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Carbon Dioxide Reduction to Methanol Catalyzed by Mn(I) PNP Pincer Complexes under Mild Reaction Conditions

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ABSTRACT: Well-defined Mn(I) hydrido carbonyl PNP pincer-type complexes were tested as efficient and selective non-precious transition metal catalysts for the reduction of CO_2 to MeOH in the presence of hydrosilanes. The choice of reaction temperature and type of silanes proved to be pivotal to achieve fast reactions and high selectivity to the methoxysilyl- *vs*. silylformate derivatives in DMSO. The catalytic data are complemented by DFT calculations, highlighting a stepwise CO_2 reduction mechanism centred on the Mn catalyst without metal-to-ligand cooperation (MLC).

KEYWORDS. CO_2 hydrosilylation • manganese pincer complexes • homogeneous catalysis • mechanistic studies • DFT calculations.

INTRODUCTION

Carbon dioxide is a known greenhouse gas, and its increasing amount in the atmosphere is causing concern. On the other hand, for small scale applications, it can be an attractive C1 carbon source for chemical synthesis as it is renewable, abundant, non-flammable and inexpensive. The combination of these two aspects has brought about a renewed interest of chemists and significant efforts have been devoted towards the development of new strategies for CO2 activation and transformation into fuels and value-added chemicals.¹ To date, a number of transition metal-based and organocatalysts have been developed, which allow the chemical reduction of carbon dioxide to formic acid, methanol or methane. In particular, the homogeneous hydrogenation of carbon dioxide to formic acid has been extensively studied due to its importance as chemical hydrogen storage method.² However, CO₂ hydrogenation to methanol, a desired bulk chemical with many different uses in industry and academia, proved to be more challenging and has so far been achieved only with a handful of homogeneous systems.³ Another important issue is process economic sustainability, suggesting the use of non-noble metals in catalysis. The first homogeneous non-noble metal catalyst for the hydrogenation of CO₂ to MeOH was described by Beller and coworkers using a catalyst formed in situ from [Co(acac)₃], triphos (triphos = 1, 1, 1-tris(diphenylphosphinomethyl)ethane) and HNTf₂.^{4a} The catalytic system works at 100 °C under a total pressure of 90 bar ($p_{H2} = 70$ bar, $p_{CO2} = 20$ bar), with a maximum TON = 50 after 24 h (TON = turnover number). A more recent study by Martins and coworkers showed that MeOH

could be obtained in up to 44% yield by reduction of CO₂ with H₂ (75 bar total pressure) in the presence of the iron scorpionate catalyst [FeCl₂{ κ^3 -HC(pz)₃}] (pz = pyrazol-1-yl) with a solvent- and amine-free mild reaction protocol.4b Another protocol, involving at first N-formylation of an amine with CO₂ and H₂ and subsequent formamide reduction to MeOH, was described by Surva Prakash and coworkers.^{5a} By use of a welldefined Mn(I) PNP pincer complex as catalyst, yields of 84% under 60 bar total pressure were obtained at 110-120 °C. Naturally, catalysts based on noble metals for CO₂ hydrogenation to MeOH are also known.^{2,3} A recent addition to the literature was made by Everett and Wass using homogeneous ruthenium catalysts in the presence of amine auxiliaries.^{5b} A TON (turnover number) of 8900 and TOF (turnover frequency) of 4500 h⁻¹ were achieved using [RuCl₂(Ph₂PCH₂CH₂NHMe)₂] as catalyst with a diisopropylamine auxiliary.

Apart from H₂ gas, that has the drawbacks of poor solubility in most solvents, the need of pressure and related safety concerns, other reagents were used to reduce CO₂, and silanes have found a renewed attention for this reaction. CO₂ hydrosilylation is a thermodynamically favored process due to the formation of strong Si-O bonds, acting as driving force for the reaction. As reported in the literature, this reaction is generally used to obtain silyl formates,⁶ versatile building blocks for organic syntheses and polymers. For silyl formate synthesis, one of the most efficient catalysts to date is the Cu complex [CuH(L)] [L = 1,2-bis(diisopropylphosphino)benzene] reported by Baba and coworkers. The catalyst, formed *in situ* by addition of the ligand to Cu salts under reducing conditions, promoted the formation of silylformates with TON of ca.

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70000 after only 24 h under 1 atm CO₂ in the presence of PMHS (PMHS = polymethylhydrosiloxane).⁷ CO₂ was also reduced, albeit under harsh conditions, using (EtO)₃SiH in the presence of the Zn catalyst [(IMes)₃Zn₃H₄(THF)](BPh₄)₂, giving silylformate as the main product.8 Room temperature, Zncatalysed CO₂ reduction to silvlformate was reported in 2018, using terminal the zinc hydride complex [Tntm]ZnH (Tntm = tris(6-tert-butyl-3-thiopyridazinyl)methanide).⁹ CO₂ reduction to CH₄ with silanes has also been achieved, in most cases in the presence of a strong Lewis acid such as $B(C_6F_5)_3$ as cocatalyst.¹⁰ Complexes { $[Tism^{PriBenz}]M$ }[HB(C₆F₅)₃] (M = Zn, Tism^{PriBenz} Mg: = tris[(1-isopropylbenzimidazol-2yl)dimethylsilyl] methyl ligand) gave efficient catalytic CO₂ hydrosilvlation in combination with B(C₆F₅)₃ and R₃SiH to afford sequentially the bis(silyl)acetal H₂C(OSiR₃)₂ and CH₄ $(R_3SiH = PhSiH_3, Et_3SiH, and Ph_3SiH)$. The selectivity to the different possible products could be switched by the choice of silane, with PhSiH₃ favoring CH₄, and Ph₃SiH favoring the bis(silyl)acetal H2C(OSiPh3)2.11 ZrIV/HfIV alkyl/amido complexes containing a tridentate N-ligand based on benzoimidazole were also used as catalysts precursors for the tandem CO2 hydrosilylation to CH4 in combination with B(C₆F₅)₃ as cocatalyst/activator and various hydrosilanes.12 Iwasawa and coworkers reported that Pd complexes bearing a Group 13 metalloligand catalyze CO₂ hydrosilylation to formates with a turnover frequency (TOF) of 19300 h⁻¹, the highest reported to date for this reaction.13

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25 The selective reduction of CO₂ to methoxysilyl derivatives, giving MeOH by simple hydrolysis, appeared to be more chal-26 lenging and, to date, few catalytic systems are capable of pro-27 moting such a reaction. The first example was reported by Ei-28 senberg et al., using [Ir(CN)(CO)(dppe)] at 40 °C, albeit with 29 sluggish reactions and low TONs [dppe = 1,2-30 bis(diphenylphosphino)ethane].¹⁴ Ying and coworkers used a 31 stable NHC organocatalyst at room temperature, reaching 32 TOFs as high as 25.5 h⁻¹ (based on Si-H), even by using air as 33 CO₂-containing feedstock.¹⁵ More recently, pyridine-decorated 34 MWCNTs (MWCNT = multi-walled carbon nanotubes) were 35 efficiently used as heterogeneous organocatalysts for this reaction, with hydroboranes as reducing agents.¹⁶ Guan reported 36 the use of a PCP pincer-type NiH(L) complex [L = 2,6-37 $(tBuPO)_2C_6H_3$] as efficient catalyst for this reaction, using an 38 organoborane as a reducing agent, obtaining a TOF = 495 h^{-1} 39 based on B-H units, and studying the reaction mechanism by 40 DFT methods.¹⁷ In 2018, Huang and coworkers showed very 41 high activity of a dearomatized (pyridyldiamino)diphosphine 42 PN³P-nickel hydride complex for the reduction of CO₂ to 43 MeOH (TON_{max} = 4900) and selective methylation and 44 formylation of amines using Ph₂SiH₂.¹⁸ Among other pincer-45 type complexes, Chirik and coworkers showed that 46 [CoH(^{tBu}PNP)] [^{tBu}PNP = 2.6-bis(di-tertbutylphosphinomethyl)pyridine] promoted the catalytic hy-47 drosilylation of CO2 with PhSiH3 to a mixture of silyl for-48 mates, bis(silyl)acetals, and methoxysilyl derivatives.¹⁹ Oes-49 treich reported that tethered Ru-S complexes of general for-50 mula [Ru(PR₃)L] (Chart 1) are able to catalyze CO₂ hydrosi-51 lylation in the presence of monohydrosilanes, with high selec-52 tivity either to bis(silyl)acetals or methoxysilyl products, re-53 spectively. It was demonstrated that the chemoselectivity of 54 the reaction depends mainly on the reaction temperature. 55 However, temperatures as high as 150 °C, long reaction times 56 (days) and high catalyst loadings (1% mol) were required.²⁰ 57 Abu-Omar and coworkers reported that the oxorhenium PNN

pincer complex [Re(PNN)(O)₂][OTf] was capable of CO₂ reduction to methoxysilyl products using a combination of PhMe₂SiH and PhSiH₃.²¹ The perruthenate salt [N(*n*-hexyl)₄][ReO₄] was also shown to be an effective catalyst for this reaction.²²



Chart 1. Selected examples of transition metal catalysts used for CO_2 hydrosilylation to MeOH.

We have recently reported that homogeneous CO_2 hydrogenation to formate could be achieved with high TONs under relatively mild reaction conditions (H₂/CO₂ = 1:1, 80 bar, 80 °C) in the presence of Mn(I) hydrido carbonyl complexes bearing PNP pincer ligands based on the 2,6-diaminopyridine scaffold (complexes 1 and 2 in Chart 1).²³ These complexes were also used as efficient catalysts for other reactions, including catalytic coupling of alcohols and amines to imines, and for the synthesis of substituted quinolines and pirimidines.²⁴ We were interested in expanding the scope of these catalysts to more challenging reactions involving the use of CO₂ as C1 building block, thus we thought of interest to test them in CO₂ hydrosilylation to MeOH. The results of the catalytic tests, together with mechanistic studies by DFT calculations, are hereby presented.

RESULTS AND DISCUSSION

Catalytic Studies.

Catalytic CO₂ hydrosilylation was at first tested at room temperature and atmospheric pressure (1 bar) in the presence of $[Mn(PNP^{NH}-iPr)(CO)_2H]$ (1) and $[Mn(PNP^{NMe}-iPr)(CO)_2H]$ (2) with PhSiH₃, using a known excess of silane respect to CO₂ (5 equiv. of Si-H bonds). It was previously demonstrated that the choice of solvent can be crucial for this kind of reactions. Li and coworkers recently reported that catalyst-free Nformylation of amines using CO₂ and silanes may be achieved under ambient conditions using polar solvents such as DMSO. It was postulated that the high polarity of this solvent was sufficient to allow the activation of chemical bonds in CO₂ and silanes.²⁵ In our previous work,²³ we demonstrated that the first step of CO₂ activation in the presence of 1 consisted in its insertion in the Mn-H bond to give the formate complex cis- $[Mn(PNP^{NH}-iPr)(CO)_2\{OC(O)H\}]$ (3). Complex 3 was found to be poorly soluble in THF, but significantly more soluble in DMSO. Accordingly, we chose DMSO as solvent for our experiments. The tests were carried out on NMR tube scale, monitoring the vatiation of products distribution in time by ¹³C{¹H} and ¹H NMR spectroscopy. ¹³CO₂ was used instead of ¹²CO₂, in line with other related studies described in the litera-

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ture. The expected product distribution is shown in Scheme 1, however formation of CH₄ was never observed in our tests.



Scheme 1. Product distribution expected for CO₂ hydrosilylation.

Initially, the catalytic tests were carried out at room temperature. The main results are summarized in Table 1. In the presence of **1** and PhSiH₃, ¹³CO₂ was rapidly converted essentially into silvlformates (95% based on ${}^{13}C{}^{1}H{}$ NMR) within the first 5 min after the addition of ${}^{13}CO_2$ to the tube containing the catalytic mixture (entry 1). The formyl units appear as a broad signal in the ¹³C NMR spectrum in the range 159-165 ppm, with the corresponding protons showing as a doublet centered at $\delta_H = 8.28$ ppm in the ¹H NMR spectrum, with a large coupling constant due to ${}^{1}\text{H}{}^{-13}\text{C}$ coupling (${}^{1}J_{\text{HC}} = 224.38$ Hz). A new ¹H NMR resonance observed at 5.0 ppm was assigned to the silvlformate PhSiH₂(O₂CH).²⁶ and it gradually decreased in intensity as the reaction proceeded. Prolonged reaction times resulted in the formation of methoxysilyl species ($\delta_{\rm H}$ = 3.0-3.5 ppm; $\delta_{\rm C}$ = ca. 50 ppm) at the expenses of silvlformates via bis(silvlacetal) intermediates ($\delta_{\rm C}$ = ca. 84 ppm), reaching 84% yield (based on ${}^{13}C{}^{1}H$ NMR) after 24 h and 93% yield after 46 h. A comparable reactivity was observed with complex 2 (entry 2). In a control experiment in the absence of catalyst (entry 3), CO₂ hydrosilylation proceeded selectively to silvlformates, but longer reaction times were needed to reach nearly quantitative CO₂ conversion. After 24 h, only minor amounts of bis(silylacetal) units (2%) and methoxysilyl species (<1%) were detected.

Table 1. Selected results for catalyst screening in CO₂ hydrosilylation with PhSiH₃ at 25 $^{\circ}$ C.^{*a*}

En-	Cata-	t [h]	%	%	%	%
try	lyst		CO_2	Si(O ₂ CH)	Si(OCH ₂ O)Si	Si(OMe)
1	1	<0.1	3	95	0	2
		1	1	79	6	14
		3	0	55	12	33
		24	0	6	10	84
		46	0	3	4	93
2	2	< 0.1	0	78	8	14
		1	0	76	14	10
		3	0	52	24	24
		24	0	7	12	81
		28	0	1	6	93
3	none	1	30	70	0	0
		3	9	91	0	0
		24	1	97	2	<1

^{*a*} Reaction conditions: ¹³CO₂ (1 bar, 0.14 mmol); catalyst, if any (0.014 mmol, catalyst:CO₂ = 1:10); PhSiH₃ (0.70 mmol, 5.0 equiv. Si-H bonds respect to CO₂, 2.0 mol% catalyst to Si-H bonds); d₆-DMSO (400 μ l); mesitylene (10 μ l) as internal standard; 25 °C. Product distribution calculated from ¹³C{¹H} NMR values (error ± 5%).

In the latter experiment, i.e. in the absence of a catalyst, soon after the addition of CO₂ to the tube, the ¹H NMR spectrum

showed two additional signals at 12.74 (s) and 8.43 ppm (brd, $J_{\rm HC} = 217.72$ Hz) which were assigned to free formic acid. The corresponding ¹³C{¹H} NMR signal appeared as a sharp singlet at 162 ppm. The origin of the proton source needed to release HCOOH from silvl formate is unclear. A plausible hypothesis could be that, under these reaction conditions, partial silvlformate decomposition by dehydration may occur, giving H₂O and CO, as observed by other authors.¹⁹ Indeed, the presence of traces of ¹³CO in solution was detected in some ¹³C{¹H} NMR spectra at 184.6 ppm (see Supporting Information). An additional doublet of low intensity centered at ca. 9.5 ppm (${}^{1}J_{\text{HC}}$ = 178.61 Hz) was also observed in the ${}^{1}\text{H}$ NMR spectrum, together with a ¹³C{¹H} NMR singlet at 197 ppm. We attribute these signals to traces of formaldehyde, by comparison with literature data. MnBr2 and Mn(CO)5Br were also used as catalysts for room temperature tests under the conditions described in Table 1, to verify the effect of the PNP ligand. They both proved to be less efficient than 1 and 2, with 43% CO₂ conversion to silvlformate only and 74% CO₂ conversion to silvlformate (64%) and silvlacetals (10%) after 3 h, respectively (see Supporting Information).

Next, the effect of temperature and type of silane were tested. A small library of silanes was screened for the hydrosilylation of ${}^{13}CO_2$ (1 bar) in d₆-DMSO at 80 °C in the presence of **1**, monitoring the reactions by NMR spectroscopy. Selected data are summarized in Table 2.

Table 2. Selected results for silane screening in CO_2 hydrosilylation with **1** at 80 °C.^{*a*}

En	Silane	t	%	%	%	%	
try		[h]	CO_2	Si(O ₂ CH)	Si(OCH ₂ O)Si	Si(OMe)	
1	PhSiH₃	1	0	4	7	89	
		3	0	2	5	93	
		6	0	0	1	99	
2	Ph_2SiH_2	1	6	8	7	79	
		3	3	6	5	84	
		24	3	3	4	88	
3 ^b	Ph₃SiH	1	55	44	0	0	
		24	8	90	0	0	
4 ^c	Et₃SiH	1	-	-	0	0	
		24	-	-	0	0	
5	PhMe₂SiH	1	69	31	0	0	
		24	28	72	0	0	

^{*a*} Reaction conditions: ¹³CO₂ (1 bar, 0.14 mmol); catalyst **1** (0.014 mmol, catalyst:CO₂ = 1:10); silane (0.70 mmol, 5.0 equiv. Si-H bonds to CO₂, 2.0 mol% catalyst to Si-H bonds); d₆-DMSO (400 µl); mesitylene (10 µl) as internal standard; 80 °C. Product distribution calculated from ¹³C{¹H} NMR values (error \pm 5%). ^{*b*} An insoluble precipitate formed during the reaction, as previously reported (ref. 10c). ^{*c*} Only traces of silylformate.

Monohydrosilanes such as Ph₃SiH and PhMe₂SiH were less active under the reaction conditions described above, giving only the silylformate product after 24 h. With Et₃SiH, a biphasic solution formed in the NMR tube, hampering monitoring of the reaction. NMR analysis of the crude mixture after 24 h and workup showed only silylformate as product in trace quantities. On the other hand, PhSiH₃ and Ph₂SiH₂ successfully afforded the desired methoxysilyl product in high yields (80-89%) after only 1 h at 80 °C. With PhSiH₃ as reducing agent, full CO₂ reduction to methoxysilyl derivatives (>99%) was achieved after 6 h at 80 °C (Table 2, entry 1). At the end of the reaction, unreacted silane was still clearly visible in the

¹H NMR spectrum (Si-H signal at 4.11 ppm), whereas all 13 CO₂ was consumed. The final silane conversion was 62%, corresponding to 0.14 mmol PhSiH₃. Considering that essentially all the CO₂ originally placed in the NMR tube (ca. 0.14 mmol) was reduced to the desired product, the experimentally observed conversion of the silane matches perfectly the expected value. In contrast, using Ph₂SiH₂, complete disappearance of the Si-H signals was observed in the ¹H NMR spectrum after 3h, although not all CO₂ was consumed judging from the corresponding ${}^{13}C{}^{1}H$ NMR data (Table 2, entry 2). This result suggests that unproductive side reactions involving Ph₂SiH₂ may take place, decreasing the overall process efficiency. Thus, we concluded that the stronger PhSiH₃ had to be preferred, and it was chosen as reducing agent in the following experiments, in agreement with Garcia and coworkers for the Ru-catalyzed CO₂ hydrosilylation to CH₄,.^{10b} and with Cantat and coworkers for the Fe-catalyzed CO₂ utilization as C1 building block to synthesize formamides and methylamines from amines.27

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Encouraged by these results, we then tested the reduction of 18 CO₂ with 1 using an excess of CO₂ respect to silane. As 19 silanes are more expensive reagents than CO₂, and excess 20 silane or silicon waste by-products are often difficult to remove by workup (whereas CO₂ can be simply vented), a pro-22 cess with total and selective conversion of silanes could be of 23 interest for practical applications. The tests were run in 24 Schlenk tubes using ¹²CO₂ and PhSiH₃ at room temperature 25 and 80 °C, to check the effect of temperature on the reaction selectivity and product distribution. For the tests at 25 °C, ¹H 26 NMR analysis of the reaction mixture after 24 h revealed full 27 consumption of PhSiH₃ and formation of formic acid (δ : 8.17, 28 s, HCOOH; 12.76, s, HCOOH) as the sole CO₂-reduction 29 product. ¹³C{¹H} NMR showed, accordingly, a broad signal 30 centered at 161.23 ppm. The signal broadness may suggest that the mixture contained both silvlformates and free 32 HCOOH. Interestingly, the ${}^{13}C{}^{1}H$ NMR spectrum showed 33 also a well-defined heptet at $\delta_{\rm C} = 16.75$ ppm and a broad dou-34 blet at $\delta_{\rm C} = 18.2$ ppm. The multiciplity of these signals is at-35 tributed to C-D coupling. The ¹³C{¹H} NMR heptet was attributed to the formation of (CD₃)₂S by comparison with litera-36 ture values (18-25 ppm depending on solvent).²⁸ (CD₃)₂S may 37 indeed form by reduction of d₆-DMSO as unproductive side 38 reaction of silanes under these experimental conditions. 39

The test was then repeated at 80 °C under otherwise identical 40 conditions. After 24 h, NMR analysis revealed the complete 41 consumption of PhSiH3 and 100% selective formation of 42 methoxysilyl species (δ_H = 3.36, br.s; δ_C = 49.81, s), without 43 any signs of undesired DMSO reduction, with TON = 50 44 based on Si-H consumption, as calculated from ¹H NMR sig-45 nal integration. Further optimization was obtained by halving 46 the catalyst content (0.007 mmol; 1 mol% respect to "Si-H") 47 and repeating the Schlenk tube test at 80 °C for 24 h. Also in 48 this case, the reaction gave the methoxysilyl product with complete selectivity, reaching TON = 100. 49

50 We also checked for the fate of the Mn complex after the reac-51 tion under excess of CO₂ in the presence of PhSiH₃ and 1 at 25 52 °C, to get information about catalyst deactivation. In the ¹H NMR spectrum, recorded at the end of the catalytic test, the 53 resonance due to Mn-H hydride had disappeared. The corre-54 sponding ³¹P{¹H} NMR spectrum showed a single P-55 containing species with a singlet at 133.7 ppm, that we assign 56 to the cationic tricarbonyl complex $[Mn(PNP^{NH}-iPr)(CO)_3]^+$ in 57

agreement with data recently reported by Sortais and coworkers.29

Mechanistic Studies.

In order to get an insight in the mechanism of CO₂ hydrosilylation catalyzed by 1, NMR experiments and DFT calculations were carried out. Insertion of CO2 into a metal-hydrogen bond constitutes the initial step in many inner-sphere reaction of CO₂ using transition metal hydrido complexes. Indeed, in our previous work on CO₂ hydrogenation to formate,²³ we demonstrated that the reaction of 1 with CO₂ proceeds rapidly at room temperature to give complex cis-[Mn(PNP^{NH}iPr)(CO)₂{OC(O)H}] (**3**) (Scheme 2a). Crystals of **3** suitable for X-ray diffraction analysis were now grown by diffusion of Et₂O into a THF/dmso (9/1) solution of **3**. A structural view of 3 is shown in Figure 1, with selected bond distances and angles given in the caption.



Figure 1. Structural view of 3 showing 50% thermal ellipsoids (most H atoms omitted for clarity). Selected bond lengths (Å) and bond angles (°): Mn1-C18 1.779(3), Mn1-C19 1.799(3), Mn1-O3 2.062(2), Mn1-N1 2.082(3), Mn1-P1 2.294(1), Mn1-P2 2.292(1), P2-Mn1-P1 164.06(4).

To establish whether 3 was involved as intermediate in the Mn-catalyzed CO₂ hydrosilylation mechanism, a Wilmad quick pressure valve NMR tube was charged with 1 (5.0 mg, 0.01 mmol) and d₆-DMSO (400 μ L). The ³¹P{¹H} NMR spectrum showed, as expected, a sharp singlet at 160.8 ppm due to 1. The tube was then charged with ${}^{13}CO_2$ (1 bar) at room temperature and transferred to the NMR probe for analysis. Quantitative formation of 3 was confirmed by the appearance of the expected singlet at 136.7 ppm in the ${}^{31}P{}^{1}H$ NMR spectrum. The tube was then evacuated and the CO₂ atmosphere replaced with N₂. PhSiH₃ (10 equiv. to Mn) was then added to the NMR tube, resulting in partial conversion (ca. 16%) of 3 into 1 after 2 h. After 24 h, the ³¹P{¹H} NMR spectrum showed only the singlet at 160.8 ppm due to the formation of 1 (Scheme 2b).



Scheme 2. Synthesis of 3 by CO₂ insertion into the M-H bond in $\mathbf{1}$ (a) and reverse reaction in the presence of PhSiH₃ (b).

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The full mechanism was then studied by DFT calculations,³⁰ leading to the proposed catalytic cycle shown in Scheme 3. 2 The complete free energy profile of the stepwise reduction of CO₂ to the methoxysilyl level is presented in the Supporting 3 Information (Figures S1-S3). The reactions composing the 4 catalytic cycle, shown in Scheme 3, correspond to the four ma-5 jor steps of the mechanism. First, hydride attack to the C-atom 6 of CO₂ occurs, resulting in a metal-coordinated formate ligand 7 in intermediate C. This part of the mechanism is common to 8 the CO₂ hydrogenation pathway previously addressed.²³ For-9 mation of **C** is an easy process with a maximum barrier of 8 10 kcal mol⁻¹ and represents an exergonic reaction, as the formate 11 complex C is 9 kcal mol⁻¹ more stable than the initial reactants. From C, the mechanism proceeds first with attack of a 12 silane molecule on the coordinated O-atom of formate, fol-13 lowed by hydride transfer from Si to Mn. The result is the silyl 14 formate (HCOO)SiH₂Ph with regeneration of the initial Mn 15 hydride complex, in intermediate H. This part of the mecha-16 nism has the highest barrier of the entire path (29 kcal mol⁻¹) 17 corresponding to the step of silane attack, but overall it is al-18 most thermoneutral with $\Delta G = 2$ kcal mol⁻¹. In the next part of 19 the mechanism, the hydride in the metallic fragment attacks 20 the carbonyl C-atom of the formate, yielding a metal-21 coordinated silvl hemiacetal, [(OCH₂O)SiH₂Ph]⁻, in interme-22 diate M. The process is comparatively more facile with a barrier of 20 kcal mol⁻¹ and a free energy balance of 3 kcal mol⁻¹. 23 The attack of a second silane molecule to the non-coordinated 24 O-atom of the hemiacetal in M, followed by hydride transfer 25 from the Si-atom to the carbonyl C-atom, results in the libera-26 tion of silyl ether (PhSiH₂)₂O, and in the formation of a meth-27 oxide Mn complex (Q). The barrier associated with this part of 28 the mechanism is significant (24 kcal mol⁻¹) but the process is 29 clearly favored from the thermodynamic point of view as indi-30 cated by a free energy balance of $\Delta G = -18$ kcal mol⁻¹. In the 31 final stage of the catalytic cycle, a third silane molecule at-32 tacks the coordinated methoxide in Q and, with a subsequent 33 hydride transfer from Si to Mn, yields the final product methoxyphenylsilane (CH₃O)SiH₂Ph giving back the initial Mn hy-34 dride A. This a fairly easy stage of the mechanism with a bar-35 rier of only 8 kcal mol⁻¹, and the closing of the cycle, from \mathbf{Q} 36 back to **A**, is clearly exergonic with $\Delta G = -28$ kcal mol⁻¹. 37



Scheme 3. Proposed (simplified) catalytic cycle. The free energy values (kcal mol⁻¹) refer to the initial reactant (A) and the values in italics represent barriers. Full details in Supporting Information.

The mechanism for the formation of the silylformate (HCOO)SiH₂Ph from CO₂ and PhSiH₃ in the absence of catalyst (in DMSO) was also studied for comparison. The reaction proceeds in a single step with concerted formation of the Si-C(CO₂) bond and H-transfer from Si to the O-atom. The corresponding profile is presented in the Supporting Information (Figure S4). The process is favored from a thermodynamic point of view ($\Delta G = -11$ kcal mol⁻¹) but the barrier involved (37 kcal mol⁻¹) is 9 kcal mol⁻¹ higher than the one obtained for the Mn-catalyxed reaction, clearly showing the role of the Mn catalyst in the process.

CONCLUSIONS

In summary, we have hereby reported the first example of efficient direct Mn(I)-catalyzed CO2 hydrosilylation to silylprotected MeOH under mild reaction conditions (80 °C, 1 bar CO₂). Catalytic tests showed that the desired product could be obtained working both in excess of silane and in excess of CO₂, respectively. It was also demonstrated that, at room temperature, the reaction gave quickly silvlformates, reaching the methoxysilyl level only after long reaction times. Alternatively, the selectivity of the process can be switched completely to the methoxysilyl products by running the reactions at 80 °C. DFT calculations showed that the catalytic cycle proceeds via stepwise reduction of CO2 to formate, acetal and methoxy species. The catalyst works in the first step as hydride transfer agent to CO₂ to afford a formato complex, and in the second step to transfer a hydride to the silvlformate to give the silvlacetal species. The first reduction step has the highest barrier of 29 kcal mol⁻¹, but the exoergonic thermodynamic balance helps to carry the reaction further to the methoxysilyl product. The latter, upon release from the metal center, regenerates the initial Mn-H complex that is thus able to start the next turnover of the catalytic cycle.

EXPERIMENTAL SECTION

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CO₂ catalytic reduction under excess silane. In a typical catalytic run, a WilmadTM quick pressure valve NMR tube fitted with a Teflon valve (total volume ca. 3.5 mL) was charged with d₆-DMSO (400 µL), silane (0.7 mmol "Si-H", ca. 5 eq "Si-H" respect to ¹³CO₂), the catalyst, if any (0.014 mmol, 2 mol% respect to "Si-H"; catalyst:CO₂ ratio = 1:10) and mesitylene (10 μ L) as internal standard. The NMR tube was then attached to a high vacuum line, frozen in ice/water, and the headspace evacuated. The tube was then charged with ${}^{13}CO_2$ (1 bar; ca. 0.14 mmol considering the headspace), thawed and quickly transferred to the NMR probe kept at 25 °C. For tests run at 80 °C, the NMR tube was kept in an oil bath set at the desired temperature, and quickly transferred to the NMR probe for analysis at the chosen time. The products distribution and silane conversion were determined by ${}^{13}C{}^{1}H$ NMR and ¹H NMR spectroscopy, respectively. All experiments were repeated at least twice to check for reproducibility (average error ca. 5%).

CO2 catalytic reduction under excess CO2. In a typical experiment, a Schlenk tube equipped with a Teflon Young valve (total volume = 15 mL) was charged with d_6 -DMSO (400 μ L), PhSiH₃ (29 µL, 0.23 mmol; 0.7 mmol "Si-H", ca. 1 equiv. "Si-H" respect to CO₂), catalyst 1 (3.0 or 6.0 mg, 0.007 or 0.014 mmol; 1 or 2 mol% respect to "Si-H"), mesitylene (10 µL) as internal standard. The resulting solution was frozen in ice/H2O, the tube evacuated and refilled with 1 bar CO2 (3 times). The tube containing the reaction mixture was then placed in an oil bath set at the desired temperature and the reaction mixture was allowed to stir for 24 h. Then, an aliquot of the reaction mixture was transferred into an NMR tube. The products distribution and silane conversion were determined by ¹³C{¹H} NMR and ¹H NMR spectroscopy, respectively. All experiments were repeated at least twice to check for reproducibility (average error ca. 5%).

ASSOCIATED CONTENT

Supporting Information. General methods and materials; selected NMR spectra; additional tables for catalytic tests; computational details and full reaction pathways; atomic coordinates for DFT optimized structures (xyz file); crystallographic data for **3** (CCDC entry 1827141). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

1. (a) Li, Y.; Cui, X.; Dong, K.; Junge, K.; Beller, M. Utilization of CO₂ as a C1 Building Block for Catalytic Methylation Reactions. ACS Catal. 2017, 7, 1077-1086; (b) Klankermayer, J.; Wesselbaum, S.; Beydoun, K.; Leitner, W. Selective Catalytic Synthesis Using the Combination of Carbon Dioxide and Hydrogen: Catalytic Chess at the Interface of Energy and Chemistry. Angew. Chem. Int. Ed. 2016, 55, 7296-7343; (c) Zhang, Z.; Sun, Q.; Xia, C.; Sun, W. CO2 as a C1 Source: B(C₆F₅)₃-Catalyzed Cyclization of *o*-Phenylene-diamines to Construct Benzimidazoles in the Presence of Hydrosilane. Org. Lett. 2016, 18, 6316-6319; (d) Aresta, M.; Dibenedetto, A.; Quaranta, E. State of the Art and Perspectives in Catalytic Processes for CO2 Conversion into Chemicals and Fuels: the Distinctive Contribution of Chemical Catalysis and Biotechnology. J. Catal. 2016, 343, 2-45; (e) Ren, D.; Song, Z.; Fu, J.; Huo, Z. in Advances in CO2 Capture, Sequestration, and Conversion, ACS Symposium Series, 2015, Vol. 1194, Chapter 4, pp 109–122; (f) Gao, X.; Yu, B.; Yang, Z.; Zhao, Y.; Zhang, H.; Hao, L.; Han, B.; Liu, Z. Ionic Liquid-Catalyzed C-S Bond Construction using CO2 as a C1 Building Block under Mild Conditions: a Metal-Free Route to Synthesis of Benzothiazoles. ACS Catal. 2015, 5, 6648-6652; (g) González-Sebastián, L.; Flores-Alamo, M.; García, J. J. Selective N-Methylation of Aliphatic Amines with CO2 and Hydrosilanes using Nickel-Phosphine Catalysts. Organometallics 2015, 34, 763-769; (h) Omae, I. Recent Developments in Carbon Dioxide Utilization for the Production of Organic Chemicals. Coord. Chem. Rev. 2012, 256, 1384-1405; (i) Sakakura, T.; Choi, J.-C.; Yasuda, H. Transformation of Carbon Dioxide. Chem. Rev. 2007, 107, 2365–2387; (j) Aresta, M. in Carbon Dioxide as Chemical Feedstock. Aresta, M., Ed.; Wiley-VCH, Weinheim; 2010; p. 1-13.

2. (a) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols. Chem. Rev. 2018, 118, 372-433; (b) Mellmann, D.; Sponholz, P.; Junge, H.; Beller, M. Formic Acid as a Hydrogen Storage Material - Development of Homogeneous Catalysts for Selective Hydrogen Release. Chem. Soc. Rev. 2016, 45, 3954-3988; (c) Dalebrook, A. F.; Gan, W.; Grasemann, M.; Moret, S.; Laurenczy, G. Hydrogen Storage: Beyond Conventional Methods. Chem. Commun. 2013, 49, 8735-8751; (d) Enthaler, S.; von Langermann, J.; Schmidt, T. Carbon Dioxide and Formic Acid-the Couple for Environmental-Friendly Hydrogen Storage? Energy Environ. Sci. 2010, 3, 1207-1217; (e) Joó, F. Breakthroughs in Hydrogen Storage-Formic Acid as a Sustainable Storage Material for Hydrogen. ChemSusChem 2008, 1, 805-808; (f) Iglesias, M.; Oro, L. A. Mechanistic Considerations on Homogeneously Catalyzed Formic Acid Dehydrogenation. Eur. J. Inorg. Chem. 2018, 2125-2138.

3. (a) Sordakis, K.; Tsurusaki, A.; Iguchi, M.; Kawanami, H.; Himeda, Y.; Laurenczy, G. Carbon Dioxide to Methanol: the Aqueous Catalytic Way at Room Temperature. Chem. Eur. J., 2016, 22, 15605-15608; (b) Du, X.-L.; Jiang, Z.; Su, D. S.; Wang, J.-Q. Research Progress on the Indirect Hydrogenation of Carbon Dioxide to Methanol. ChemSusChem, 2016, 9, 322-332; (c) Wang, W.-H.; Himeda, Y.; Muckerman, J. T.; Manbeck, G. F.; Fujita, E. CO₂ Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO₂ Reduction. Chem. Rev. 2015, 115, 12936-12973; (d) Singh, A. K.; Singh, S.; Kumar, A. Hydrogen Energy Future with Formic Acid: a Renewable Chemical Hydrogen Storage System. Catal. Sci. Technol. 2016, 6, 12-40; (e) Wesselbaum, S.; Moha, V.; Meuresch, M.; Brosinski, S.; Thenert, K. M.; Kothe, J.; vom Stein, T.; Englert, U.; Hölscher, M.; Klankermayer, J.; Leitner, W. Hydrogenation of Carbon Dioxide to Methanol using a Homogeneous Ruthenium-Triphos Catalyst: from Mechanistic Investigations to Multiphase Catalysis Chem. Sci. 2015, 6, 693-704; (f) Khusnutdinova, J. R.; Garg, J. A.; Milstein, D. Combining Low-Pressure CO₂ Capture and Hydrogenation to Form Methanol. ACS Catal. 2015, 5, 2416-2422; (g) Olah, G. A. Towards Oil Independence through Renewable Methanol Chemistry. Angew. Chem. Int. Ed. 2013, 52, 104-107; (h) Huff, C. A.; Sanford, M. S. Cascade Catalysis for the Homogeneous Hydrogenation of CO2 to Methanol. J. Am. Chem. Soc. 2011, 133, 18122-18125.

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 (a) Schneidewind, J.; Adam, R.; Baumann, W.; Jackstell, R.; Beller, M. Low-Temperature Hydrogenation of Carbon Dioxide to Methanol with a Homogeneous Cobalt Catalyst. *Angew. Chem. Int. Ed.* 2017, *56*, 1890-1893; (b) Ribeiro, A. P. C.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. Carbon Dioxide-to-Methanol Single-Pot Conversion using a C-scorpionate Iron(II) Catalyst. *Green Chem.* 2017, *19*, 4811-4815.

(a) Kar, S.; Goeppert, A.; Kothandaraman, J.; Surya Prakash, G.
K. Manganese-Catalyzed Sequential Hydrogenation of CO₂ to Methanol via Formamide. *ACS Catal.* 2017, 7, 6347–6351; (b) Everett, M.; Wass, D. F. Highly Productive CO₂ Hydrogenation to Methanol – a Tandem Catalytic Approach via Amide Intermediates. *Chem. Commun.* 2017, *53*, 9502-9504.

6. (a) Julian, A.; Guzman, J.; Jaseer, E. A.; Fernandez-Alvarez, F. J.; Royo, R.; Polo, V.; Garcia-Orduña, P.; Lahoz, F. J.; Oro, L. A. Mechanistic Insights on the Reduction of CO₂ to Silylformates Catalyzed by Ir-NSiN Species. *Chem. Eur. J.* 2017, *23*, 11898 – 11907; (b) Rios, P.; Diez, J.; Lopez-Serrano, J.; Rodriguez, A.; Conejero, S. Cationic Platinum(II) σ-SiH Complexes in Carbon Dioxide Hydrosilation. *Chem. Eur. J.* 2016, *22*, 16791 – 16795; (c) For a review article see: Fernandez-Alvarez, F. J.; Oro, L. A. *ChemCatChem* 2018, *10*, 4783-4796.

 Motokura, K.; Kashiwame, D.; Takahashi, N.; Miyaji, A.; Baba,
T. Highly Active and Selective Catalysis of Copper Diphosphine Complexes for the Transformation of Carbon Dioxide into Silyl Formate. *Chem. Eur. J.* 2013, *19*, 10030–10037.

8. Rit, A.; Zanardi, A.; Spaniol, T. P.; Maron, L.; Okuda, J. A Cationic Zinc Hydride Cluster Stabilized by an N-Heterocyclic Carbene: Synthesis, Reactivity, and Hydrosilylation Catalysis. *Angew. Chem. Int. Ed.* **2014**, *53*, 13273–13277.

 Tüchler, M.; Gärtner, L.; Fischer, S.; Boese, A. D.; Belaj, F.; Mösch-Zanetti, N. C. Efficient CO₂ Insertion and Reduction Catalyzed by a Terminal Zinc Hydride Complex. *Angew. Chem. Int. Ed.* **2018**, *57*, 6906-6909.

10. (a) Jiawei, C.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y.-X. Selective Reduction of CO2 to CH4 by Tandem Hydrosilylation with Mixed Al/B Catalysts. J. Am. Chem. Soc. 2016, 138, 5321-5333; (b) Jurado-Vazquez, T.; Ortiz-Cervantes, C.; García, J. J. Catalytic Reduction of CO2 with Organo-silanes using [Ru3(CO)12]. J. Organomet. Chem. 2016, 823, 8-13; (c) Park, S.; Bézier, D.; Brookhart, M. An Efficient Iridium Catalyst for Reduction of Carbon Dioxide to Methane with Trialkylsilanes. J. Am. Chem. Soc. 2012, 134, 11404-11407; (d) Berkefeld, A.; Piers, W. E.; Parvez, M. Tandem Frustrated Lewis Pair/Tris(pentafluorophenyl)borane-Catalyzed Deoxygenative Hydrosilylation of Carbon Dioxide. J. Am. Chem. Soc. 2010, 132, 10660-10661; (e) Mitton, S. J.; Turculet, L. Mild Reduction of Carbon Dioxide to Methane with Tertiary Silanes Catalyzed by Platinum and Palladium Silyl Pincer Complexes. Chem. Eur. J. 2012, 18, 15258-15262; (f) Matsuo, T.; Kawaguchi, H. From Carbon Dioxide to Methane: Homogeneous Reduction of Carbon Dioxide with Hydrosilanes Catalyzed by Zirconium-Borane Complexes. J. Am. Chem. Soc. 2006, 128, 12362-12363.

11. Rauch, M.; Parkin, G. Zinc and Magnesium Catalysts for the Hydrosilylation of Carbon Dioxide. *J. Am. Chem. Soc.* **2017**, *139*, 18162-18165.

 Luconi, L.; Rossin, A.; Tuci, G.; Gafurov, Z.; Lyubov, D. M.; Trifonov, A. A.; Cicchi, S.; Ba, H.; Pham-Huu, C.; Yakhvarov, D.; Giambastiani, G. Benzoimidazole-Pyridylamido Zirconium and Hafnium Alkyl Complexes as Homogeneous Catalysts for Tandem Carbon Dioxide Hydrosilylation to Methane. *ChemCatChem* in press. DOI: 10.1002/cctc.201800077.

13. Takaya, J.; Iwasawa, N. Synthesis, Structure, and Catalysis of Palladium Complexes Bearing a Group 13 Metalloligand: Remarkable Effect of an Aluminum-Metalloligand in Hydrosilylation of CO₂. *J. Am. Chem. Soc.* **2017**, *139*, 6074–6077.

14. Eisenschmid, T. G.; Eisenberg, R. The Iridium Complex Catalyzed Reduction of Carbon Dioxide to Methoxide by Alkylsilanes. *Organometallics* **1989**, *8*, 1822-1824. 15. Riduan, S. N.; Zhang, Y.; Ying, J. Y. Conversion of Carbon Dioxide into Methanol with Silanes over N-heterocyclic Carbene Catalysts. *Angew. Chem. Int. Ed.* **2009**, *121*, 3322–3325.

16. Tuci, G.; Rossin, A.; Luconi, L.; Pham-Huu, C., Cicchi, S.; Ba, H.; Giambastiani, G. Pyridine-Decorated Carbon Nanotubes as a Metal-Free Heterogeneous Catalyst for Mild CO₂ Reduction to Methanol with Hydroboranes. *Catal. Sci. Technol.* **2017**, *7*, 5833-5837.

17. (a) Huang, F.; Zhang, C.; Jiang, J.; Wang, Z.-X.; Guan, H. How Does the Nickel Pincer Complex Catalyze the Conversion of CO₂ to a Methanol Derivative? A Computational Mechanistic Study. *Inorg. Chem.* **2011**, *50*, 3816–3825; (b) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. An Efficient Nickel Catalyst for the Reduction of Carbon Dioxide with a Borane. *J. Am. Chem. Soc.* **2010**, *132*, 8872–8873.

18. Lia, H.; Gonçalves, T. P.; Zhao, Q.; Gong, D.; Lai, Z.; Wang, Z.; Zheng, J.; Huang, K.-W. Diverse Catalytic Reactivity of a Dearomatized PN³P*–Nickel Hydride Pincer Complex towards CO₂ Reduction. *Chem. Commun.* **2018**, *54*, 11395-11398.

19. Scheuermann, M. L.; Semproni, S. P.; Pappas, I.; Chirik, P. J. Carbon Dioxide Hydrosilylation Promoted by Cobalt Pincer Complexes. *Inorg. Chem.* **2014**, *53*, 9463–9465.

20. Metsänen, T. T.; Oestreich, M. Temperature-Dependent Chemoselective Hydrosilylation of Carbon Dioxide to Formaldehyde or Methanol Oxidation State. *Organometallics* **2015**, *34*, 543–546.

21. Mazzotta, M. G.; Xiong, M.; Abu-Omar, M. M. Carbon Dioxide Reduction to Silyl-Protected Methanol Catalyzed by an Oxorhenium Pincer PNN Complex. *Organometallics* **2017**, *36*, 1688–1691.

22. Morris, D. S.; Weetman, C.; Wennmacher, J. T. C.; Cokoja, M.; Drees, M.; Kühn, F. E.; Love, J. B. Reduction of Carbon Dioxide and Organic Carbonyls by Hydrosilanes Catalyzed by the Perrhenate Anion. *Catal. Sci. Technol.* **2017**, *7*, 2838–2845.

23. Bertini, F.; Glatz, M.; Gorgas, N.; Stöger, B.; Peruzzini, M.; Veiros, L. F.; Kirchner, K.; Gonsalvi, L. Carbon Dioxide Hydrogenation Catalysed by Well-defined Mn(I) PNP Pincer Hydride Complexes. *Chem. Sci.* **2017**, *8*, 5024-5029.

24. (a) Mastalir, M.; Glatz, M.; Gorgas, N.; Stöger, B.; Pittenauer, E.; Allmaier, G.; Veiros, L. F.; Kirchner, K. Divergent Coupling of Alcohols and Amines Catalyzed by Isoelectronic Hydride Mn^I and Fe^{II} PNP Pincer Complexes. *Chem. Eur. J.* **2016**, *22*, 12316–12320; (b) Mastalir, M.; Glatz, M.; Pittenauer, E.; Allmaier, G.; Kirchner, K. Sustainable Synthesis of Quinolines and Pyrimidines Catalyzed by Manganese PNP Pincer Complexes. *J. Am. Chem. Soc.* **2016**, *138*, 15543–15546.

25. Li, H.; Xing, Q.; Yue, C.; Lei, Z.; Li, F. Solvent-Promoted Catalyst-Free N-formylation of Amines using Carbon Dioxide under Ambient Conditions. *Chem. Commun.* **2016**, *52*, 6545–6548.

26. Mukherjee, D.; Sauer, D. F.; Zanardi, A.; Okuda, J. Selective Metal-Free Hydrosilylation of CO₂ Catalyzed by Triphenylborane in Highly Polar, Aprotic Solvent. *Chem. Eur. J.* **2016**, *22*, 7730 – 7733.

27. Frogneux, X.; Jacquet, O.; Cantat, T. Iron-Catalysed Hydrosilylation of CO₂: CO₂ Conversion to Formamides and Methylamines. *Catal. Sci. Technol.* **2014**, *4*, 1529-1533.

28. Avella-Moreno, E.; Nunes-Dallos, N.; Garzon-Tovar, L.; Duarte-Ruiz, A. Reactions and Products Revealed by NMR Spectra of Deuterated Dimethylsulfoxide with Iodomethane in Neutral and Basic Media. J. Sulfur Chem. **2015**, *36*, 535-543.

29. Bruneau-Voisine, A.; Wang, D.; Roisnel, T.; Darcel, C.; Sortais, J.-B. Hydrogenation of Ketones with a Manganese PN³P Pincer Pre-Catalyst. *Catal. Commun.* **2017**, *92*, 1–4.

30. a) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989; b) Calculations performed at the PBE0/(SDD, 6-31G**) level using the GAUSSIAN 09 package. All calculations included solvent effects (DMSO) using the PCM/SMD model and the free energy values are corrected for dispersion using the DFT-D3 method. A full account of the computational details and a complete list of references are provided as Supporting Information.

59 60 Table of Contents (TOC)

Well-defined Mn(I) hydridocarbonyl PNP pincer complexes catalyze the direct CO₂ hydrosilylation up to the methoxysilyl level, i.e. MeOH precursors, in DMSO under mild reaction conditions (1 bar, 80 °C) with high yields, in a stepwise, inner-sphere mechanism fully described by DFT calculations.



