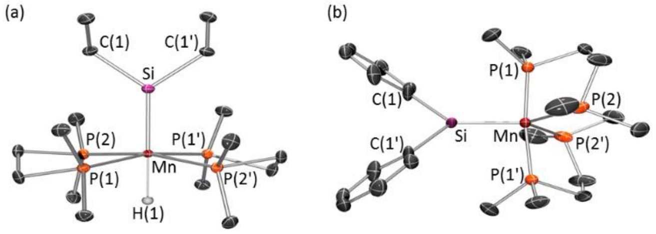


Figure 1. X-ray crystal structures of (a) *trans*-[(dmpe)$_2$MnH(=SiEt$_2$)] (***trans*-2a**) and (b) *cis*-[(dmpe)$_2$MnH(=SiPh$_2$)] (***cis*-2b**) with ellipsoids at 50% probability. Most hydrogen atoms have been omitted for clarity. Compound **cis-2b** co-crystallized with [(dmpe)$_2$MnH$_2$(SiHPh$_2$)] (**3b**), with superimposed (dmpe)$_2$Mn and phenyl groups. Only the structure of **cis-2b** is shown in this Figure; an X-ray structure of pure **3b** was independently obtained and is shown in Figure 2.

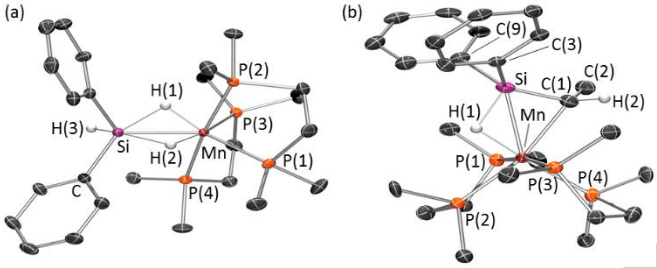


Figure 2. X-ray crystal structures of (a) [(dmpe)$_2$MnH$_2$(SiHPh$_2$)] (**3b**) and (b) *cis*-[(dmpe)$_2$MnH(Ph$_2$Si=CHMe)] (**4b**) with ellipsoids drawn at 50% probability. Most hydrogen atoms have been omitted for clarity.

The reaction to form **2a** and ethane likely occurs via an undetected 5-coordinate manganese ethyl complex, [(dmpe)$_2$MnEt], formed by isomerization of **1** to place the hydride and alkene *cis* to one another, followed by 1,2-insertion. This ethyl complex can undergo σ-bond metathesis with Et$_2$SiH$_2$ {or Si–H bond oxidative addition (OA) followed by C–H bond forming reductive elimination (RE)} to form a low-coordinate hydrosilyl intermediate, [(dmpe)$_2$Mn(SiHR$_2$)] (**A**; R = Et), which isomerizes to **2a** by α-hydride elimination.

Compound **1** also reacted with Ph$_2$SiH$_2$ at 60 °C to afford [(dmpe)$_2$MnH(=SiPh$_2$)] (**2b**) as an approximate 50:50 mixture with [(dmpe)$_2$MnH$_2$(SiHPh$_2$)] (**3b**), releasing ethane and Ph$_2$EtSiH (Scheme 1); **3b** may form via initial σ-bond metathesis (or OA/RE) between [(dmpe)$_2$MnEt] and Ph$_2$SiH$_2$ to afford "(dmpe)$_2$MnH" and Ph$_2$EtSiH, followed by oxidative addition of a second equivalent of Ph$_2$SiH$_2$.[30] Compounds **2b** and **3b** could not be separated, but the mixture could be converted entirely to **3b** by reaction with H$_2$. Similarly, compound **2a** reacted cleanly with H$_2$ to generate [(dmpe)$_2$MnH$_2$(SiHEt$_2$)] (**3a**) (Scheme 1), and in solution, **3a** and **3b** each exist as an equilibrium mixture of two isomers, one of which was structurally characterized for **3b** (Figure 2). Compound **2b** was characterized in solution, and shown to exist as an 88:12 mixture of interconverting silylene hydride isomers: a major C_1-symmetric *cis* isomer with a hydride ^{1}H NMR signal at –16.22 ppm, a ^{29}Si NMR shift of 210.2 ppm, and four broad ^{31}P environments at –20 °C; and a minor C_{2v} *trans* isomer with one ^{31}P environment, a hydride ^{1}H NMR signal at –9.78 ppm, and a ^{29}Si NMR shift of 285.1 ppm.

Maintaining a toluene solution of **2b**/**3b** at –30 °C afforded crystals containing a 50:50 mixture of ***cis*-2b** and **3b** (confirmed by NMR spectroscopy) with superimposed (dmpe)$_2$Mn fragments and phenyl rings. Distinct silicon atom positions are observed for ***cis*-2b** and **3b**, but the resulting structures are only suitable to establish connectivity. In the structure of ***cis*-2b** (Figure 1), the four phosphorus atoms and silicon form an approximate trigonal bipyramid, with the *Si*-phenyl groups in the equatorial plane. Silicon is trigonal planar, and electron density consistent with the hydride ligands in ***cis*-2b** and co-crystallized **3b** was located on either side of the Mn–Si bond (due to crystallographic disorder in the case of ***cis*-2b**), above and below the C(1)/Si/C(1') plane. DFT calculations (gas phase, all-electron, PBE, TZ2P, ZORA, D3-BJ) support a close interaction between the hydride ligand and the silicon atom in ***cis*-2b**, yielding distances of 2.168 and 1.665 Å for the Mn–Si and Mn–H bonds, a Si–H distance of 1.726 Å, and angles of 51.5 and 49.0° for the H–Mn–Si and H–Si–Mn linkages. These values compare well with those of other silylene hydride complexes featuring strong Si-H interactions, including the X-ray structures of [(C$_5$Me$_4$Et)(CO)$_2$WH-{=SiHC(SiMe$_3$)$_3$}] and [(1,2-C$_2$H$_4$(P^{t}Bu$_2$)$_2$}NiH(=SiMes$_2$)]$^+$,[7] and the Neutron structure of [Cp*(dmpe)Mo(H)(=SiEt$_2$)][8] (Si–H = 1.71(6), 1.64(7) and 1.68(1) Å; H–M–Si = 46(2), 49(2) and 45.5(4)°; and H–Si–M = 50(2), 51(2) and 51.5(4)°, respectively).

Compound **2b** is the first silylene hydride complex observed to exist as distinct isomers with and without an M–H–Si interaction, providing a unique opportunity to probe the nature of the Mn–Si and Si–H interactions. Surprisingly, DFT calcul-ations show slightly shorter Mn–Si distances in ***cis*-2a,b** versus ***trans*-2a,b** (Mn–Si = 2.168-2.175 Å for *cis* vs 2.184-2.187 Å for *trans*). However, the Mn–Si Mayer bond orders for ***cis*-2a** and ***cis*-2b** (1.25 and 1.19) are notably less than those for ***trans*-2a** and ***trans*-2b** (1.54 and 1.52), and the same trend is observed in Nalewajski-Mrozek and Gopinathan-Jug bond orders.

Fragment analysis of ***cis*-** and ***trans*-2a** using the combined Extended Transition State and Natural Orbitals for Chemical Valence (ETS-NOCV) method revealed similarities in the bonding between the (dmpe)$_2$MnH and SiEt$_2$ fragments in both isomers of **2a** (Figures 3-4). In particular, bonding in both complexes involves σ-donation from the silylene HOMO to the (dmpe)$_2$MnH LUMO, accompanied by $\pi_{\parallel}$-backdonation into a silylene orbital that is σ-antibonding with respect to the Si–C bonds. However, $\pi_{\perp}$-backdonation primarily involves the silylene LUMO and a filled Mn-H σ-bonding orbital (HOMO-3) in ***cis*-2a**, versus a filled manganese d-orbital in ***trans*-2a**. The Hirshfeld charge on the SiEt$_2$ fragment is more negative in ***trans*-2a** than ***cis*-2a** (–0.29 vs –0.18), indicative of less effective σ-donation and/or more effective π-backdonation in the former. Nevertheless, the silicon atoms in both isomers of **2a** and **2b** are electrophilic, based on positive Hirshfeld charges on the silicon atoms (0.20 to 0.22), negative Hirshfeld charges on manganese (–0.25 to –0.27), and positive electrostatic potentials at silicon.

Both **2a** and **2b** reacted with ethylene (1.7 atm, 25 °C) to form silene hydride products, *cis*-[(dmpe)$_2$MnH(R$_2$Si=CHMe)] {R = Et (**4a**) and Ph (**4b**)} (Scheme 2), conceptually achieving addition of the carbene isomer of ethylene (CHMe) to the silylene (SiEt$_2$ or SiPh$_2$); compound **4a** was isolated in pure form, whereas **4b** was isolated as an approximate 50:50 mixture with **3b** which was present in the starting material. Compounds **4a** and **4b** gave hydride ^{1}H NMR signals at –15.30 and –14.56 ppm, ^{29}Si resonances at –2.95 and 1.47 ppm, and characteristic silene ^{13}C NMR signals at –19.37 and –22.93 ppm, respectively.

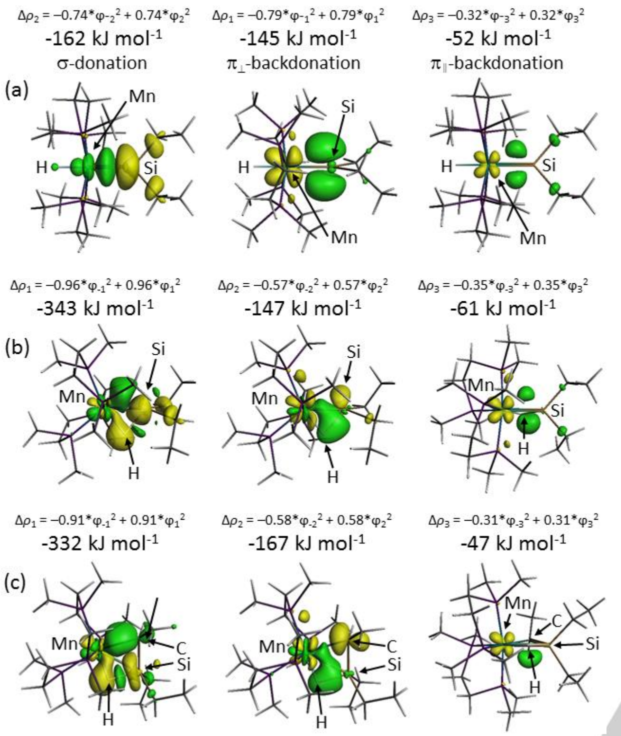


Figure 3. Deformation density contributions Δρ$_1$, Δρ$_2$ and Δρ$_3$ to bonding between the SiEt$_2$ and (dmpe)$_2$MnH fragments in (a) ***trans*-2a**, (b) ***cis*-2a** and (c) **4a**; green and yellow represent increased and decreased electron density, respectively, relative to the fragments; isosurfaces are set to 0.003.

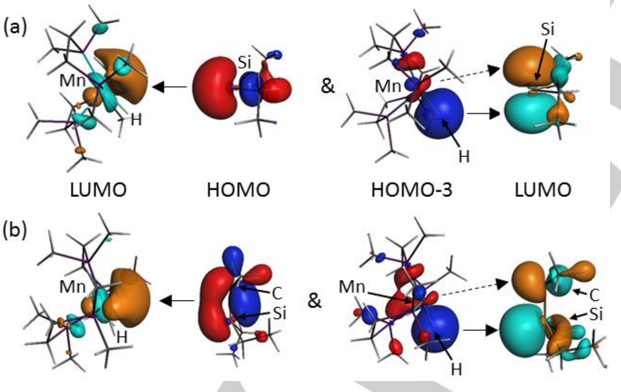
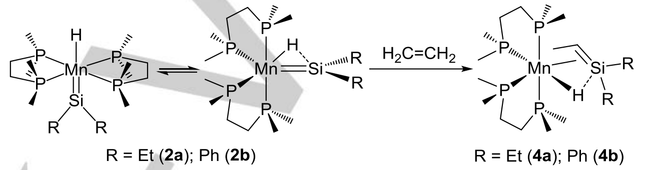


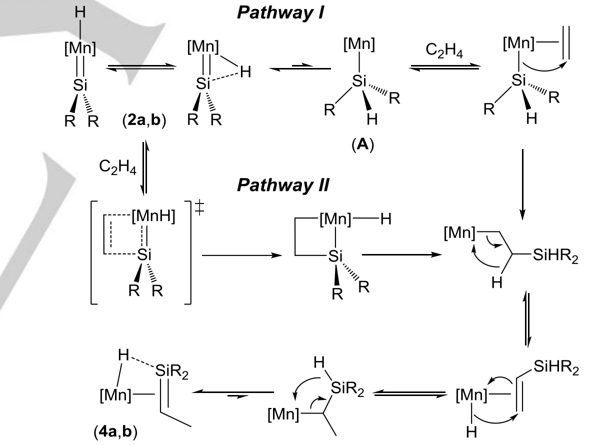
Figure 4. Key fragment orbitals contributing to Δρ$_1$ and Δρ$_2$ in (a) ***cis*-2a** and (b) **4a**; isosurfaces are set to 0.04.

An X-ray crystal structure of **4b** (Figure 2) revealed a distorted octahedral geometry in which the hydride interacts with the silicon atom of the silene. The silene Si–C(1) distance in **4b** is 1.781(5) Å, which is at the short end of the range previously reported for silene complexes (1.773(4)-1.838(11) Å),[13-22] and the Mn–C(1) distance is over 0.10 Å shorter than the M–Si distance {2.270(4) vs 2.409(2) Å}, as observed for all other silene complexes. The sum of the X–C(1)–X (X = Si, H or C) and C–Si–C angles (346(2) and 343.5(2)°) are also consistent with considerable silene character. However, the Mn–H and H–Si distances of 1.56(5) and 1.55(4) Å (calcd. 1.653 and 1.648 Å), as well as a large $^1J_{\mathrm{Si,H}}$ coupling of 90 Hz in **4b**, clearly indicate a significant interaction between the hydride ligand and silicon.

Fragment interaction and ETS-NOCV calculations on **4a** (Figures 3-4) reveal three major interactions between the silene and (dmpe)$_2$MnH fragments. The first two contributions involve σ-donation from the silene π-bond (HOMO) to the LUMO of the (dmpe)$_2$MnH fragment, combined with π∥-backdonation from a filled Mn–H σ-bonding orbital (HOMO-3) into the silene π* orbital (LUMO), whereas the 3rd contribution involves π⊥-back-donation to the silene. Parallels in the bonding descriptions for ***cis*-2b** and **4b** arise from the very similar geometries of the (dmpe)$_2$MnH fragments in these complexes, and the analogous symmetries and orientations of the HOMO and LUMO of the silylene and silene fragments relative to the M–H bond.



Scheme 2. Reaction of [(dmpe)$_2$MnH(=SiR$_2$)] (**2a**,**b**) with ethylene to form [(dmpe)$_2$MnH(R$_2$Si=CHMe)] {R = Et (**4a**) and Ph (**4b**)}.



Scheme 3. Two potential pathways for the formation of [(dmpe)$_2$MnH-(R$_2$Si=CHMe)] {R = Et (**4a**) and Ph (**4b**)} via reaction of [(dmpe)$_2$MnH(=SiR$_2$)] (**2a**,**b**) with ethylene. [Mn] = "(dmpe)$_2$Mn" and [MnH] = "(dmpe)$_2$MnH".

Several mechanisms could be proposed for the formation **4a** and **4b**, but the reactions of **2a** and **2b** with d_4-ethylene to form *cis*-[(dmpe)$_2$MnH(R$_2$Si=CDCD$_3$)] rule out a mechanism involving initial insertion of ethylene into a Mn–H bond. Alternative possibilities are shown in Scheme 3. In mechanism I, a low-coordinate silyl complex, [(dmpe)$_2$Mn(SiHR$_2$)] (**A**), is accessed from the *cis*-silylene hydride complex, and from this point, two cycles of 1,2-insertion and β-hydride elimination would afford the silene hydride product. In mechanism II, the Si=C double bond of the silene initially engages in 2+2 cycloaddition with ethylene to form a metallasilacyclobutane which then undergoes Si–H bond-forming reductive elimination.

Mechanism II lacks precedent in silicon chemistry, although silylene 2+2 cycloaddition chemistry has been obser-ved for isocyanates,[31] proposed as a possibility for nitriles,[32] isothiocyanates,[33] and ketones,[34] and observed for alkynes in combination with Schrock-type titanium silylene complexes.[10] By contrast, mechanism I is supported by: (a) the likely intermediacy of species **A** in the reaction to form **2a** from **1** (*vide supra*), (b) DFT calculations, which show that low-coordinate hydrosilyl isomers of **2a** and **2b**, $[(dmpe)_2Mn(SiHR_2)]$ (**A**; R=Et or Ph), exist as minima located 25 and 42 kJ mol^{-1} higher in energy than ***cis*-2a** and ***cis*-2b** respectively, and (c) the reactions of **2a** and **2b** with D_2 which exclusively form $[(dmpe)_2MnD_2(SiHR_2)]$ (R=Et; **d$_2$-3a**, R=Ph; **d$_2$-3b**), indicative of reactivity stemming from intermediate **A** rather than directly from a silylene hydride.

Future work will probe the scope of the stoichiometric reactions of **1** with hydrosilanes followed by alkenes. Additionally, silene complex **4a** is an active catalyst or pre-catalyst for alkene hydrosilylation (2 mol% of **4a** effected >60% conversion of ethylene and diethylsilane to triethylsilane after 24 h at 60 °C). However appreciable amounts of **1**, **2a** and **3a** were formed as the reaction progressed, and additional studies will be undertaken to evaluate the role of these species in catalysis.

Experimental Section

Full experimental and characterization details for new complexes, details of DFT calculations, NMR spectra of new compounds and selectively deuterated analogues, and powder X-ray diffractograms for a **2b**/**3b** mixture and pure **3b** are included in the Supporting Information. CCDC 1529213-1529216 contain the supplementary crystallographic data for **4b**, ***trans*-2a**, **3b** and ***cis*-2b**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: Hydride ligands • Manganese • Si ligands • Silene ligands • Silylene ligands

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[30] Formation of Ph_2EtSiH in the reaction to form **2b** and **3b** could alternatively occur via the following sequence: (i) dissociation of ethylene from $[(dmpe)_2MnH(C_2H_4)]$, and oxidative addition of Ph_2SiH_2 to form **3b**, (ii) concurrent formation of **2b** (cis and trans isomers) via the mechanism proposed in the text, (iii) reaction of **2b** with ethylene (formed in step i) to generate silene complex **4b**, and (iv) an equilibrium between **4b** and $[(dmpe)_2Mn(CHMeSiPh_2H)]$ or $[(dmpe)_2Mn(SiPh_2Et)]$, either of which could undergo σ-bond metathesis with additional Ph_2SiH_2 to form Ph_2EtSiH and $[(dmpe)_2Mn(SiHPh_2)]$ (**A**), which would isomerize to **2b** by α-hydride elimination. Indeed, **4b** does react rapidly and cleanly with Ph_2SiH_2 at 60 °C to form **2b** and Ph_2EtSiH.
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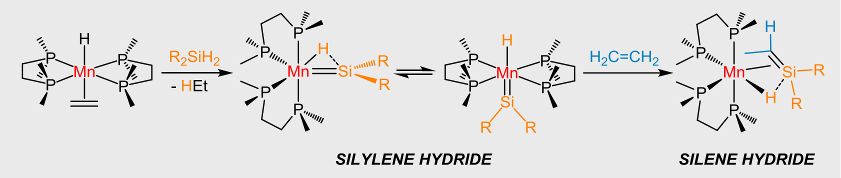
Layout 2:

COMMUNICATION



The alkene hydride complex, *trans*-[(dmpe)$_2$MnH(C_2H_4)] eliminates ethane upon reaction with secondary silanes, yielding both *cis*- and *trans*-isomers of the silylene hydride complexes [(dmpe)$_2$MnH(=SiR$_2$)]. Subsequent reaction with ethylene yielded silene hydride complexes, [(dmpe)$_2$MnH(R$_2$Si=CHMe)], most likely via an undetected low-coordinate silyl isomer, [(dmpe)$_2$Mn(SiHR$_2$)], in equilibrium with the silylene hydrides.

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