Reactions of Manganese Silyl and Silylene Complexes with CO_2 and $C(N^iPr)_2$: Synthesis of Mn(I) Formate and Amidinylsilyl Complexes

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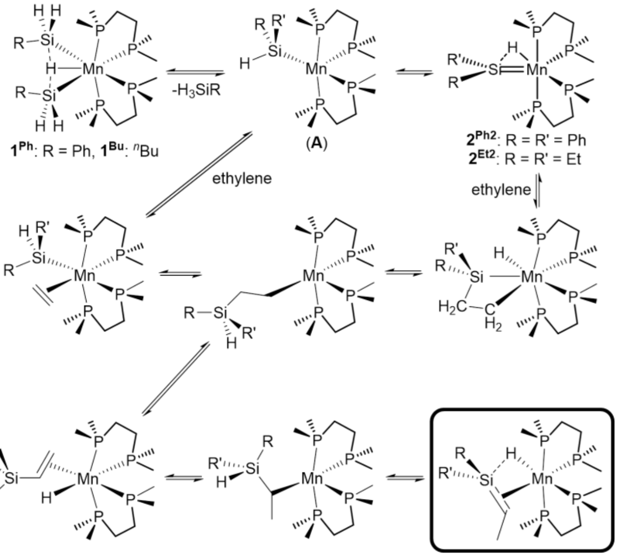
ABSTRACT: Reactions of the disilyl hydride complexes $[(dmpe)_2MnH(SiH_2R)_2]$ ($\mathbf{1^{Ph}}$: R = Ph, $\mathbf{1^{Bu}}$: R = ^{n}Bu) or the silylene hydride complexes $[(dmpe)_2MnH(=SiR_2)]$ ($\mathbf{2^{Ph2}}$: R = Ph, $\mathbf{2^{Et2}}$: R = Et) with the heterocumulenes carbon dioxide (CO_2) and diisopropylcarbodiimide $\{C(N^iPr)_2\}$ were investigated. With CO_2, these reactions yielded the manganese(I) formate complex *trans*-$[(dmpe)_2Mn(CO)(\kappa^1\text{-}O_2CH)]$ (**3**), with polysiloxane byproducts. Compound **3** was found to undergo reversible CO_2 elimination at room temperature, and was only stable under an atmosphere of CO_2. By contrast, reactions with $C(N^iPr)_2$ afforded manganese(I) amidinylsilyl complexes $[(dmpe)_2Mn\{\kappa^2\text{-}SiRR'(N^iPrCHN^iPr)\}]$ $\{\mathbf{5^{Ph,H}}$: R = Ph, R' = H, $\mathbf{5^{Bu,H}}$: R = ^{n}Bu, R' = H, $\mathbf{5^{Ph2}}$: R = R' = Ph, $\mathbf{5^{Et2}}$: R = R' = Et$\}$. Complexes **3**, $\mathbf{5^{Ph,H}}$ and $\mathbf{5^{Ph2}}$ were crystallographically characterized. DFT calculations and analysis of XRD bond metrics suggest that the structure of **5** involves a contribution from a resonance structure featuring a neutral base-stabilized silylene and an anionic amido donor on manganese.

INTRODUCTION

Our group has recently reported the manganese disilyl hydride complexes $[(dmpe)_2MnH(SiH_2R)_2]$ ($\mathbf{1^{Ph}}$: R = Ph, $\mathbf{1^{Bu}}$: R = ^{n}Bu) and silylene hydride complexes $[(dmpe)_2MnH(=SiR_2)]$ ($\mathbf{2^{Ph2}}$: R = Ph, $\mathbf{2^{Et2}}$: R = Et).[1,2] Exposure of either set of complexes to ethylene resulted in an unprecedented transformation to afford manganese silene hydride complexes $[(dmpe)_2MnH(RR'Si{=}CHMe)]$ (Scheme 1).[1,3] Reaction schemes were proposed for this transformation involving either a 5-coordinate silyl complex (**A**; formed from $\mathbf{1^R}$ by hydrosilane elimination, or from $\mathbf{2^{R2}}$ by 1,1-insertion) or a silylene hydride complex (formed from $\mathbf{1^R}$ by hydrosilane elimination to form **A**, followed by α-hydride elimination); Scheme 1. DFT calculations and trapping experiments were conducted, and demonstrated the thermodynamic and kinetic accessibility of 5-coordinate silyl and silylene hydride species from disilyl hydride complexes $\mathbf{1^R}$.[3]

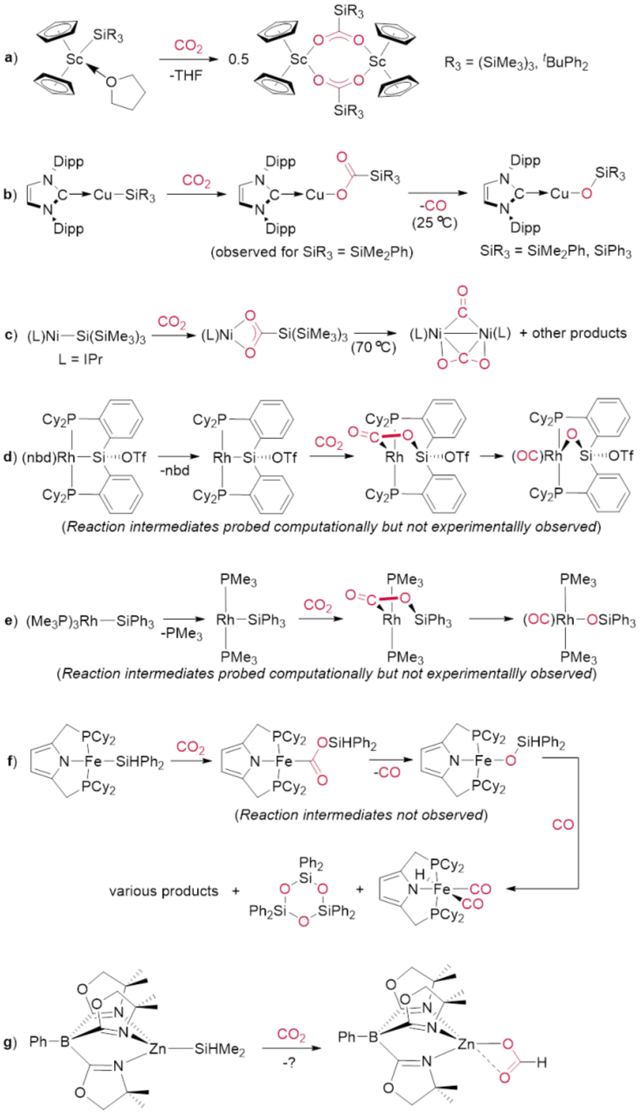
Given the unique reactivity of $\mathbf{1^R}$ and $\mathbf{2^{R2}}$ with ethylene, we were motivated to investigate their reactivity with other unsaturated molecules, such as carbon dioxide and carbodiimides. Studies which shed light on the reactivity of CO_2 with organometallic complexes are of interest given that CO_2 is a widely available and inexpensive C1 synthon,[4] and large-scale consumption of atmospheric CO_2 could potentially disrupt anthropogenic climate change.[5] While carbon dioxide is often described as thermodynamically and kinetically inert, the polar unsaturated C=O bonds in CO_2 have proven highly reactive towards various d-block complexes.[6,7] Consequently, significant effort has been directed towards both catalytic and stoichiometric CO_2 activation by d-block metals, often involving insertion of CO_2 into M–H, M–O, or M–N bonds.[7] By contrast, reactions between CO_2 and d-block silyl or silylene moieties are scarce (*vide infra*), despite the potential for reaction pathways which ultimately generate strong Si–O bonds (Si–O BDE = 798(8) kJ mol^{-1}).[8]

Scheme 1. Proposed pathways for reactions of disilyl hydride complexes $[(dmpe)_2MnH(SiH_2R)_2]$ ($\mathbf{1^{Ph}}$: R = Ph, $\mathbf{1^{Bu}}$: R = ^{n}Bu) and silylene hydride complexes $[(dmpe)_2MnH(=SiR_2)]$ ($\mathbf{2^{Ph2}}$: R = Ph, $\mathbf{2^{Et2}}$: R = Et) with ethylene to form silene hydride complexes $[(dmpe)_2MnH(RR'Si{=}CHMe)]$. Only one isomer is shown for all species. R' = H for reactions involving $\mathbf{1^R}$ and R' = R for reactions involving $\mathbf{2^{R2}}$.[1,3]



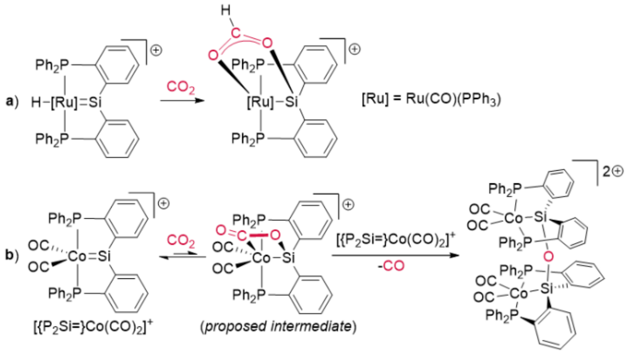
In 1990, the Tilley group reported the first examples of CO_2 insertion into a d-block silyl bond {in $[Cp_2Sc(SiR_3)(THF)]$, $SiR_3 = Si(SiMe_3)_3$, Si^tBuPh_2}, forming bridging silanecarboxylate complexes (a in Scheme 2).[9] In the past decade, examples of CO_2 insertion into Cu–silyl[10] and Ni–silyl[11] groups have also been reported, and in both cases the observed silanecarboxylate products proved susceptible to decomposition via C–O bond lysis (b and c, respectively, in Scheme 2). In contrast, the Whited group reported Si–O bond forming CO_2 insertion into Rh–silyl bonds, followed by CO extrusion to afford siloxide complexes (d and e in Scheme 2).[12] Similar reactivity was also reported by Tonzetich for Fe–silyl bonds, although in this case an iron siloxide complex was not observed due to decomposition to various products including an iron carbonyl hydride complex and a cyclic siloxane (f in Scheme 2).[13] In addition, a tris(oxazolinyl)borato zinc silyl complex reacted with CO_2 to afford a formate species (g in Scheme 2), possibly via initial CO_2 insertion into the Zn–Si bond.[14]

Scheme 2. Reactions of CO_2 with the M–Si bonds in d-block silyl complexes.[9–14]



A small number of reactions between silylene complexes and CO_2 have also been reported. For example, in 2017, Whited et al. described the reaction of a Ru(II) silylene hydride cation and carbon dioxide to yield a structure with a formate moiety bridging ruthenium and silicon (a in Scheme 3).[15] Two potential mechanisms were proposed, one of which involved initial isomerization to a 5-coordinate silyl species. The same group also recently reported the reaction of CO_2 with another cationic pincer silylene complex, $[\{P_2Si{=}\}Co(CO)_2]^+$, which proceeded via 2+2 cycloaddition of a C=O bond across the silylene Si=Co bond, followed by CO extrusion and coordination to a second equivalent of $[\{P_2Si{=}\}Co(CO)_2]^+$ (b in Scheme 3).[16]

Scheme 3. Reactions of CO_2 with the M=Si bonds in d-block silylene complexes.[15,16]

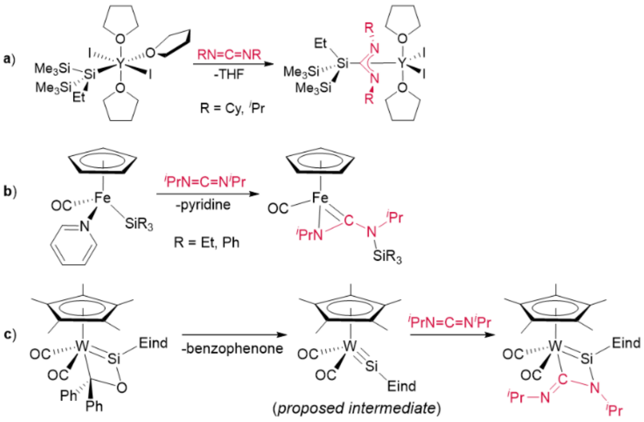


Carbodiimides {$C(NR)_2$} are isoelectronic with CO_2, and reactions involving these compounds may be of utility in modelling the initial steps in reactions of d-block silyl or silylene complexes with CO_2, given than subsequent reactivity (which for CO_2 generally involves C–O bond lysis and Si–O bond formation; Schemes 2 and 3) may be disfavored due to a weaker thermodynamic driving force for Si–E bond formation (the BDE for an Si–N bond is 359 kJ mol^{-1} lower than that for an Si–O bond),[8] potentially in combination with increased steric hindrance.

To our knowledge, the only reported reactions of carbodiimides at a d-block silyl moiety involve overall Si–C bond forming 1,2-insertion into a Y–Si bond in $[(THF)_2YI_2\{SiEt(SiMe_3)_2\}]$[17] or Si–N bond forming 1,2-insertion into an Fe–Si bond in $[(OC)(py)CpFe(SiR_3)]$ (R = Et, Ph),[18] yielding amidinate or η^2-amidino complexes, respectively (a and b in Scheme 4). In addition, the Tobita group has reported that a tungsten silylene complex featuring a W=Si–O–C metallacycle reacts with diisopropylcarbodiimide to form a new silylene complex, though it proceeds via an unusual mechanism; initial ketone extrusion to form a silylyne intermediate {observed in the absence of $C(N^iPr)_2$}, with subsequent 2+2 cycloaddition between the C=N bond in $C(N^iPr)_2$ and the W≡Si silylyne bond (c in Scheme 4).[19]

Herein we report the first reactions of mangansese silyl and silylene complexes with carbon dioxide and a carbodiimide.

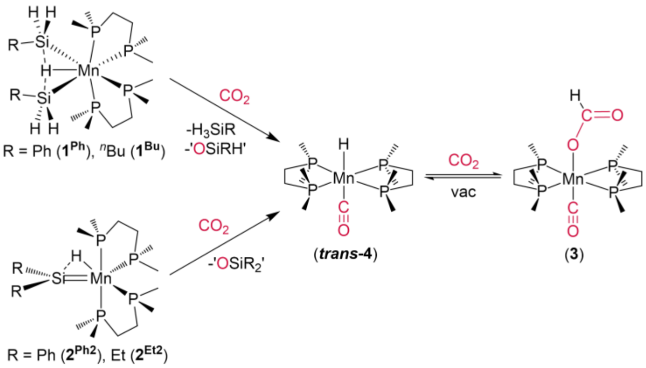
Scheme 4. Reactions of carbodiimides with d-block silyl (a-b)[17,18] or silylene (c)[19] complexes. The silylyne intermediate in c is shown as a monomer for clarity, though exists in solution in equilibrium with a (dominant) dimer species. Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hyndrindacen-4-yl.



RESULTS AND DISCUSSION

Reactions with Carbon Dioxide: Reactions of disilyl hydride complexes $[(dmpe)_2MnH(SiH_2R)_2]$ ($\mathbf{1^{Ph}}$: R = Ph, $\mathbf{1^{Bu}}$: R = ^{n}Bu) and silylene hydride complexes $[(dmpe)_2MnH(=SiR_2)]$ ($\mathbf{2^{Ph2}}$: R = Ph, $\mathbf{2^{Et2}}$: R = Et) with carbon dioxide afforded, in each case, *trans*-$[(dmpe)_2Mn(CO)(\kappa^1\text{-}O_2CH)]$ (**3**; Scheme 5), in which one equivalent of CO_2 has been converted to CO.[20] In the reactions of $\mathbf{1^R}$, one equivalent of free silane (H_3SiR) was eliminated. Furthermore, all of these reactions afforded benzene-soluble byproducts assigned as polysiloxanes $\{(SiR'RO)_n$, R = Ph, Et, or ^{n}Bu, R' = R or H};[21] the ^{29}Si NMR chemical shifts ranged from –21 to –45 ppm,[22] and for reactions with $\mathbf{1^R}$ (R' = H), ^{1}H NMR signals were located at 4.8-5.5 ppm in the Si*H* region.[23] For reactions of $\mathbf{2^{Ph2}}$ and $\mathbf{2^{Et2}}$, ^{13}C and ^{29}Si NMR spectra of polysiloxane byproducts matched those of commercial cyclosiloxane samples.

Scheme 5. Reactions of disilyl hydride complexes $[(dmpe)_2MnH(SiH_2R)_2]$ ($\mathbf{1^{Ph}}$: R = Ph, $\mathbf{1^{Bu}}$: R = ^{n}Bu) or silylene hydride complexes $[(dmpe)_2MnH(=SiR_2)]$ ($\mathbf{2^{Ph2}}$: R = Ph, $\mathbf{2^{Et2}}$: R = Et) with carbon dioxide to afford the formate complex *trans*-$[(dmpe)_2Mn(CO)(\kappa^1\text{-}O_2CH)]$ (**3**). Only one isomer is shown for $\mathbf{2^{R2}}$.



Compound **3** was obtained in pure form by sublimation to afford a 60 : 40 mixture of **3** and known *trans*-$[(dmpe)_2MnH(CO)]$ (***trans*-4**),[24] the product of CO_2 elimination from the formate ligand, followed by re-exposure to CO_2 (in solution or the solid state) to re-form **3**. In fact, **3** was only stable at room temperature under an atmosphere of CO_2, eliminating CO_2 slowly under argon (either as a solid or in solution) or under vacuum (approx. 2% conversion to ***trans*-4** after 20 min.). It is notable that CO_2 insertion into transition metal–hydride bonds is a key step in many catalytic processes, and is therefore the subject of considerable investigation.[25] NMR spectra of **3** feature a single ^{31}P NMR environment at 68.3 ppm, and only five ^{1}H NMR signals {four from the dmpe ligands between 1.23 and 1.90 ppm, and one (a quintet with $J_{31P\text{-}1H}$ of 2 Hz) from the formyl proton at 8.68 ppm}.

X-ray quality crystals of **3** were obtained from a concentrated toluene solution layered with hexamethyldisiloxane, and confirmed the expected octahedral geometry with *trans*-disposed carbonyl and κ^1-formate ligands (Figure 1). The phosphorus donors form a statistically perfect plane ($\sum$P–Mn–P = 359.98(4)-360.01(4)°), the C–Mn–O angles are 172.23(5)-173.31(5)°, and the various bonding parameters related to the terminal formate unit fall within the range previously observed for terminal manganese formate complexes.[26]

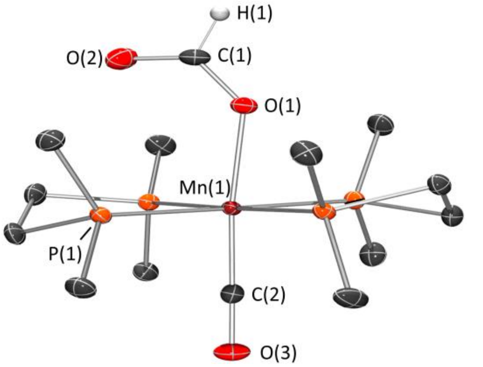


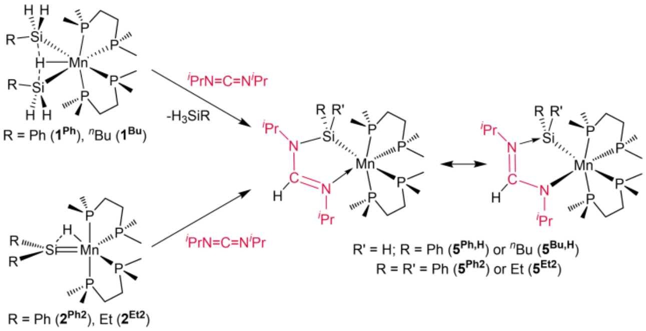
Figure 1. X-ray crystal structure of *trans*-$[(dmpe)_2Mn(CO)(\kappa^1\text{-}O_2CH)]$ (**3**), with ellipsoids drawn at 50% probability. H(1) was located from the difference map and refined isotropically. Most hydrogen atoms have been omitted for clarity. The unit cell contains two independent and essentially isostructural molecules, only one of which is shown. Atom labels with the suffix A correspond to the second molecule (not shown) in the unit cell. Bond distances (Å) and angles (deg): Mn(1)–O(1) 2.096(1), Mn(1A)–O(1A) 2.086(1), Mn(1)–C(2) 1.751(1), Mn(1A)–C(2A) 1.742(1), O(1)–C(1) 1.275(2), O(1A)–C(1A) 1.266(2), C(1)–O(2) 1.229(2), C(1A)–O(2A) 1.237(2), C(1)–H(1) 0.97(2), C(1A)–H(1A) 0.98(2), C(2)–O(3) 1.191(2), C(2A)–O(3A) 1.175(2), C(2)–Mn(1)–O(1) 173.31(5), C(2A)–Mn(1A)–O(1A) 172.23(5), Mn(1)–C(2)–O(3) 178.5(1), Mn(1A)–C(2A)–O(3A) 179.3(1), Mn(1)–O(1)–C(1) 133.78(9), Mn(1A)–O(1A)–C(1A) 133.53(9), O(1)–C(1)–O(2) 128.8(1), O(1A)–C(1A)–O(2A) 128.9(1), O(1)–C(1)–H(1) 116(1), O(1A)–C(1A)–H(1A) 114(1), O(2)–C(1)–H(1) 115(1), O(2A)–C(1A)–H(1A) 117(1).

Formate complexes have sometimes been shown to be catalytically active towards hydrosilylation of carbon dioxide.[27] However, complex **3** displayed limited (using H_3SiPh) or no (using H_3Si^nBu, H_2SiPh_2, or $HSiPh_3$) utility for catalytic CO_2 hydrosilylation (in C_6D_6 under one atmosphere of CO_2 up to 90 °C).[28]

Reactions with Diisopropylcarbodiimide: Whereas the reactions of $\mathbf{1^R}$ or $\mathbf{2^{R2}}$ with carbon dioxide yielded identical structures where a C–O bond in one equivalent of CO_2 has been cleaved (*vide supra*), disilyl hydride complexes

$[(dmpe)_2MnH(SiH_2R)_2]$ ($\mathbf{1^{Ph}}$: R = Ph, $\mathbf{1^{Bu}}$: R = ^{n}Bu) and silylene hydride complexes $[(dmpe)_2MnH(=SiR_2)]$ ($\mathbf{2^{Ph2}}$: R = Ph, $\mathbf{2^{Et2}}$: R = Et) reacted with diisopropylcarbodiimide $\{C(N^iPr)_2\}$ to form a family of manganese(I) amidinylsilyl complexes $[(dmpe)_2Mn\{\kappa^2\text{-}SiRR'(N^iPrCHN^iPr)\}]$ {R' = H and R = Ph ($\mathbf{5^{Ph,H}}$) or ^{n}Bu ($\mathbf{5^{Bu,H}}$), R' = R = Ph ($\mathbf{5^{Ph2}}$) or Et ($\mathbf{5^{Et2}}$)}; Scheme 6. These metallacycles feature a 5-membered M–Si–N–C–N ring, where one of the hydrogen substituents originating from a silyl ligand in $\mathbf{1^R}$, or the metal hydride in $\mathbf{2^{R2}}$, is located on the central carbon atom of the ^{i}PrNCN^{i}Pr unit. For reactions involving $\mathbf{1^R}$, one equivalent of free silane (H_3SiPh or H_3Si^nBu) was also observed spectroscopically. NMR spectra of $\mathbf{5^{R,H}}$ and $\mathbf{5^{R2}}$ feature a ^{29}Si NMR peak between 77.9 and 87.1 ppm, as well as an NC(*H*)N ^{1}H NMR signal at 7.58-7.87 ppm. Complexes $\mathbf{5^{R,H}}$ are chiral at the metal center and silicon, and in solution, two diastereomers were observed {in thermodynamic ratios of 2.8:1 ($\mathbf{5^{Ph,H}}$) and 2.3:1 ($\mathbf{5^{Bu,H}}$)}.[29] For $\mathbf{5^{R,H}}$, an Si*H* signal at 5.50-6.26 ppm was also observed in the ^{1}H NMR spectra.

Scheme 6. Reactions of disilyl hydride complexes $[(dmpe)_2MnH(SiH_2R)_2]$ ($\mathbf{1^{Ph}}$: R = Ph, $\mathbf{1^{Bu}}$: R = ^{n}Bu) or silylene hydride complexes $[(dmpe)_2MnH(=SiR_2)]$ ($\mathbf{2^{Ph2}}$: R = Ph, $\mathbf{2^{Et2}}$: R = Et) with diisopropylcarbodiimide to afford the amidinylsilyl complexes $[(dmpe)_2Mn\{\kappa^2\text{-}SiRR'(N^iPrCHN^iPr)\}]$ ($\mathbf{5^{Ph,H}}$: R = Ph, R' = H; $\mathbf{5^{Bu,H}}$: R = ^{n}Bu, R' = H; $\mathbf{5^{Ph2}}$: R = R' = Ph; $\mathbf{5^{Et2}}$: R = R' = Et). Only one isomer of $\mathbf{2^{R2}}$ and one diastereomer of $\mathbf{5^{R,H}}$ are shown, and complexes **5** are shown as two canonical structures.



The ^{29}Si NMR chemical shifts for **5** (*vide supra*) are comparable to those of base-stabilized silylene complexes, and a similarly high frequency resonance (65.4 ppm) has been used (in combination with crystallographic data) to suggest that the bonding environment in $[Cp^*(OC)_2Mo(\kappa^2\{Si,N\}\text{-}Si\{p\text{-}Tol\}_2\{N(H)C_5H_4N\})]$ (which contains a comparable M–Si–N–C–N metallacycle) involves a contribution from a base-stabilized silylene resonance structure.[30] However, ^{29}Si resonances at only slightly lower frequencies have also been reported for aminosilyl complexes such as $[Cp^*(OC)_2Fe\{SiMe_2(NR_2)\}]$ (R = Me, ^{i}Pr, Ph; ^{29}Si δ = 53-47 ppm).[31]

X-ray quality crystals of amidinylsilyl complex $\mathbf{5^{Ph,H}}$ were obtained from a concentrated hexanes solution layered with hexamethyldisiloxane at –30 °C. The resulting structure (Figure 2) contains two independent but essentially isostructural molecules in the unit cell, one of which is disordered due to two overlapping diastereomers of $\mathbf{5^{Ph,H}}$. Structural parameters derived from the X-ray crystal structure and DFT calculations[32] reveal Mn–N distances of 2.137(3)-2.141(3) Å (calcd. 2.12 Å, Mayer b.o. 0.58-0.59) and Mn–Si distances of 2.347(1)-2.358(1) Å (calcd. 2.32 Å, Mayer b.o. 0.93-0.95). These Mn–Si distances lie at the shorter end of the range observed for Mn(I) silyl complexes with dmpe co-ligands {e.g. 2.35-2.44 Å in $[(dmpe)_2Mn(SiH_2R)(CNR')]$ (R = Ph or ^{n}Bu, R' = *o*-xylyl or ^{t}Bu)},[3] and are longer than those in related NHC-stabilized silylene hydride complexes {2.26-2.30 Å in $[(dmpe)_2MnH\{=SiR(NHC)\}]$ (R = Ph or ^{n}Bu, NHC = 1,3-diisopropylimidazolin-2-ylidene or 1,3,4,5-tetramethyl-4-imidazolin-2-ylidene)}.[3] However, the two C–N distances in the metallacycle are more similar than would be expected for localized single and double bonds. The C–N bonds closer to silicon and manganese are 1.350(4)-1.350(5) Å (calcd. 1.34-1.35 Å, Mayer b.o. 1.23-1.24) and 1.296(6)-1.299(5) Å (calcd. 1.31 Å, Mayer b.o. of 1.50), respectively; cf. 1.46 Å for a typical C–N single bond and 1.21 Å for a typical C–N double bond.[33] In addition, the Si–N distances of 1.805(3)-1.813(3) Å (calcd. 1.82 Å, Mayer b.o. 0.74) are longer than those in free aminosilanes (1.70-1.76 Å).[34] Furthermore, the sum of bond angles about the silicon center excluding those involving the N donor (347(3)-349(3)°; calcd. 348.8-349.3°) are intermediate between what would be expected for sp^2 or sp^3 Si hybridization.

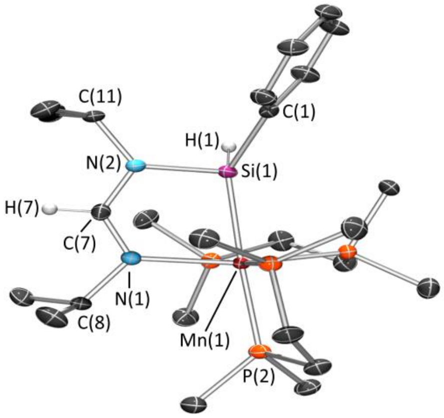


Figure 2. X-ray crystal structure of $[(dmpe)_2Mn\{\kappa^2\text{-}SiHPh(N^iPrCHN^iPr)\}]$ ($\mathbf{5^{Ph,H}}$) with ellipsoids at 50% probability. Most hydrogen atoms have been omitted for clarity. H(1), H(1A), H(7), and H(7A) were located from the difference map and refined isotropically. The unit cell contains two independent and essentially isostructural molecules, only one of which is shown. For one of the two molecules (not shown), the dmpe ligands were disordered over two positions and modelling this disorder allowed the two different diastereomers of $\mathbf{5^{Ph,H}}$ to be observed. Atom labels with the suffix A correspond to the second molecule (not shown) in the unit cell. Bond distances (Å) and angles (deg): Mn(1)–Si(1) 2.347(1), Mn(1A)–Si(1A) 2.358(1), Mn(1)–N(1) 2.137(3), Mn(1A)–N(1A) 2.141(3), Si(1)–H(1) 1.44(5), Si(1A)–H(1A) 1.50(6), Si(1)–C(1) 1.934(4), Si(1A)–C(1A) 1.938(3), Si(1)–N(2) 1.815(3), Si(1A)–N(2A) 1.805(4), N(2)–C(7) 1.348(4), N(2A)–C(7A) 1.349(5), N(2)–C(11) 1.478(6), N(2A)–C(11A) 1.482(6), N(1)–C(7) 1.301(6), N(1A)–C(7A) 1.298(6), N(1)–C(8) 1.490(4), N(1A)–C(8A) 1.485(6), C(7)–H(7) 0.98(4), C(7A)–H(7A) 0.96(6), N(1)–Mn(1)–Si(1) 80.14(9), N(1A)–Mn(1A)–Si(1A) 79.45(9), Mn(1)–Si(1)–C(1) 136.4(1), Mn(1A)–Si(1A)–C(1A) 132.8(1), Mn(1)–Si(1)–H(1) 118(2), Mn(1A)–Si(1A)–H(1A) 120(2), Mn(1)–Si(1)–N(2) 100.5(1), Mn(1A)–Si(1A)–N(2A) 100.6(1), Si(1)–N(2)–C(7) 114.6(3), Si(1A)–N(2A)–C(7A) 115.1(3), Si(1)–N(2)–C(11) 126.2(2), Si(1A)–N(2A)–C(11A) 125.7(2), N(2)–C(7)–N(1) 123.9(3), N(2A)–C(7A)–N(1A) 123.3(3), C(7)–N(1)–Mn(1) 120.4(3), C(7A)–N(1A)–

Mn(1A) 121.1(3), C(7)–N(1)–C(8) 114.0(3), C(7A)–N(1A)–C(8A) 113.8(3), C(11)–N(2)–C(7) 117.9(3), C(11A)–N(2A)–C(7A) 119.2(3), C(8)–N(1)–Mn(1) 125.5(2), C(8A)–N(1A)–Mn(1A) 125.1(3).

A crystal structure was also obtained of **5**$^{\mathbf{Ph2}}$, though it was of poor quality and only suitable to determine connectivity (which matches that of **5**$^{\mathbf{Ph,H}}$; Figure S1), and crystal structures were not obtained for the other two analogues (**5**$^{\mathbf{Bu,H}}$ and **5**$^{\mathbf{Et2}}$). DFT calculations were carried out on **5**$^{\mathbf{Ph2}}$, **5**$^{\mathbf{Et2}}$, and **5**$^{\mathbf{Et,H}}$ (**5**$^{\mathbf{Et,H}}$ was used as a model for **5**$^{\mathbf{Bu,H}}$, in which the ^{n}Bu group has been replaced by an Et group). These calculations yielded distances and Mayer bond orders similar to calculated values described above for **5**$^{\mathbf{Ph,H}}$ (within 0.07 Å and 0.09, respectively; Table S1).[32] Together, these bond metrics suggest that **5** is well described using a combination of the two resonance structures in Scheme 6; one with anionic amidinylsilyl and neutral imine donors (left), and the other with a neutral base-stabilized silylene and an anionic amido donor (right). Similar resonance structures have been employed to describe the bonding situation in a pair of M–Si–N–C–N metallacycles (M = Mo, Ru) where the N donor on the metal is part of a pyridine ring, as well as in related M–Si–O–C–E (M = Mo, W, Fe, Ru; E = O, N) metallacycles.[30,35,36]

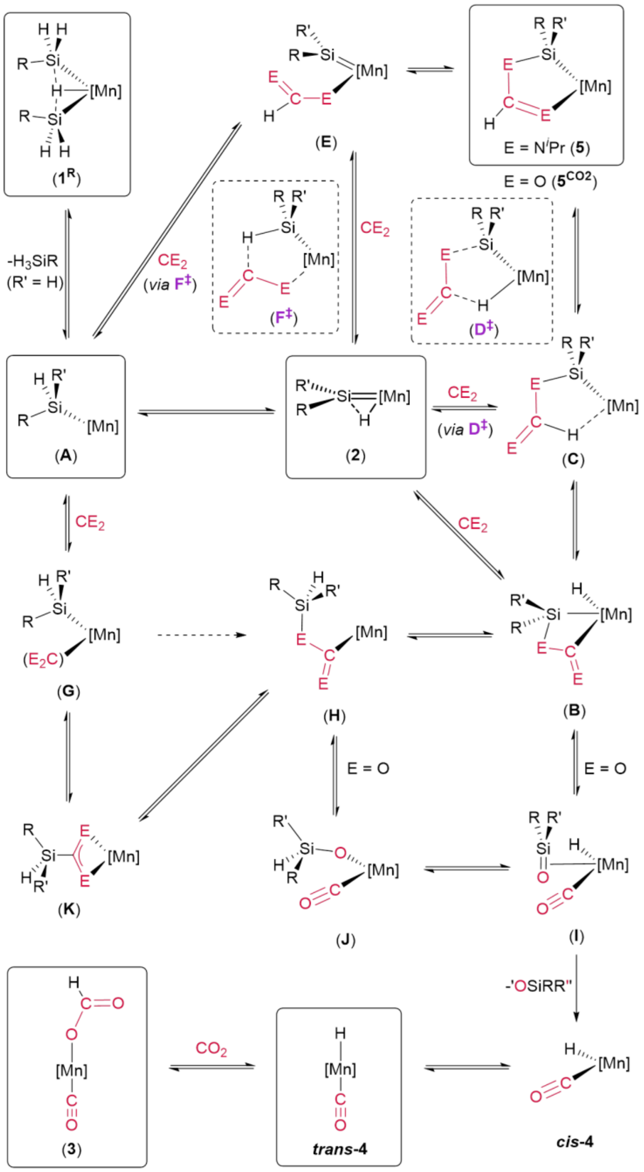
Potential Pathways for Reactions of Disilyl Hydride (1$^{\mathbf{R}}$) or Silylene Hydride (2$^{\mathbf{R2}}$) Complexes with CO$_2$ or C(N^{i}Pr)$_2$: The reactions described in this work (Schemes 5 and 6) could proceed via a 5-coordinate silyl species (**A**) or a silylene hydride complex (**2**); Scheme 7. Both of these species have previously been shown to be accessible from disilyl hydride complexes **1**$^{\mathbf{R}}$ through combined computational studies, high temperature ^{1}H NMR spectroscopy, and trapping reactions with isonitriles and NHCs.[3] In addition, silyl isomers have been shown to be accessible from isolated silylene hydride complexes **2**$^{\mathbf{R2}}$ by DFT calculations.[1]

The silylene hydride species (**2**) present several plausible reaction pathways to the observed reaction products (Scheme 7). One possibility involves initial 2+2 cycloaddition of the Mn=Si double bond and a C=E (E = O, N^{i}Pr) bond to afford intermediate **B** (with Si–E and Mn–C bond formation, given the electrophilic nature of Si in **2**).[1] This cycloaddition reaction could proceed either in a concerted or two-step process (via initial O or N coordination to the silicon center), and similar mechanistic steps have been proposed for reactions of ruthenium silylene hydride complexes with RC≡N,[37] RNCO,[38] and MesNCS,[36,39] as well as for a cobalt silylene complex with CO$_2$ (b in Scheme 3).[16] Subsequent C–H bond forming reductive elimination from **B** would then generate intermediate **C**, and isomerization would afford compound **5**; the observed product in reactions with C(N^{i}Pr)$_2$.

It is also conceivable that intermediate **C** could be formed directly from **2** and CE$_2$ via an outer sphere mechanism involving formal 2+3 cycloaddition of the Si=M–H unit across one of the C=E bonds (i.e. via transition state **D**‡). Such a process (either concerted or two-step), via a transition state with a M–Si–E–C–H ring system (analogous to **D**‡), has been suggested for reactions of ruthenium silylene complexes with CO$_2$ (a in Scheme 3)[15] and MesNCO,[36,39] and a similar transition state was also suggested for the reaction of a tungsten silylene hydride complex with acetone.[40] Furthermore, an analogous reaction was proposed as a step in the catalytic reductive formylation of amines by CO$_2$ and H$_2$SiPh$_2$ using a cationic Rh(I) carbene pre-catalyst.[41]

An alternative route to compound **5** could involve CE$_2$ insertion into the Mn–H bond of a silylene hydride complex (**2**) to afford silylene formate or formamidinate {HC(NR)$_2$} intermediate **E**, with subsequent cyclization (involving nucleophilic attack of the formate or formamidinate anion on the silylene).

Scheme 7. Potential pathways for the reactions of disilyl hydride complexes [(dmpe)$_2$MnH(SiH$_2$R)$_2$] (**1**$^{\mathbf{Ph}}$: R= Ph, **1**$^{\mathbf{Bu}}$: R = ^{n}Bu) or silylene hydride complexes [(dmpe)$_2$MnH(=SiR$_2$)] (**2**$^{\mathbf{Ph2}}$: R = Ph, **2**$^{\mathbf{Et2}}$: R = Et) with E=C=E (E = O, N^{i}Pr). [Mn] = Mn(dmpe)$_2$. For some compounds, more than one isomer is likely to be accessible (e.g. *cis* vs *trans*, the presence/absence of an interaction between silicon and an adjacent hydride ligand, or coordination/lack of coordination of lone pairs on E to the metal center), but for clarity, only one isomer is shown. Solid boxes indicate known complexes and intermediates.



The reactions of **1**$^{\mathbf{R}}$ or **2**$^{\mathbf{R2}}$ with CO$_2$ and C(N^{i}Pr)$_2$ could also proceed via 5-coordinate silyl intermediate **A** as the reactive species (Scheme 7).[42] In one such mechanism, intermediate **E** could be accessed directly via 2+3 cycloaddition of the Mn–Si–H moiety in **A** across one of the E=C bonds {with a transition state containing a M–Si–H–C–E ring system (**F**‡)}. This is analogous to mechanisms proposed by Whited et al. in the reaction of a ruthenium silylene hydride with CO_2 (a in Scheme 3),[15] and computationally investigated (though discarded as higher in energy) by Wu and Lin et al. for the reactions of a tungsten silylene hydride complex with acetonitrile and acetone.[43]

Alternatively, reactions of **A** could involve initial CO_2/$C(N^iPr)_2$ coordination to afford intermediate **G**, followed by Si–E bond forming 1,2-insertion to generate **H**, and subsequent oxidative addition of an Si–H bond to form previously described **B**. However, in the reactions of metal silyl complexes with CO_2 or $C(NR)_2$, Si–E bond-forming 1,2-insertion (d-f in Scheme 2, and b in Scheme 4)[12,13,18] has only been observed for metal–silyl complexes in which the electronegativity of the metal (Rh or Fe) is greater than, or similar to, that of silicon. Therefore, for manganese, this pathway (1,2-insertion reactivity to convert **G** to **H**) seems unlikely.[44]

Conversion of **G** to **H** could alternatively proceed via Si–C bond forming 1,2-insertion to generate silanecarboxylate (R_3SiCO_2) or silyl amidinate {$R_3SiC(NR)_2$} complex **K**, followed by an outer-sphere 1,2-shift of the silyl group from C to E. DFT calculations[45] have suggested that a related mechanism is pertinent in the reactions of Cu(I) silyl complexes with CO_2 to form siloxide compounds (b in Scheme 2).[10] For E = O, the initial silanecarboxylate-forming step has also been observed for Ni(I) silyl complexes (c in Scheme 2),[11] while the latter 1,2-silyl shift step bears a resemblance to the Brook rearrangement.[46] It is also notable that the products formed in the previously reported reactions of transition metal silyl complexes with carbodiimides (a-b in Scheme 4) contain amidino and silyl amidinate ligands related to those in **H** and **K**.

The above reaction pathways provide access to structure **5**; the final product in reactions with carbodiimides. However, in the case of CO_2, further (or alternative) reactivity ensues to generate **3**, where CO ligand formation is accompanied by polysiloxane {$(RR'SiO)_n$} elimination; this reactivity bears some resemblance to the C–S bond cleavage observed upon reaction of [Cp*(CO)RuH{=SiHC($SiMe_3$)$_3$}] with MesNCS.[36,39]

One potential route to compound **3** involves cleavage of the O–C bond in **B** to afford intermediate **I**, containing a hydride and a neutral silaaldehyde or silanone ligand, followed by RR'Si=O elimination {yielding a polsiloxane, $(RR'SiO)_n$} to afford compound **4** (*cis* or *trans*), which we have shown reversibly inserts CO_2 to afford **3** (*vide supra*). Silaaldehyde complexes of Mn are unknown, but Tobita recently reported a stable W complex with a η^2-coordinated silaaldehyde ligand.[47] Silanone complexes have been reported for Al, Zn, W, and Mo, although in all cases the silanone ligand bridges between two metals or features Lewis-base coordination to the Si center.[48] Silanone complexes have also been proposed as reactive intermediates in reactions which afford polysiloxane byproducts.[49]

An additional pathway could be envisaged to generate intermediate **I**, proceeding via intermediate **J**, which contains a siloxide (OSiHRR') and a carbonyl ligand. The C(O)OSiHRR' ligand in compound **H** could undergo α-siloxide elimination to form **J**, which could generate compound **I** by β-hydride elimination. The overall process (**H**→**J**→**I**) resembles reactivity proposed by Tonzetich et al. to explain siloxane byproducts observed in the reaction of an iron(II) silyl complex with CO_2 (f in Scheme 2).[13] In addition, the initial **H** to **J** transformation resembles the CNMes extrusion reaction observed for a C(NMes){$SSiH_2C(SiMe_3)_3$} ligand on ruthenium,[36,39] and a related transformation has been proposed, based on DFT calculations, as the final step in CO extrusion from Cu(I) silanecarboxylate complexes (b in Scheme 2).[45]

SUMMARY AND CONCLUSIONS

This work describes the reactivity of manganese disilyl hydride (**1**) and silylene hydride (**2**) complexes with CO_2 and $C(N^iPr)_2$. Carbon dioxide is a widely available and inexpensive C1 synthon, and large-scale consumption of atmospheric CO_2 could potentially disrupt anthropogenic climate change. However, reactions between CO_2 and d-block silyl or silylene moieties are scarce, despite the potential for reaction pathways which ultimately generate strong Si–O bonds. All reactions of **1**-**2** with CO_2 afforded the carbonyl formate complex *trans*-[(dmpe)$_2$Mn(CO)(κ^1-O_2CH)] (**3**), presumably formed via [(dmpe)$_2$Mn(CO)H] (**4**). In previous reactions of d-block silyl or silylene complexes with CO_2, only one example of formate complex formation has been reported, in the chemistry of zinc, although formation of a carbonyl hydride complex has been reported for iron. Direct reactions of silyl or silylene complexes with carbodiimides are even more scarce than those with carbon dioxide, exclusively forming amidinate or η^2-amidino complexes. In this work, reactions of **1**-**2** with $C(N^iPr)_2$ afforded amidinylsilyl complexes (**5**) featuring a 5-membered M–Si–N–C–N ring. It is notable that in reactions with $C(N^iPr)_2$, the C–N linkages remained intact, whereas in reactions with CO_2, C–O bond cleavage afforded a carbonyl ligand, likely due to steric differences and/or the greater strength of Si–O versus Si–N bonds.

EXPERIMENTAL SECTION

General Methods. An argon-filled MBraun UNIlab glove box equipped with a –30 °C freezer was employed for the manipulation and storage of all oxygen- and moisture- sensitive compounds. Air-sensitive preparative reactions were performed on a double-manifold high-vacuum line equipped with a two stage Welch 1402 belt-drive vacuum pump (ultimate pressure 1×10^{-4} torr) using standard techniques.[50] The vacuum was measured periodically using a Kurt J. Lesker 275i convection enhanced Pirani gauge. Residual oxygen and moisture were removed from the argon stream by passage through an Oxisorb-W scrubber from Matheson Gas Products.

Benzene and hexamethyldisiloxane were purchased from Aldrich, hexanes and toluene were purchased from Caledon, and deuterated solvents were purchased from ACP Chemicals. Benzene, hexamethyldisiloxane, hexanes and toluene were initially dried and distilled at atmospheric pressure from sodium/benzophenone (first three) and sodium (toluene). All solvents were stored over an appropriate drying agent (hexamethyldisiloxane, benzene, toluene, C_6D_6 = Na/Ph_2CO; hexanes = Na/Ph_2CO/tetraglyme) and introduced to reactions or solvent storage flasks via vacuum transfer with condensation at –78 °C.

Dmpe, H_3SiPh, H_3Si^nBu, H_2SiEt_2, H_2SiPh_2, 1,4-dioxane, CO_2, $C(N^iPr)_2$, and ethylmagnesium chloride solution (2.0 M in diethyl ether) were purchased from Sigma-Aldrich. Manganese dichloride was purchased from Strem Chemicals. Hexaphenylcyclotrisiloxane, octaphenylcyclotetrasiloxane, and diethylcyclosiloxanes were purchased from Gelest. Argon was purchased from PraxAir. [(dmpe)$_2$MnH(C_2H_4)],[51] [(dmpe)$_2$MnH(SiH_2Ph)$_2$] (**1**$^{\mathbf{Ph}}$),[2] [(dmpe)$_2$MnH($SiH_2{}^nBu$)$_2$] (**1**$^{\mathbf{Bu}}$),[2] [(dmpe)$_2$MnH(=$SiPh_2$)] (**2**$^{\mathbf{Ph2}}$),[1] and [(dmpe)$_2$MnH(=$SiEt_2$)] (**2**$^{\mathbf{Et2}}$)[1] were prepared using literature procedures. **2**$^{\mathbf{Ph2}}$ was obtained in a mixture with the reaction byproduct [(dmpe)$_2$MnH_2($SiHPh_2$)];[1] in multiple repetitions of this reaction, recrystallization yielded **2**$^{\mathbf{Ph2}}$ content ranging from 26-83%.

NMR spectroscopy was performed on Bruker AV-500 and AV-600 spectrometers. Spectra were obtained at 298 K unless otherwise indicated. All ^{1}H NMR spectra were referenced relative to SiMe$_4$ through a resonance of the protio impurity of the solvent used: C_6D_6 (δ 7.16 ppm). Also, all ^{13}C NMR spectra were referenced relative to SiMe$_4$ through a resonance of the ^{13}C in the solvent: C_6D_6 (δ 128.06 ppm). The ^{29}Si and ^{31}P NMR spectra were referenced using an external standard {of hexamethyldisiloxane in $CDCl_3$ (6.53 ppm) or 85% H_3PO_4 in D_2O (0.0 ppm), respectively} or by indirect referencing from a ^{1}H NMR spectrum.[52]

Combustion elemental analyses were performed by Midwest Microlabs in Indianapolis.

Single-crystal X-ray crystallographic analyses were performed on crystals coated in Paratone oil and mounted on a Bruker SMART APEX II diffractometer with a 3 kW sealed-tube Mo generator and APEX II CCD detector in the McMaster Analytical X-Ray (MAX) Diffraction Facility. A semi-empirical absorption correction was applied using redundant and symmetry related data. Raw data was processed using XPREP (as part of the APEX v2.2.0 software), and solved by intrinsic (SHELXT)[53] methods. Structures were completed by difference Fourier synthesis and refined with full-matrix least-squares procedures based on F^2. In all cases, non-hydrogen atoms were refined anisotropically and hydrogen atoms were generated in ideal positions and then updated with each cycle of refinement (with the exception of hydrogen atoms on C(1) of complex **3,** on Si(1), Si(1A), C(7) and, C(7A) of complex **5$^{\mathbf{Ph,H}}$**, or on C(13) and C(13A) of complex **5$^{\mathbf{Ph2}}$**, which were located from the difference map and refined isotropically). Refinement was performed with SHELXL[54] in Olex2.[55]

All prepared complexes are air sensitive, and their products upon reaction with air are malodorous. Therefore, all syntheses were conducted under an atmosphere of argon. In lists of NMR environments below, C_β refers to the ^{i}Pr carbon bound to the nitrogen atom directly bonded to Mn, and C_γ refers to the ^{i}Pr carbon bound to the nitrogen atom directly bonded to Si.

***trans*-[(dmpe)$_2$Mn(CO)(κ^1-O$_2$CH)] (3)**. Method a.) 128.1 mg (0.224 mmol) of [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] (**1$^{\mathbf{Ph}}$**) was dissolved in 10 mL of benzene. The reaction mixture was freeze/pump/thawed in a 50 mL storage flask three times, placed under 1 atm of CO_2 at room temperature, and then sealed. After stirring at room temperature overnight, the solvent was removed *in vacuo* and the resulting solid was sublimed at 80 °C at 5 mTorr. The sublimed solid was dissolved in approx. 0.6 mL of C_6D_6, and the reaction mixture was freeze/pump/thawed in a NMR tube with a J-young valve three times, before again being placed under 1 atm of CO_2 and sealed. NMR characterization was carried out *in situ* under an atmosphere of CO_2 because removal of CO_2 (and also removal of solvent) led to partial conversion to [(dmpe)$_2$MnH(CO)] (**4**); approx. 2% after 20 min. under vacuum. X-ray quality crystals were obtained by washing the crude (pre-sublimation) solid with hexamethyldisiloxane followed by dissolution of the solid in a small volume of toluene, layering with hexamethyldisiloxane, and cooling to –30 °C. Methods b-d; Approx. 10 mg of [(dmpe)$_2$MnH(SiH$_2{}^n$Bu)$_2$] (**1$^{\mathbf{Bu}}$**), [(dmpe)$_2$MnH(=SiEt$_2$)] (**2$^{\mathbf{Et2}}$**), or a mixture of [(dmpe)$_2$MnH$_2$(SiHPh$_2$)] and [(dmpe)$_2$MnH(=SiPh$_2$)] (**2$^{\mathbf{Ph2}}$**) was dissolved in approx. 0.6 mL of C_6D_6. The resulting solutions were then placed in a NMR tube with a J-Young Teflon valve and was freeze-pump-thawed (×3). The NMR tubes were then placed under an atmosphere of carbon dioxide, sealed, and allowed to sit for 1.5 h (b), 1.25 h (c), or 5 minutes (d). The resulting mixtures (b-d) were analyzed *in situ* without purification, with 100% conversion to complex **3** and the proposed polysiloxane byproducts observed by NMR spectroscopy (in the case of **2$^{\mathbf{Ph2}}$**, the [(dmpe)$_2$MnH$_2$(SiHPh$_2$)] impurity in the starting material also reacted with CO_2 under the same conditions to yield impurities in the reaction mixture). **^{1}H NMR (C_6D_6, 600 MHz, 298 K):** δ 8.68 (p, 1H, $^4J_{H,P}$ 1.8 Hz, OC($\underline{H}$)O), 1.90, 1.36 (2 × m, 4H, PC$\underline{H}_2$), 1.26, 1.23 (2 × s, 12H, PC$\underline{H}_3$). **^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K):** δ 167.93 (s, O$\underline{C}$(H)O), 30.94 (p, $J_{C,P}$ 11.6 Hz, P$\underline{C}$H$_2$), 17.95 (m, P$\underline{C}$H$_3$), 15.54 (s, P$\underline{C}$H$_3$). **^{31}P{^{1}H} NMR (C_6D_6, 243 MHz, 298 K):** δ 68.33 (s).

[(dmpe)$_2$Mn{κ^2-SiHPh(N^{i}PrCHN^{i}Pr)}] (5$^{\mathbf{Ph,H}}$). An excess of diisopropylcarbodiimide {C(N^{i}Pr)$_2$} (67 mg, 0.531 mmol) was added to a solution containing 60.4 mg (0.106 mmol) of [(dmpe)$_2$MnH(SiH$_2$Ph)$_2$] (**1$^{\mathbf{Ph}}$**) in 8 mL of benzene. The reaction mixture was stirred in a sealed flask at 65 °C for two days, leading to a bright red solution which turned a clear orange upon cooling to room temperature. The solvent, hydrosilane by-product, and excess carbodiimide were then removed *in vacuo*. The resulting orange solid was recrystallized from a concentrated solution of hexanes layered with hexamethyldisiloxane at –30 °C, giving a yield of 55.8 mg (0.095 mmol, 90%). X-ray quality crystals were obtained from a saturated solution of **5$^{\mathbf{Ph,H}}$** in hexanes layered with hexamethyldisiloxane at –30 °C. **Dominant isomer**: **^{1}H NMR (C_6D_6, 600 MHz, 298 K):** δ 8.09 (d, 2H, $^3J_{H,H}$ 6.8 Hz, *o*), 7.67 (s with shoulders, 1H, NC($\underline{H}$)N), 7.34 (t, 2H, $^3J_{H,H}$ 7.6 Hz, *m*), 7.24 (t, 1H, $^3J_{H,H}$ 7.3 Hz, *p*), 6.26 (d of d with ^{29}Si sat., 1H, $^3J_{H,P}$ 17.9 Hz, $^3J_{H,P}$ 8.0 Hz, $^1J_{H,Si}$ 136.5, Si$\underline{H}$), 3.45 (septet, 1H, $^3J_{H,H}$ 6.8 Hz, C$_\gamma\underline{H}$(CH$_3$)$_2$), 2.91 (septet, 1H, $^3J_{H,H}$ 6.6 Hz, C$_\beta\underline{H}$(CH$_3$)$_2$), 1.99, 0.78 (2 × m, 1H, PC$\underline{H}_2$), 1.83–1.37 (m, 6H, PC$\underline{H}_2$), 1.47 (d, 3H, $^3J_{H,P}$ 6.2 Hz, PC$\underline{H}_3$), 1.45 (d, 3H, $^3J_{H,P}$ 5.5 Hz, PC$\underline{H}_3$), 1.39 (d, 3H, $^3J_{H,P}$ 4.3 Hz, PC$\underline{H}_3$), 1.33 (d, 3H, $^3J_{H,P}$ 3.1 Hz, PC$\underline{H}_3$), 1.17 (m, 9H, PC$\underline{H}_3$), 1.06, 0.99 (2 × d, 3H, $^3J_{H,H}$ 6.7 Hz, CH(C$\underline{H}_3$)$_2$), 1.02 (d, 3H, $^3J_{H,H}$ 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 0.94 (d, 3H, $^3J_{H,H}$ 6.5 Hz, CH(C$\underline{H}_3$)$_2$), 0.73 (d, 3H, $^3J_{H,P}$ 4.7 Hz, PC$\underline{H}_3$). **^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K):** δ 159.93 (s, N$\underline{C}$(H)N), 153.11 (s, *ipso*), 137.37 (s, *o*), 127.01 (s, *m*), 126.66 (s, *p*), 59.53 (d, $^4J_{C,P}$ 8.7 Hz, $\underline{C_\beta}$H(CH$_3$)$_2$), 50.08 (s, $\underline{C_\gamma}$(CH$_3$)$_2$), 35.24 (m, P$\underline{C}$H$_2$), 29.90 (d, $^1J_{C,P}$ 16.6 Hz, P$\underline{C}$H$_3$), 29.11 (d of d, $^1J_{C,P}$ 26.5 Hz, $^3J_{C,P}$ 15.7 Hz, P$\underline{C}$H$_2$), 26.96, 20.51 (2 × m, P$\underline{C}$H$_3$), 26.12, 24.46, 24.34, 24.26 (4 × s, CH($\underline{C}$H$_3$)$_2$), 24.37, 23.87 (2 × s, P$\underline{C}$H$_3$), 23.73 (d, $^1J_{C,P}$ 4.8 Hz, P$\underline{C}$H$_3$), 13.40 (d, $^1J_{C,P}$ 11.8 Hz, P$\underline{C}$H$_3$). **^{29}Si{^{1}H} NMR (C_6D_6, 119 MHz, 298 K):** δ 81.11 (m). **^{31}P{^{1}H} NMR (C_6D_6, 243 MHz, 298 K):** δ 74.49, 72.09, 66.19, 55.10 (4 × s, 1P). **Minor isomer**: **^{1}H NMR (C_6D_6, 600 MHz, 298 K):** δ 8.22 (d, 2H, $^3J_{H,H}$ 7.8 Hz, *o*), 7.70 (s, 1H, NC($\underline{H}$)N), 7.37 (t, 2H, $^3J_{H,H}$ 7.4 Hz, *m*), 7.24 (t, 1H, $^3J_{H,H}$ 7.2 Hz, *p*), 6.23 (d of d with ^{29}Si sat., 1H, $^3J_{H,P}$ 27.6 Hz, $^3J_{H,P}$ 9.5 Hz, $^1J_{H,Si}$ 140.1, Si$\underline{H}$), 3.48 (septet, 1H, $^3J_{H,H}$ 6.8 Hz, C$\underline{H}$(CH$_3$)$_2$), 3.07 (septet, 1H, $^3J_{H,H}$ 6.7 Hz, C$\underline{H}$(CH$_3$)$_2$), 1.94–0.72 (many multiplets, 8H, PC$\underline{H}_2$), 1.72 (d, 3H, $^3J_{H,P}$ 6.0 Hz, PC$\underline{H}_3$), 1.53 (d, 3H, $^3J_{H,P}$ 4.9 Hz, PC$\underline{H}_3$), 1.32 (3H, PC$\underline{H}_3$), 1.28, 0.77 (2 × d, 3H, $^3J_{H,P}$ 4.2 Hz, PC$\underline{H}_3$), 1.24 (d, 3H, $^3J_{H,P}$ 2.9 Hz, PC$\underline{H}_3$), 1.24 (d, 3H, $^3J_{H,P}$ 2.8 Hz, PC$\underline{H}_3$), 1.08 (d, 3H, $^3J_{H,P}$ 5.3 Hz, PC$\underline{H}_3$), 1.04, 1.03 (2 × d, 3H, $^3J_{H,H}$ 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 1.01 (d, 3H, $^3J_{H,H}$ 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 0.88 (d, 3H, $^3J_{H,H}$ 6.5 Hz, CH(C$\underline{H}_3$)$_2$). **^{13}C{^{1}H} NMR (C_6D_6, 151 MHz, 298 K):** δ 159.93 (s, N$\underline{C}$(H)N), 153.11 (s, *ipso*), 137.68 (s, *o*), 127.37 (s, *m*), 126.66 (s, *p*), 59.39 (d, $^4J_{C,P}$ 8.3 Hz, $\underline{C}$H(CH$_3$)$_2$), 50.02 (s, $\underline{C}$H(CH$_3$)$_2$), 36.32, 32.40 (2 × m, P$\underline{C}$H$_2$), 34.28 (d of d, $^1J_{C,P}$ 25.0 Hz, $^3J_{C,P}$ 13.4 Hz, P$\underline{C}$H$_2$), 30.45 (d, $^1J_{C,P}$ 10.7 Hz, P$\underline{C}$H$_3$), 26.54, 21.26, 13.62 (3 × m, P$\underline{C}$H$_3$), 26.35, 24.95, 24.12 (3 × s, P$\underline{C}$H$_3$), 26.16 (s, CH($\underline{C}$H$_3$)$_2$), 24.64–24.19 (m, CH($\underline{C}$H$_3$)$_2$), 22.06 (d, $^1J_{C,P}$ 10.0 Hz, P$\underline{C}$H$_3$). **^{29}Si{^{1}H} NMR (C_6D_6, 119 MHz, 298 K):** δ 81.11 (m). **^{31}P{^{1}H} NMR (C_6D_6, 243 MHz, 298 K):** δ 72.09 (s, 2P), 69.03, 56.00 (2 × s, 1P). **Anal.** Found (calcd.): C, 51.09 (51.01); H, 9.28 (9.08); N, 4.74 (4.76).

[(dmpe)$_2$Mn{κ^2-SiH^{n}Bu(N^{i}PrCHN^{i}Pr)}] (5$^{\mathbf{Bu,H}}$). An excess of diisopropylcarbodiimide {C(N^{i}Pr)$_2$} (165 mg, 1.307 mmol) was added to a solution containing 135.5 mg (0.255 mmol) of [(dmpe)$_2$MnH(SiH$_2{}^n$Bu)$_2$] (**1$^{\mathbf{Bu}}$**) in 10 mL of benzene. The reaction mixture was stirred in a sealed flask overnight at room temperature, after which the solvent, hydrosilane by-product, and excess carbodiimide were removed *in vacuo*. The resulting orange solid was recrystallized from a concentrated solution of **5$^{\mathbf{Bu,H}}$** in hexanes giving a yield of 35.3 mg (0.062 mmol, 24%). X-ray quality crystals could not be obtained. **Dominant isomer**: **^{1}H NMR (C_6D_6, 600 MHz, 298 K):** δ 7.58 (s, 1H, NC($\underline{H}$)N), 5.50 (d of d with ^{29}Si sat., 1H, $^3J_{H,P}$ 24.2 Hz, $^3J_{H,P}$ 9.3 Hz, $^1J_{H,Si}$ 136.5 Hz, Si$\underline{H}$), 3.81 (septet, 1H, $^3J_{H,H}$ 6.8 Hz, C$\underline{H}$(CH$_3$)$_2$), 3.09 (septet, 1H, $^3J_{H,H}$ 6.7 Hz, C$\underline{H}$(CH$_3$)$_2$), 0.9-2.1 (various m, 8H, PC$\underline{H}_2$), 1.95 (m, 2H, SiHCH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 1.65 (m, 2H, SiHCH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 1.45 (d, 3H, $^2J_{H,P}$ 5.8 Hz, PC$\underline{H}_3$), 1.44, 1.18 (2 × d, 3H, $^2J_{H,P}$ 5.7 Hz, PC$\underline{H}_3$), 1.38 (d, 3H, $^2J_{H,P}$ 4.9 Hz, PC$\underline{H}_3$), 1.32 (d, 3H, $^2J_{H,P}$ 3.9 Hz, PC$\underline{H}_3$), 1.24 (d, 3H, $^2J_{H,P}$ 2.5 Hz, PC$\underline{H}_3$), 1.21 (d, 3H, $^3J_{H,H}$ 6.8 Hz, CH(C$\underline{H}_3$)$_2$), 1.18, 0.83 (2 × d, 3H, $^3J_{H,H}$ 6.6 Hz, CH(C$\underline{H}_3$)$_2$), 1.13 (m, 5H, SiHC$\underline{H}_2$CH$_2$CH$_2$CH$_3$ and SiHCH$_2$CH$_2$CH$_2$C$\underline{H}_3$), 1.11 (d, 3H, $^2J_{H,P}$ 4.2 Hz, PC$\underline{H}_3$), 0.97 (d, 3H, $^3J_{H,H}$ 6.9 Hz, CH(C$\underline{H}_3$)$_2$), 0.86 (d, 3H, $^2J_{H,P}$ 4.4 Hz, PC$\underline{H}_3$). **^{13}C{^{1}H}**

NMR (C_6D_6, 151 MHz, 298 K): δ 159.10 (s, $N\underline{C}(H)N$), 58.81, 50.28 (2 × s, $\underline{C}H(CH_3)_2$), 36.28 (app. q, $^{1}J_{C,P}$ 20 Hz, $P\underline{C}H_2$), 35.48 (s, $SiHCH_2\underline{C}H_2CH_2CH_3$), 34.17 (d of d, $^{1}J_{C,P}$ 24.5 Hz, $^{2}J_{C,P}$ 13.1 Hz, $P\underline{C}H_2$), 31.87 (d of d, $^{1}J_{C,P}$ 22.7 Hz, $^{2}J_{C,P}$ 17.5 Hz, $P\underline{C}H_2$), 28.21 (m, $P\underline{C}H_3$), 28.13 (s, $SiHCH_2CH_2\underline{C}H_2CH_3$), 26.67 (d, $^{2}J_{C,P}$ 7.8 Hz, $P\underline{C}H_3$), 25.76, 24.68, 24.04 (3 × s, $CH(\underline{C}H_3)_2$), 25.39 (d, $^{2}J_{C,P}$ 4.5 Hz, $P\underline{C}H_3$), 25.19 (s, $SiH\underline{C}H_2CH_2CH_2CH_3$), 24.99 (s, $P\underline{C}H_3$ and $CH(\underline{C}H_3)_2$), 24.42 (br. s, $P\underline{C}H_3$), 21.45 (d, $^{2}J_{C,P}$ 20.8 Hz, $P\underline{C}H_3$), 20.77 (d, $^{2}J_{C,P}$ 12.1 Hz, $P\underline{C}H_3$), 14.46 (s, $SiHCH_2CH_2CH_2\underline{C}H_3$), 13.70 (d, $^{2}J_{C,P}$ 11.5 Hz, $P\underline{C}H_3$). **$^{29}Si\{^{1}H\}$ NMR (C_6D_6, 119 MHz, 298 K):** δ 87.09 (m). **$^{31}P\{^{1}H\}$ NMR (C_6D_6, 243 MHz, 298 K):** δ 76.19, 73.51, 72.21, 53.57 (4 × s, 1P). **Minor isomer**: **^{1}H NMR (C_6D_6, 600 MHz, 298 K):** δ 7.58 (s, 1H, $NC(\underline{H})N$), 5.59 (d of d with ^{29}Si sat., 1H, $^{3}J_{H,P}$ 16.7 Hz, $^{3}J_{H,P}$ 8.4 Hz, $^{1}J_{H,Si}$ 129.3 Hz, $Si\underline{H}$), 3.85 (septet, 1H, $^{3}J_{H,H}$ 6.8 Hz, $C\underline{H}(CH_3)_2$), 3.04 (septet, 1H, $^{3}J_{H,H}$ 6.6 Hz, $C\underline{H}(CH_3)_2$), 0.9-2.1 (various m, 8H, $PC\underline{H}_2$), 2.05 (m, 2H, $SiHCH_2C\underline{H}_2CH_2CH_3$), 1.65 (m, 2H, $SiHCH_2CH_2C\underline{H}_2CH_3$), 1.42 (d, 3H, $^{2}J_{H,P}$ 6.3 Hz, $PC\underline{H}_3$), 1.39 (d, 3H, $^{2}J_{H,P}$ 5.8 Hz, $PC\underline{H}_3$), 1.33 (d, 3H, $^{2}J_{H,P}$ 3.7 Hz, $PC\underline{H}_3$), 1.33 (d, 3H, $^{2}J_{H,P}$ 3.3 Hz, $PC\underline{H}_3$), 1.31 (d, 3H, $^{2}J_{H,P}$ 5.7 Hz, $PC\underline{H}_3$), 1.25 (d, 3H, $^{2}J_{H,P}$ 2.5 Hz, $PC\underline{H}_3$), 1.21, 0.92 (2 × d, 3H, $^{3}J_{H,H}$ 6.8 Hz, $CH(C\underline{H}_3)_2$), 1.20 (d, 3H, $^{3}J_{H,H}$ 4.6 Hz, $CH(C\underline{H}_3)_2$), 1.13 (m, 5H, $SiHC\underline{H}_2CH_2CH_2CH_3$ and $SiHCH_2CH_2CH_2C\underline{H}_3$), 1.10 (d, 3H, $^{2}J_{H,P}$ 3.4 Hz, $PC\underline{H}_3$), 0.88 (d, 3H, $^{2}J_{H,P}$ 4.0 Hz, $PC\underline{H}_3$), 0.87 (d, 3H, $^{3}J_{H,H}$ 6.9 Hz, $CH(C\underline{H}_3)_2$). **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 151 MHz, 298 K):** δ 159.10 (s, $N\underline{C}(H)N$), 58.75, 50.15 (2 × s, $\underline{C}H(CH_3)_2$), 35.48 (s, $SiHCH_2\underline{C}H_2CH_2CH_3$), 28.91 (m, $P\underline{C}H_2$), 28.13 (s, $SiHCH_2CH_2\underline{C}H_2CH_3$), 27.69 (m, $P\underline{C}H_3$), 26.53 (d, $^{2}J_{C,P}$ 8.9 Hz, $P\underline{C}H_3$), 25.50 (d, $^{2}J_{C,P}$ 4.2 Hz, $P\underline{C}H_3$), 25.19 (s, $SiH\underline{C}H_2CH_2CH_2CH_3$), 25.07, 24.68 (2 × s, $CH(\underline{C}H_3)_2$), 24.84 (s, $P\underline{C}H_3$ and $CH(\underline{C}H_3)_2$), 24.42 (br. s, $P\underline{C}H_3$), 24.04 (s, $P\underline{C}H_3$ and $CH(\underline{C}H_3)_2$), 17.65 (d, $^{2}J_{C,P}$ 10.4 Hz, $P\underline{C}H_3$), 14.46 (s, $SiHCH_2CH_2CH_2\underline{C}H_3$), 13.09 (d, $^{2}J_{C,P}$ 11.5 Hz, $P\underline{C}H_3$). **$^{29}Si\{^{1}H\}$ NMR (C_6D_6, 119 MHz, 298 K):** δ 87.09 (m). **$^{31}P\{^{1}H\}$ NMR (C_6D_6, 243 MHz, 298 K):** δ 73.51, 73.02, 69.35, 52.84 (4 × s, 1P). **Anal.** Found (calcd.): C, 48.31 (48.58); H, 9.88 (10.10); N, 5.05 (4.93).

$[(dmpe)_2Mn\{\kappa^2\text{-}SiPh_2(N^iPrCHN^iPr)\}]$ (5^{Ph2}). 14.1 mg of a 0.35:1 mixture of $[(dmpe)_2MnH(=SiPh_2)]$ (2^{Ph2}) and $[(dmpe)_2MnH_2(SiHPh_2)]$ (containing 0.01 mmol of 2^{Ph2}) was dissolved in approx. 0.6 mL of C_6D_6. Upon addition of 15 mg (0.12 mmol) of diisopropylcarbodiimide $\{C(N^iPr)_2\}$, the dark purple solution turned orange. The solvent and excess $C(N^iPr)_2$ were removed *in vacuo*, and the resulting orange oil dissolved in approx. 0.6 mL of C_6D_6 and analysed *in situ* by NMR spectroscopy. 100% conversion of 2^{Ph2} to 5^{Ph2} was observed by NMR spectroscopy within minutes, and $[(dmpe)_2MnH_2(SiHPh_2)]$ present in the starting material remained un-reacted in the product mixture. Attempts to isolate 5^{Ph2} from this mixture were unsuccessful. X-ray quality crystals were obtained by recrystallization of the 5^{Ph2}/$[(dmpe)_2MnH_2(SiHPh_2)]$ mixture from hexanes at –30 °C. **^{1}H NMR (C_6D_6, 500 MHz, 298 K):** δ 7.89, 7.79 (2 × d, 2H, $^{3}J_{H,H}$ 7.7 Hz, *o*), 7.87 (s, 1H, $NC(\underline{H})N$), 7.20-7.33 (m, 6H, *m* and *p*), 3.91 (septet, 1H, $^{3}J_{H,H}$ 6.6 Hz, $C_\gamma\underline{H}(CH_3)_2$), 3.12 (septet, 1H, $^{3}J_{H,H}$ 6.5 Hz, $C_\beta\underline{H}(CH_3)_2$), 2.45, 1.99, 1.83 (3 × m, 1H, $P(C\underline{H}_2)$), 1.53-1.77 (m, 2H, $P(C\underline{H}_2)$), 1.60 (d, 3H, $^{2}J_{H,P}$ 5.4 Hz, $P(C\underline{H}_3)$), 1.43 (d, 3H, $^{2}J_{H,P}$ 3.7 Hz, $P(C\underline{H}_3)$), 1.40 (d, 3H, $^{2}J_{H,P}$ 5.3 Hz, $P(C\underline{H}_3)$), 1.32 (d, 3H, $^{2}J_{H,P}$ 5.8 Hz, $P(C\underline{H}_3)$), 1.24 (m, 6H, $P(C\underline{H}_3)$ and $C_\gamma H(C\underline{H}_3)_2$), 1.16, 0.76 (2 × d, 3H, $^{2}J_{H,P}$ 3.9 Hz, $P(C\underline{H}_3)$), 1.02 (d, 3H, $^{3}J_{H,H}$ 6.3 Hz, $C_\beta H(C\underline{H}_3)_2$), 0.89 (3H, $C_\beta H(C\underline{H}_3)_2$),[56] 0.80 (d, 3H, $^{2}J_{H,P}$ 5.7 Hz, $P(C\underline{H}_3)$), 0.62 (d, 3H, $^{3}J_{H,H}$ 6.5 Hz, $C_\gamma H(C\underline{H}_3)_2$). **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 126 MHz, 298 K):** δ 160.89 (s, $N\underline{C}(H)N$), 154.99, 150.64 (2 × *i*),[56] 139.38, 137.22 (2 × s, *o*), 127.07, 126.59, 126.22, 126.11 (4 × s, *m* or *p*), 59.11 (d, $^{3}J_{C,P}$ 9.1 Hz, $\underline{C}_\beta H(CH_3)_2$), 47.81 (s, $\underline{C}_\gamma H(CH_3)_2$), 36.34 (m, $P(\underline{C}H_2)$), 32.45, 26.24 (2 × $P(\underline{C}H_2)$),[56] 28.10 (t, $J_{C,P}$ 9.8 Hz, $P(\underline{C}H_3)$), 26.40, 24.48 (2 × s, $C_\beta H(\underline{C}H_3)_2$), 25.42, 25.01 (2 × s, $C_\gamma H(\underline{C}H_3)_2$), 25.30, 18.30 (2 × m, $P(\underline{C}H_3)$), 23.05, 22.44 (2 ×, $P(\underline{C}H_3)$).[56] **$^{29}Si\{^{1}H\}$ NMR (C_6D_6, 99 MHz, 298 K):** δ 77.9.[56] **$^{31}P\{^{1}H\}$ NMR (C_6D_6, 202 MHz, 298 K):** δ 80.13, 78.95, 65.28, 56.70 (4 × s, 1P).

$[(dmpe)_2Mn\{\kappa^2\text{-}SiEt_2(N^iPrCHN^iPr)\}]$ (5^{Et2}). Method a) 16.1 mg (0.04 mmol) of $[(dmpe)_2MnH(=SiEt_2)]$ (2^{Et2}) and an excess of diisopropylcarbodiimide $\{C(N^iPr)_2\}$ (22 mg, 0.17 mmol) were dissolved in approx. 0.6 mL of C_6D_6, and complete conversion of 2^{Et2} to 5^{Et2} was observed by NMR spectroscopy within 6 hours of sitting at room temperature. Method b) Excesses of diisopropylcarbodiimide $\{C(N^iPr)_2\}$ (280 mg, 2.22 mmol) and H_2SiEt_2 (400 mg, 4.53 mmol) were added to a solution containing 116.3 mg (0.303 mmol) of $[(dmpe)_2MnH(C_2H_4)]$ in 15 mL of benzene {the latter two species react to form $[(dmpe)_2MnH(=SiEt_2)]$ (2^{Et2}) *in situ*}.[1] After heating this solution at 35 °C for 1 week, followed by 45 °C for one day, the solvent, as well as the excess hydrosilane and carbodiimide, were removed *in vacuo* from the resulting deep orange solution. 2 mL of hexamethyldisiloxane was added to the resulting orange solid, and centrifuged to remove solid impurities. The solid residue was extract with an additional 1 mL of hexamethyldisiloxane (insoluble impurities were also removed by centrifugation). Allowing the clear orange supernatants to stand at –30 °C for a few days yielded a total of 41.6 mg of 5^{Et2} as large orange X-ray quality crystals or orange powder. Storing the mother liquor from the initial recrystallization at –30 °C for two weeks afforded another 29.4 mg of 5^{Et2}, and concentrating the resulting mother liquor before storage at –30 °C for two weeks provided an additional 14.7 mg of 5^{Et2}, for a total combined yield of 85.7 mg (0.151 mmol, 50 %). **^{1}H NMR (C_6D_6, 500 MHz, 298 K):** δ 7.65 (s, 1H, $NC(\underline{H})N$), 3.95 (septet, 1H, $^{3}J_{H,H}$ 6.7 Hz, $C_\gamma\underline{H}(CH_3)_2$), 3.08 (septet, 1H, $^{3}J_{H,H}$ 6.6 Hz, $C_\beta\underline{H}(CH_3)_2$), 1.57-1.98 (m, 5H, $P(C\underline{H}_2)$), 1.50 (t, 3H, $^{3}J_{H,H}$ 7.8 Hz, $SiCH_2C\underline{H}_3$), 1.49 (t, 3H, $^{3}J_{H,H}$ 8.5 Hz, $SiCH_2C\underline{H}_3$), 1.45 (d, 3H, $^{2}J_{H,P}$ 5.8 Hz, $P(C\underline{H}_3)$), 1.42 (2H, $SiC\underline{H}_2CH_3$),[56] 1.40 (d, 3H, $^{2}J_{H,P}$ 5.2 Hz, $P(C\underline{H}_3)$), 1.33 (3H, $P(C\underline{H}_3)$),[56] 1.32 (d, 3H, $^{2}J_{H,P}$ 5.4 Hz, $P(C\underline{H}_3)$), 1.30 (d, 3H, $^{2}J_{H,P}$ 4.0 Hz, $P(C\underline{H}_3)$), 1.15-1.29 (m, 4H, $SiC\underline{H}_2CH_3$ and $P(C\underline{H}_2)$), 1.21 (d, 3H, $^{2}J_{H,P}$ 1.8 Hz, $P(C\underline{H}_3)$), 1.17 (d, 3H, $^{2}J_{H,P}$ 4.3 Hz, $P(C\underline{H}_3)$), 1.16, 1.14 (2 × d, 3H, $^{3}J_{H,H}$ 6.7 Hz, $C_\gamma H(C\underline{H}_3)_2$), 1.00 (m, 1H, $P(C\underline{H}_2)$), 0.94 (d, 3H, $^{3}J_{H,H}$ 6.8 Hz, $C_\beta H(C\underline{H}_3)_2$), 0.87 (d, 3H, $^{2}J_{H,P}$ 4.6 Hz, $P(C\underline{H}_3)$), 0.86 (d, 3H, $^{3}J_{H,H}$ 6.7 Hz, $C_\beta H(C\underline{H}_3)_2$). **$^{13}C\{^{1}H\}$ NMR (C_6D_6, 126 MHz, 298 K):** δ 160.29 (s, $N\underline{C}(H)N$), 58.91 (d, $^{3}J_{C,P}$ 10.1 Hz, $\underline{C}_\beta H(CH_3)_2$), 47.70 (s, $\underline{C}_\gamma H(CH_3)_2$), 36.33, 36.05 (2 × m, $P(\underline{C}H_2)$), 33.13, 27.50, 25.00, 19.22 (4 × m, $P(\underline{C}H_3)$), 32.22 (d of d, $J_{C,P}$ 21.9 Hz, $J_{C,P}$ 16.7 Hz, $P(\underline{C}H_2)$), 26.03 (d of d, $J_{C,P}$ 16.2 Hz, $J_{C,P}$ 4.1 Hz, $P(\underline{C}H_3)$), 25.77, 25.26 (2 × s, $C_\gamma H(\underline{C}H_3)_2$), 25.38 (s, $P(\underline{C}H_3)$), 25.13, 24.36 (2 × s, $C_\beta H(\underline{C}H_3)_2$), 17.11 (d, $^{2}J_{C,P}$ 8.9 Hz, $P(\underline{C}H_3)$), 16.57, 16.16 (2 × m, $Si\underline{C}H_2CH_3$), 11.94, 11.81 (2 × s, $SiCH_2\underline{C}H_3$). **$^{29}Si\{^{1}H\}$ NMR (C_6D_6, 99 MHz, 298 K):** δ 84.6 (s). **$^{31}P\{^{1}H\}$ NMR (C_6D_6, 202 MHz, 298 K):** δ 74.27, 73.11, 69.84, 52.93 (4 × s, 1P). **Anal.** Found (calcd.): C, 48.63 (48.58); H, 9.93 (10.10); N, 5.01 (4.97)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Computational methods and results, visualization of the crystal structure for 5^{Ph2} and calculated structures, tables of crystal data/crystal structure refinement, and selected NMR spectra for prepared complexes, solutions generated by exposure of 1^{R} or 2^{R2} to CO_2, and commercially obtained polysiloxanes (PDF).

Cartesian coordinates for the calculated structures (XYZ).

Accession Codes

CCDC 2034691-2034693 contain the supplementary crystallographic data for complexes **3**, $5^{Ph,H}$, and 5^{Ph2}. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

D. J. H. E. thanks NSERC of Canada for a Discovery Grant, and Compute Canada for an RAC (Resource Allocation Competition). We are also grateful to Dr. Jim Britten for assistance with the analysis of X-ray crystal structure data.

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20. For reactions of $\mathbf{2^{Ph2}}$ with CO$_2$, **3** was only observed as a minor component of the resulting reaction mixture due to competing reactions of CO$_2$ with [(dmpe)$_2$MnH$_2$(SiHPh$_2$)] present in the starting material.

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22. For each reaction with CO$_2$, either one or three ^{29}Si NMR environments were located, and each environment was attributed to a different polysiloxane oligomer (from $\mathbf{1^{Ph}}$: –27.0 ppm; from $\mathbf{1^{Bu}}$: –21.1, –33.6, and –35.7 ppm; from $\mathbf{2^{Ph2}}$: –33.3, –42.5, and –45.2 ppm; from $\mathbf{2^{Et2}}$: –22.7 ppm).

23. For R = ^{n}Bu and R' = H, the Si$\underline{H}$ polysiloxane ^{1}H NMR environments cumulatively integrated to a single SiH residue per equivalent of **3**. However, for R = Ph and R’ = H, further reactivity between the byproducts ensued and accurate integration of the Si$\underline{H}$ polysiloxane environments relative to the environments arising from **3** could not be done.

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29. No EXSY NMR cross-peaks were observed to show chemical inter-change between the two diastereomers of $\mathbf{5}^{\mathbf{R,H}}$ (up to 60 °C). However, such an equilibrium was inferred by heating solutions starting with different ratios of the two isomers (obtained from preferential recrystallization), yielding solutions with consistent (i.e. thermodynamic) ratios.

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