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Catalytic Reduction of Carbon Dioxide by a Zinc Hydride Compound, [Tptm]ZnH, and Conversion to the Methanol Level

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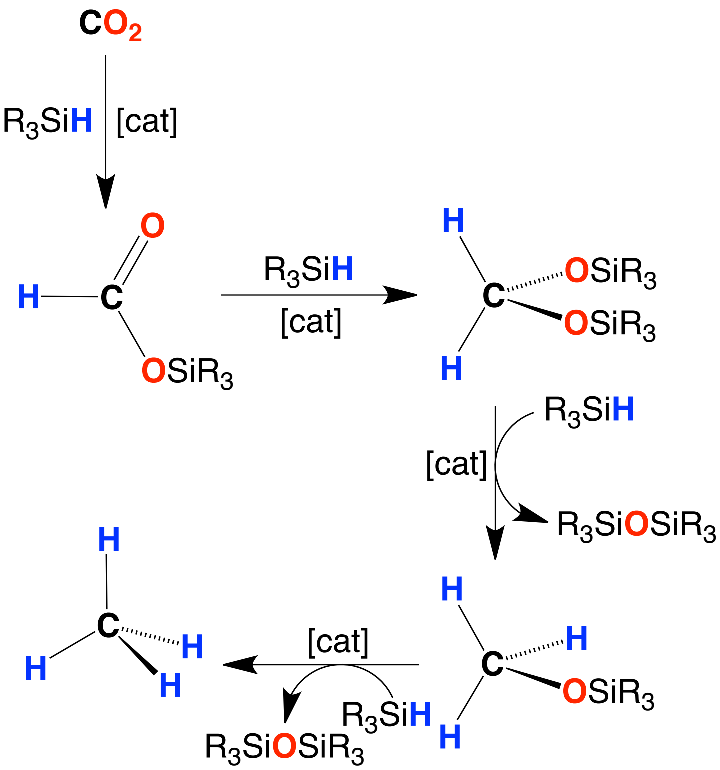
Abstract: The zinc hydride compound, [Tptm]ZnH, may achieve the reduction of CO_2 by $(RO)_3SiH$ (R = Me, Et) to the methanol oxidation level, $(MeO)_xSi(OR)_{4-x}$, *via* the formate species, $HCO_2Si(OR)_3$. However, because insertion of CO_2 into the Zn–H bond is more facile than insertion of $HCO_2Si(OR)_3$, conversion of $HCO_2Si(OR)_3$ to the methanol level only occurs to a significant extent in the absence of CO_2.

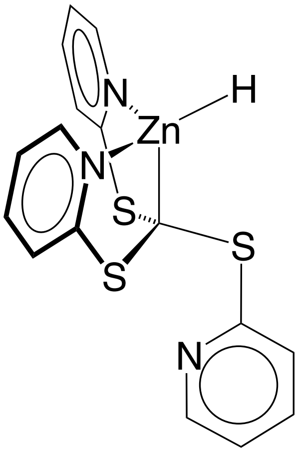
INTRODUCTION

The discovery and development of transformations of carbon dioxide is not only of considerable interest with respect to the use of this molecule as a renewable C_1 source for the synthesis of value added organic chemicals, but is also of relevance to efforts to mitigate the rising levels of atmospheric carbon dioxide, *i.e.* carbon capture and utilization (CCU).[1-6] Major difficulties, however, are associated with the fact that CO_2 is both kinetically and thermodynamically resistant to chemical transformations. In this regard, the hydrosilylation of CO_2 is of particular interest because, in contrast to the thermodynamically unfavorable addition of the H–H bond to CO_2,[7] the addition of a Si–H bond is thermodynamically favorable and can occur in a stepwise manner to afford a series of products with different carbon oxidation levels, which include silyl formates (HCO_2SiR_3), silyl acetals ($H_2C(OSiR_3)_2$), methoxysilanes (R_3SiOCH_3), and methane, as illustrated in Scheme 1.[8,9] The use of hydrosilanes to reduce CO_2 is also of relevance because inexpensive and environmentally benign hydrosilanes are available as by-products of the silicone industry.[8,10]

An important objective pertaining to hydrosilylation of CO_2 is the ability to control the degree of reduction because each derivative has distinct chemical properties.[8,11] For example, the reduction of CO_2 to the methanol level is of interest because of the potential applications for the methanol economy[12] and the use of methanol as a liquid organic hydrogen carrier for the hydrogen economy.[13,14,15] The ability to control the degree of reduction of CO_2 by hydrosilylation depends critically on the use of catalysts.[8,11] However, since many of these catalysts employ precious metals, there is interest in discovering catalysts that employ nonprecious metals, such as zinc.[8,16,17,18] Therefore, we describe here the use of a zinc hydride compound, namely [*tris*(2-pyridylthio)methyl]zinc hydride, [Tptm]ZnH (Figure 1),[19] to serve as a catalyst for the hydrosilylation of CO_2 to the methanol level.



Scheme 1. Reduction of CO_2 *via* hydrosilylation.



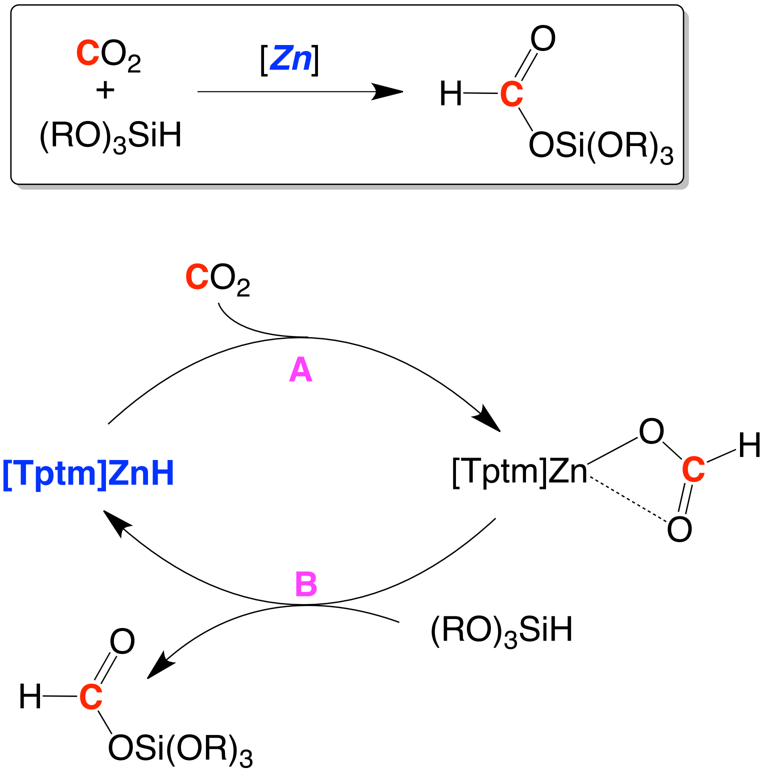
[Tptm]ZnH

Figure 1. [Tptm]ZnH, a mononuclear zinc hydride catalyst.

RESULTS AND DISCUSSION

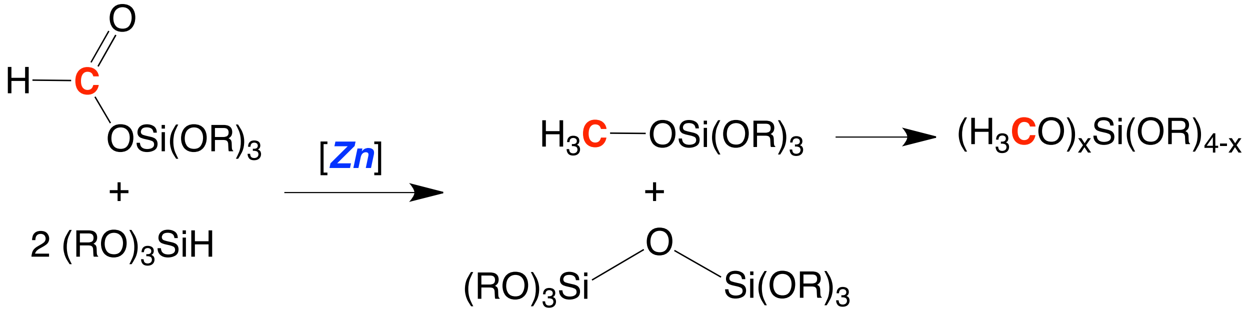
We previously reported the first example of the use of a zinc hydride compound as a catalyst for the reduction of CO_2 *via* hydrosilylation,[16a] in which [Tptm]ZnH catalyzes the hydrosilylation of CO_2 by $(RO)_3SiH$ (R = Me, Et) to afford the silyl formate,

$HCO_2Si(OR)_3$ (Scheme 2).[19,20] Specifically, CO_2 inserts into the Zn–H bond of [Tptm]ZnH to form the zinc formate species, [Tptm]Zn(O_2CH),[21,22] which subsequently undergoes metathesis with $(EtO)_3SiH$ to release $HCO_2Si(OEt)_3$ and regenerate [Tptm]ZnH, a mechanism which is analogous to that proposed for other hydrosilylation reactions.[17,23] The catalytic synthesis of silyl formates is of interest because such compounds have a variety of applications, including uses in organic syntheses.[24,25] The zinc catalyzed synthesis of $HCO_2Si(OEt)_3$ may also be conducted without the need of additional solvent; in this regard, the solvent-free conversion of CO_2 to silyl formates has been recognized as an important advance[26] according to the principles of Green Chemistry,[27,28] since it minimizes the use of unnecessary solvent.[29]



Scheme 2. Catalytic reduction of CO_2 to $HCO_2Si(OR)_3$.

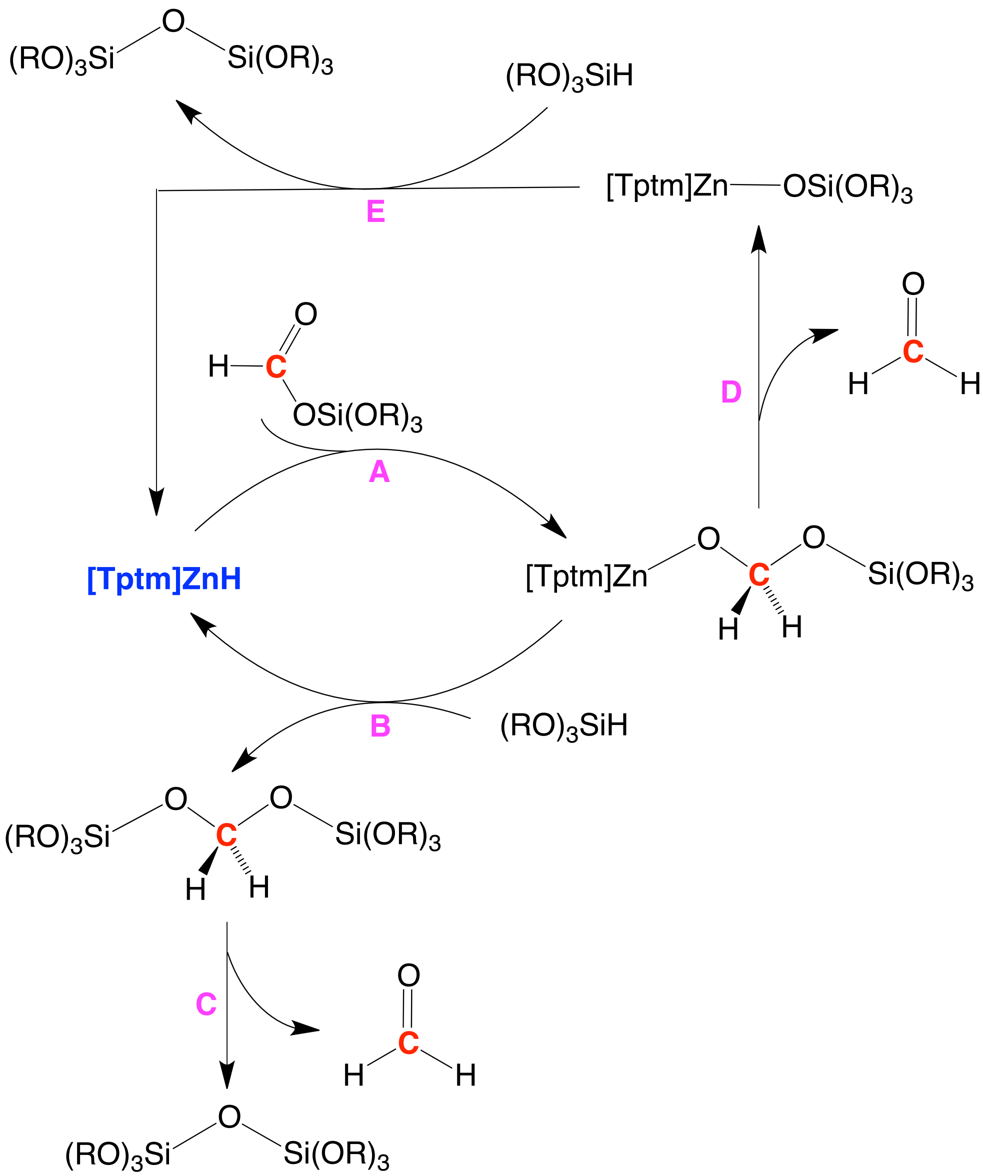
In addition to the hydrosilylation of CO_2, we have also reported that [Tptm]ZnH is an effective catalyst for the hydrosilylation of aldehydes and ketones.[30,31] On the basis of this observation, we considered the possibility that [Tptm]ZnH could likewise serve as a catalyst for the reduction of $HCO_2Si(OR)_3$, thereby providing a means to effect the overall reduction of CO_2 to lower oxidation levels. Therefore, it is significant that we report that [Tptm]ZnH is indeed a catalyst for the reduction of $HCO_2Si(OEt)_3$ to the methanol level (Scheme 3).[32,33] In this regard, while the initial methoxysilane product is $MeOSi(OEt)_3$,[34] the latter undergoes redistribution reaction to form $(MeO)_xSi(OEt)_{4-x}$, as previously noted for such compounds.[35,36] In addition, the zinc system also catalyzes the reduction of $HCO_2Si(OMe)_3$ by $(MeO)_3SiH$ to afford $Si(OMe)_4$.



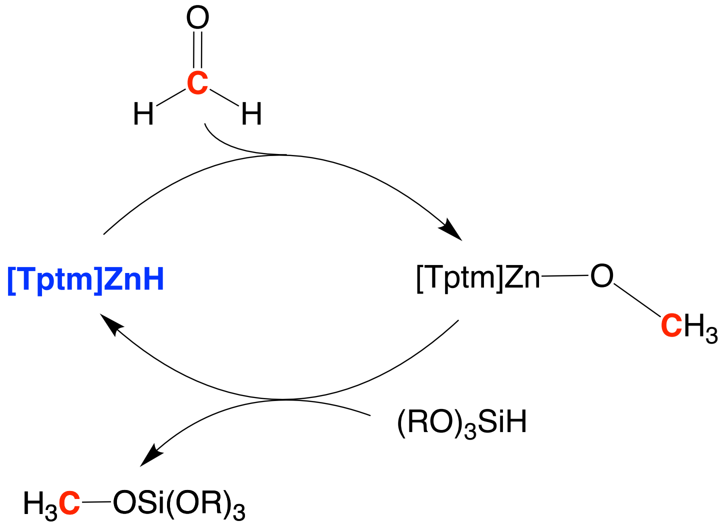
Scheme 3. Reduction of $HCO_2Si(OR)_3$ to methoxy species.

Although reduction of CO_2 to methoxysilanes is known,[37,38] the mechanisms of zinc-hydride catalyzed reductions to the methanol oxidation level have received no attention. Therefore, we have investigated this transformation computationally.

The formation of a methoxysilane derivative from the silyl formate compound, $HCO_2Si(OR)_3$, conceptually requires two cycles of hydrosilylation; the first cycle involves reduction to the formaldehyde level (Scheme 4) while the second cycle involves reduction to the methanol level (Scheme 5). On the basis of the mechanisms discussed previously for hydrosilyation of CO_2[8,16,39,40] and R_2CO,[30] the initial step of the first cycle of the reduction of $HCO_2Si(OR)_3$ is proposed to involve insertion of the C=O double bond into the Zn–H bond to afford the alkoxide, [Tptm]ZnOCH$_2$OSi(OR)$_3$ (Scheme 4; step A).



Scheme 4. Possible mechanisms for the reduction of HCO$_2$Si(OMe)$_3$ to formaldehyde.



Scheme 5. Reduction of formaldehyde to the methanol level.

The energy profile for insertion of $HCO_2Si(OMe)_3$ into the Zn–H bond of [Tptm]ZnH to form $[Tptm]ZnOCH_2OSi(OMe)_3$ is illustrated in Figure 2, which indicates that it is a kinetically feasible transformation with $\Delta G^{\ddagger} = 21.4$ kcal mol^{-1}. However, since the reduction of $HCO_2Si(OR)_3$ does not proceed effectively in the presence of CO_2, it suggests that insertion of the C=O bond of $HCO_2Si(OR)_3$ into the Zn–H bond is less facile than that of CO_2. Support for this notion is provided by density functional theory calculations, which indicate that the barrier for insertion of CO_2 (14.4 kcal mol^{-1}) into the Zn–H bond is lower than that for $HCO_2Si(OMe)_3$, as illustrated in Figure 2.

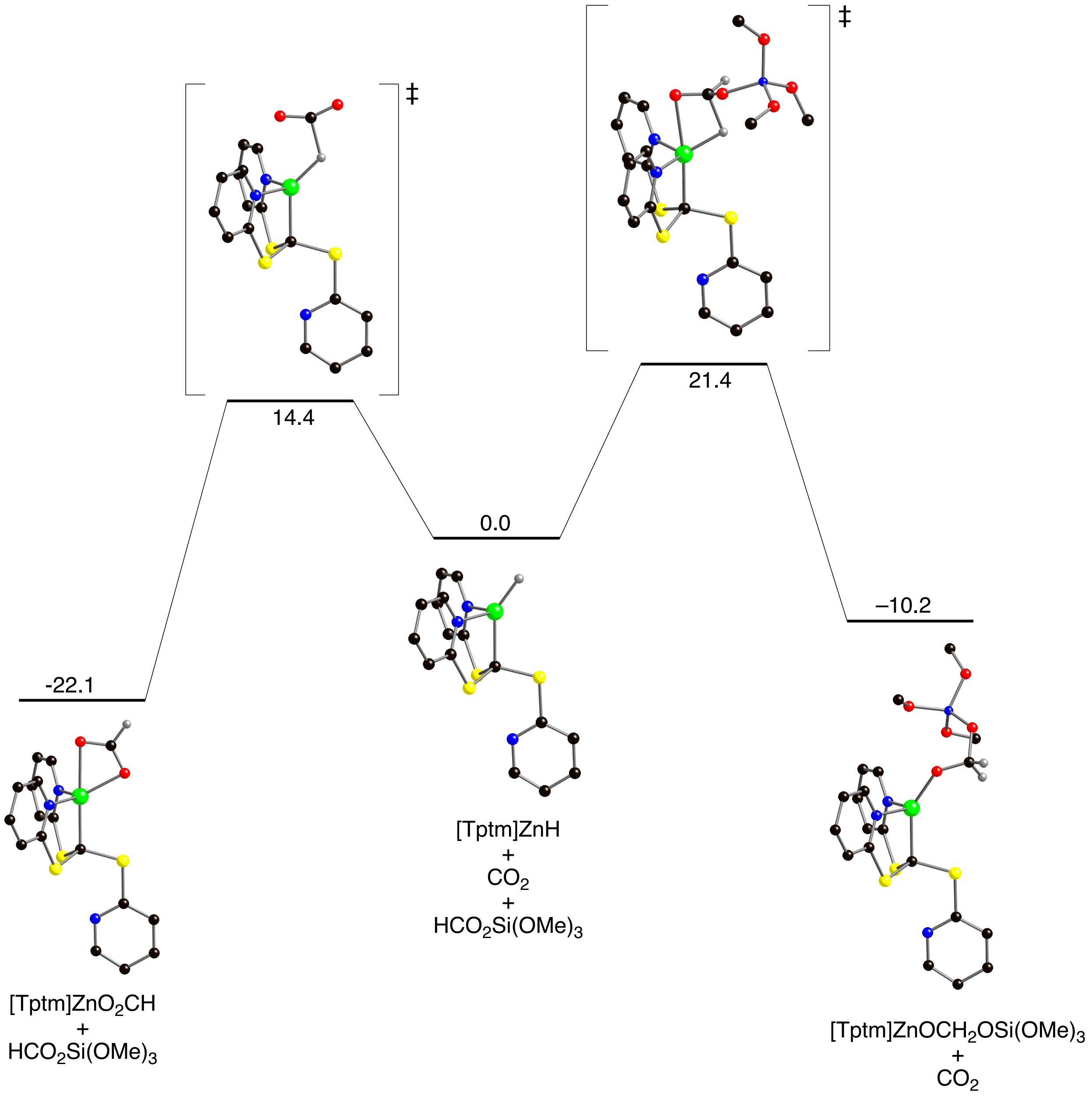
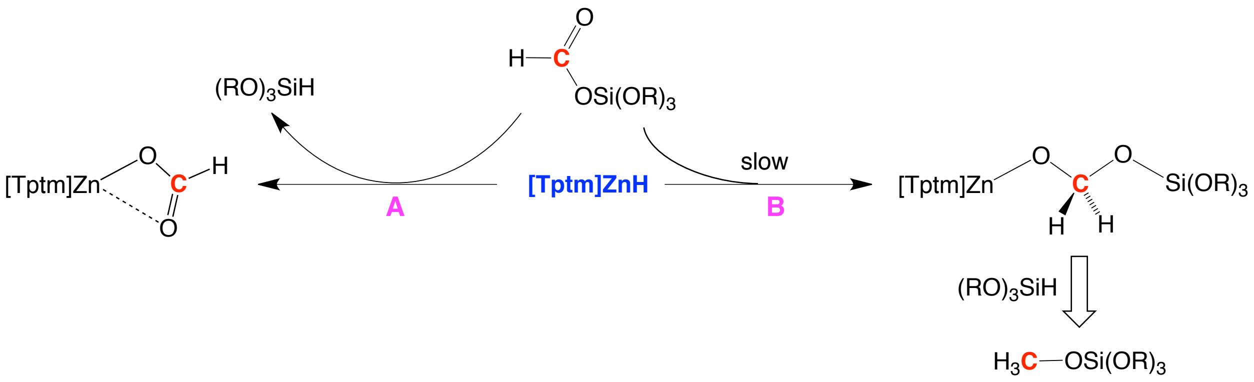


Figure 2. Insertion of CO_2 versus $HCO_2Si(OMe)_3$ into the Zn–H bond of [Tptm]ZnH (ΔG values in kcal mol^{-1} at 25°C).

Thus, the preferential formation of $[Tptm]ZnO_2CH$ over $[Tptm]ZnOCH_2OSi(OMe)_3$ is consistent with there being a selectivity for the catalytic formation of the silyl formate, $HCO_2Si(OR)_3$, in the presence of excess CO_2. As such, the hydrosilylation of $HCO_2Si(OR)_3$ only becomes efficient when the CO_2 is depleted and insertion of the C=O bond of $HCO_2Si(OR)_3$ becomes kinetically competent.

Interestingly, while the insertion of $HCO_2Si(OR)_3$ into the Zn–H bond of [Tptm]ZnH (Scheme 6, step B) becomes more significant when CO_2 is depleted, this transformation is not the favored reaction between [Tptm]ZnH and $HCO_2Si(OR)_3$. Specifically, rather than undergoing insertion of the C=O bond, [Tptm]ZnH reacts preferentially with $HCO_2Si(OR)_3$ to afford the formate complex, [Tptm]ZnO_2CH (Scheme 6, step A), which is the microscopic reverse of the product forming step of the hydrosilylation reaction to form $HCO_2Si(OR)_3$ (Scheme 2; step B), clearly demonstrating that this step of the catalytic cycle for hydrosilylation of CO_2 is reversible.[37c] Thus, it is evident that formation of the zinc formate compound by both insertion of CO_2 into the Zn–H bond and by metathesis of the Zn–H bond with $HCO_2Si(OR)_3$ is more facile than insertion of the C=O bond of $HCO_2Si(OR)_3$ into the Zn–H bond. The facile generation of the zinc formate complex [Tptm]ZnO_2CH by these reactions thereby contributes to the selectivity of the formation of $HCO_2Si(OR)_3$ during the initial stages of the hydrosilylation of CO_2. In the absence of CO_2, however, [Tptm]ZnO_2CH does react with $(EtO)_3SiH$ to form $(MeO)_xSi(OEt)_{4-x}$, *via* a sequence that is proposed to involve generation of [Tptm]ZnH and $HCO_2Si(OR)_3$ (Scheme 2), followed by the subsequent reduction of the latter (Scheme 4 and Scheme 5).



Scheme 6. Insertion of $HCO_2Si(OR)_3$ into the Zn–H bond *versus* more favorable metathesis to afford [Tptm]ZnO_2CH.

Following insertion of $HCO_2Si(OR)_3$ into the Zn–H bond to achieve reduction to the formaldehyde level, several mechanisms may be considered to achieve overall reduction to the methanol level. For example, by analogy to mechanisms proposed for the hydrosilylation of CO_2 and R_2CO,[8,30] metathesis of $[Tptm]ZnOCH_2OSi(OR)_3$ with $(RO)_3SiH$ would release the bis(silyl)acetal, $H_2C[OSi(OR)_3]_2$, thereby regenerating the zinc hydride catalyst, [Tptm]ZnH (Scheme 4; step B).[41] The formation of $H_2C[OSi(OR)_3]_2$ as a reactive intermediate is reasonable on the basis that there is literature precedent for the generation of such molecules during hydrosilylation of CO_2.[42,43] For example, we recently reported that a catalytic system comprised of $[Tism^{Pr^iBenz}]MX$ (M = Mg, Zn; X = H, Me)[44] and $B(C_6F_5)_3$ was effective for the selective hydrosilylation of CO_2 to afford the bis(silyl)acetal, $H_2C(OSiPh_3)_2$.[45] Bis(silyl)acetal compounds possess carbon in the formaldehyde oxidation level and, as demonstrated by several studies, provide a potential means of generating incipient formaldehyde (Scheme 4; step C).[46,47]

In addition to generating formaldehyde *via* a bis(silyl)acetal intermediate, it is also possible that the formaldehyde could be extruded directly from $[Tptm]ZnOCH_2OSi(OR)_3$ to form the siloxide, $[Tptm]ZnOSi(OR)_3$, which in turn reacts with $(RO)_3SiH$ to regenerate [Tptm]ZnH (Scheme 4; steps D and E). Such release of formaldehyde from $[Tptm]ZnOCH_2OSi(OR)_3$ (Scheme 4, step D) bears an analogy to the dissociation of CO_2 from the silylcarbonate complex $[Tptm]ZnO_2COSiMe_3$ to afford the siloxide, $[Tptm]ZnOSiMe_3$.[19] Furthermore, the transformation is analogous to the proposed elimination of formaldehyde from a boryl counterpart, namely $[\{2,6\text{-}C_6H_3(OPBu^t{}_2)_2\}Ni]OCH_2OBCat$.[48] Therefore, we have investigated the ability of $[Tptm]ZnOCH_2OSi(OR)_3$ to dissociate formaldehyde by using DFT calculations, which indicates that the process is facile (Figure 3), and is thereby a potential pathway that is more facile than dissociation of formaldehyde from $R_3SiOCH_2OSiR_3$ species.[18e,f]

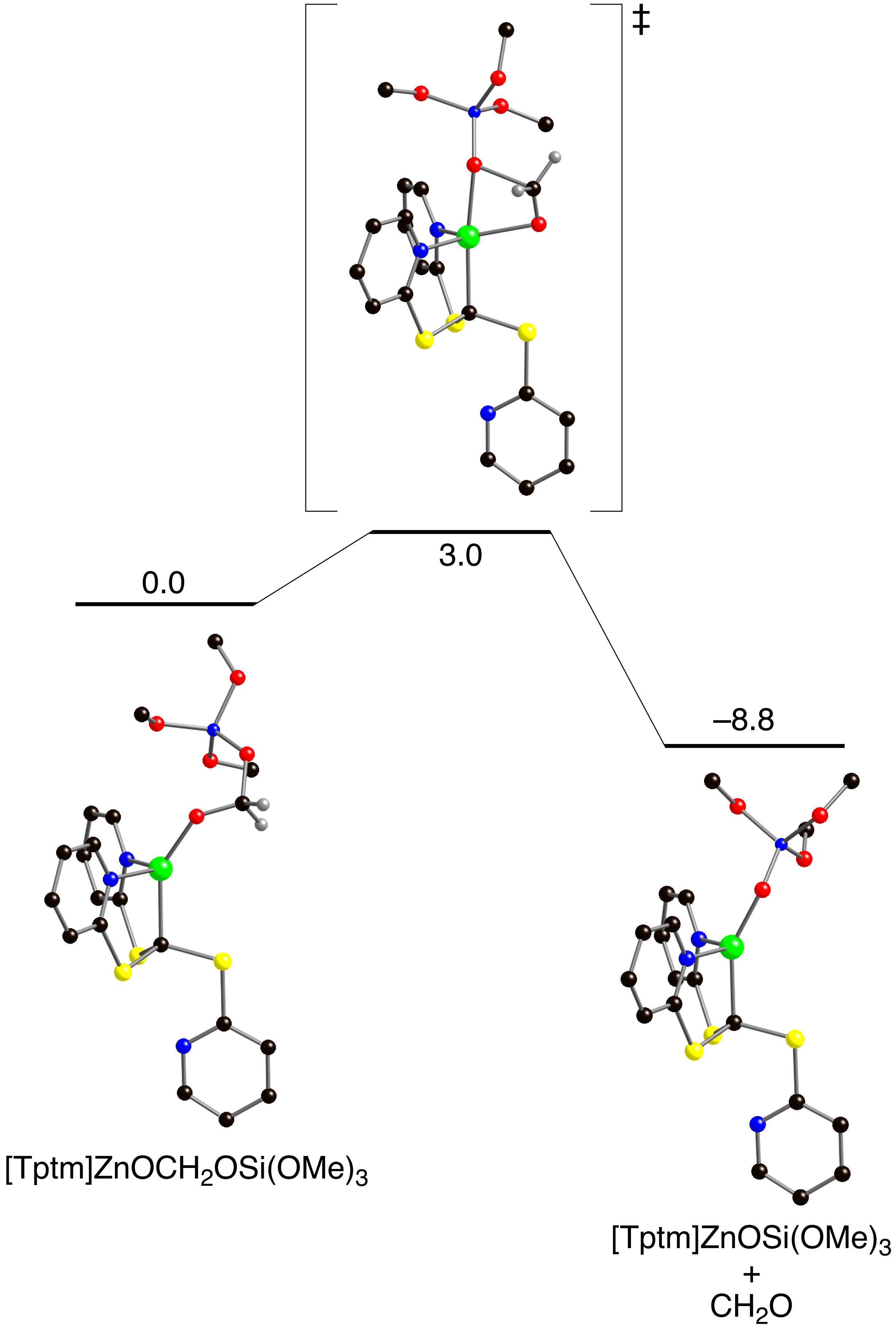

‡
3.0
0.0
–8.8
[Tptm]ZnOCH$_2$OSi(OMe)$_3$
[Tptm]ZnOSi(OMe)$_3$
+
CH$_2$O

Figure 3. Release of formaldehyde from [Tptm]ZnOCH$_2$OSi(OMe)$_3$ (ΔG values in kcal mol^{-1}).

Regardless of the mode of generation, the liberated formaldehyde would be subject to a subsequent hydrosilylation cycle *via* a mechanism akin to those for CO$_2$ and R$_2$CO, namely insertion into the Zn–H bond to form a methoxide, [Tptm]ZnOMe, followed by metathesis with the silane (RO)$_3$SiH to release the methoxysilane, MeOSi(OR)$_3$, and regenerate [Tptm]ZnH (Scheme 5).

The ability to reduce CO$_2$ to the methanol oxidation level in this system is of significance because it provides further information as to how the degree of reduction of CO$_2$ may be controlled. Thus, while examination of the literature indicates that the product distribution is influenced by the hydrosilane and the nature of the catalyst/cocatalyst,[8,11,49] the present study serves to emphasize how CO$_2$ concentration can have an impact by inhibiting reduction of formate species to lower oxidation levels.

SUMMARY

In summary, while [Tptm]ZnH catalyzes the hydrosilylation of CO$_2$ by (RO)$_3$SiH to afford the formate HCO$_2$Si(OR)$_3$, it is capable of effecting the overall reduction to the methanol level, (MeO)$_x$Si(OR)$_{4-x}$, which is promoted in the absence of CO$_2$. The preferential formation of HCO$_2$Si(OR)$_3$ in the presence of CO$_2$ may be attributed to insertion of CO$_2$ into the Zn–H bond of [Tptm]ZnH being more facile than the corresponding insertion of HCO$_2$Si(OR)$_3$.

EXPERIMENTAL SECTION

General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under an argon or nitrogen atmosphere unless otherwise specified.[50] Solvents were purified and degassed by using standard procedures. ^{1}H NMR spectra were measured on Bruker 400 Cyber-enabled Avance III, Bruker 500 DMX and Bruker AVIII 500 spectrometers. [Tptm]ZnH, [Tptm]ZnOSiMe$_3$, and [Tptm]ZnO$_2$CH were prepared by the literature methods.[19]

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 8.9 (release 15) suite of *ab initio* quantum chemistry programs.[51] Geometry optimizations were performed with the B3LYP density functional using the LACVP** basis sets that were also used for obtaining thermodynamic data. Cartesian coordinates are provided in the Supporting Information.

Zinc catalyzed reduction of HCO$_2$Si(OR)$_3$ by (RO)$_3$SiH

(a) A mixture of [Tptm]ZnH (3 mg, 0.0073 mmol) and (EtO)$_3$SiO$_2$CH (15 mg, 0.071 mmol) in benzene (*ca.* 0.5 mL) in an NMR tube equipped with a J. Young valve was treated with (EtO)$_3$SiH (15 mg, 0.091 mmol). The sample was monitored by ^{1}H NMR spectroscopy, thereby demonstrating the immediate formation of [Tptm]ZnO$_2$CH. The sample was heated at 100˚C , thereby resulting in the conversion of (EtO)$_3$SiO$_2$CH to (EtO)$_3$SiOMe and (MeO)$_x$Si(OEt)$_{4-x}$ redistribution products (TON = 10, TOF 0.2 h ^{1}); see Supporting Information.

(b) A solution of [Tptm]ZnOSiMe$_3$ (1 mg, 0.002 mmol) in C$_6$D$_6$ (*ca.* 0.5 mL) in an NMR tube equipped with a J. Young valve was treated with (MeO)$_3$SiH (20 mg, 0.164 mmol), resulting in the formation of [Tptm]ZnH. CO$_2$ (1 atm) was added and the solution was heated at 100˚C for 24 hours and was monitored by ^{1}H NMR spectroscopy, resulting in the formation of $(MeO)_3SiO_2CH$ (TOF = 0.4 h^{-1}). The sample was degassed, and additional $(MeO)_3SiH$ (20 mg, 0.164 mmol) was added. The solution was heated at 100˚C for 20 hours, resulting in the complete consumption of $(MeO)_3SiO_2CH$ (TOF = 0.5 h^{-1}); see Supporting Information.

Evidence that $HCO_2Si(OEt)_3$ does not undergo facile reduction by $(EtO)_3SiH$ in the presence of CO_2

A mixture of [Tptm]ZnH (3 mg, 0.0073 mmol), $(EtO)_3SiH$ (15 mg, 0.091 mmol), and $(EtO)_3SiO_2CH$ (15 mg, 0.071 mmol) in benzene (*ca*. 0.5 mL) in an NMR tube equipped with a J. Young valve was monitored by ^1H NMR spectroscopy, thereby resulting in the immediate formation of $[Tptm]ZnO_2CH$. The solution was treated with CO_2 (1 atm) and heated at 100˚C for 1 day. Over this period, conversion of CO_2 to $(EtO)_3SiO_2CH$ was observed but there was no formation of $(MeO)_xSi(OEt)_{4-x}$; see Supporting Information.

Reaction of [Tptm]ZnH with $(RO)_3SiO_2CH$: Formation of $[Tptm]ZnO_2CH$

(a) A mixture of [Tptm]ZnH (3 mg, 0.0073 mmol) and $(EtO)_3SiO_2CH$ (15 mg, 0.071 mmol) in benzene (*ca*. 0.5 mL) in an NMR tube equipped with a J. Young valve was monitored by ^1H NMR spectroscopy, thereby demonstrating the immediate formation of $[Tptm]ZnO_2CH$; see Supporting Information.

(b) A mixture of [Tptm]ZnH (3 mg, 0.0073 mmol) and $(MeO)_3SiH$ (15 mg, 0.123 mmol) in benzene (*ca*. 0.5 mL) in an NMR tube equipped with a J. Young valve was treated with CO_2 (1 atm). The sample was heated at 80°C and monitored by ^1H NMR spectroscopy, thereby demonstrating the formation of $(MeO)_3SiO_2CH$ over 2 days. The CO_2 was removed and the sample was treated with [Tptm]ZnH, which converted immediately to $[Tptm]ZnO_2CH$ as demonstrated by ^1H NMR spectroscopy.

Reaction of $[Tptm]ZnO_2CH$ with $(EtO)_3SiH$: Formation of $(MeO)_xSi(OEt)_{4-x}$

A mixture of [Tptm]ZnH (3 mg, 0.0073 mmol) and $(EtO)_3SiH$ (15 mg, 0.071 mmol) in benzene (*ca.*0.5 mL) in an NMR tube equipped with a J. Young valve was treated with CO_2 (1 atm), resulting in the *in situ* generation of $TptmZnO_2CH$. The tube was immediately degassed and heated at 60˚C for 1 day and 80°C for 2 days, showing the formation of $(EtO)_3SiOMe$ and $(MeO)_xSi(OEt)_{4-x}$ redistribution products; see Supporting Information.

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REFERENCES

(1) (a) Song, Q.-W.; Zhou, Z.-H.; He, L.-N. *Green Chem.* **2017**, *19*, 3707-3728.

(b) Yuan, G.; Qi, C.; Wu, W.; Jiang, H. *Curr. Opin. Green Sustain. Chem.* **2017**, *3*, 22-27.

(c) Omae, I. *Coord. Chem. Rev.* **2012**, *256*, 1384-1405.

(d) Riduan, S. N.; Zhang, Y. *Dalton Trans.* **2010**, *39*, 3347-3357.

(e) Mikkelsen, M.; Jorgensen, M.; Krebs, F. C. *Ener. Env. Sci.* **2010**, *3*, 43-81.

(f) Goeppert, A.; Czaun, M.; Jones, J.-P.; Surya Prakash, G. K.; Olah, G. A. *Chem. Soc. Rev.* **2014**, *43*, 7995-8048.

(g) Liu, Q.; Wu, L. P.; Jackstell, R.; Beller, M. *Nat. Commun.* **2015**, *6*, #5933.

(h) Pan, S.-Y.; Chiang, P.-C.; Pan, W.; Kim, H. *Crit. Rev. Environ. Sci. Technol.* **2018**, *48*, 471-534.

(i) Bao, J.; Yang, G.; Yoneyama, Y.; Tsubaki, N. *ACS Catal.* **2019**, *9*, 3026-3053.

(j) Fraga, E. S.; Ng, M. *Faraday Discuss.* **2015**, *183*, 309-326

(k) Cherubini-Celli, A.; Mateos, J.; Bonchio, M.; Dell'Amico, L.; Companyo, X. *ChemSusChem* **2018**, *11*, 3056-3070.

(l) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem. Int. Edit.* **2009,** *48*, 9839-9843.

(m) Darensbourg, D. J. *Green Chem.* **2019**, *21*, 2214-2223.

(n) Wang, Y.; Darensbourg, D. J. *Coord. Chem. Rev.* **2018,** *372*, 85-100.

(o) Coates, G. W.; Moore, D. R. *Angew. Chem. Int. Edit.* **2004,** *43*, 6618-6639.

(p) Beydoun, K.; Klankermayer, J. *Top. Organomet. Chem.* **2019**, *63*, 39-76.

(2) (a) Aresta, M., Ed. *Carbon Dioxide as a Chemical Feedstock*; Wiley-VCH: Weinheim, 2010.

(b) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975-2992.

(i) Aresta, M. *Coord. Chem. Rev.* **2017**, *334*, 150-183.

(3) (a) Tlili, A.; Blondiaux, E.; Frogneux, X.; Cantat, T. *Green Chem.* **2015**, *17*, 157-168.

(b) Chauvier, C.; Cantat, T. *ACS Catal.* **2017**, *7*, 2107-2115.

(4) (a) Klankermayer, J.; Wesselbaum, S.; Beydoun, K.; Leitner, W. *Angew. Chem. Int. Edit.* **2016**, *55*, 7296-7343.

(b) Peters, M.; Köhler, B.; Kuckshinrichs, W.; Leitner, W.; Markewitz, P.; Müller, T. E. *ChemSusChem* **2011**, *4*, 1216-1240.

(5) (a) Dabral, S.; Schaub, T. *Adv. Synth. Catal.* **2019**, *361*, 223-246.

(b) Schaub, T. *Phys. Sci. Rev.* **2018**, *3*, #20170015.

(6) For biological approaches to CO_2 reduction, see: Gamba, I. *Bioinorg. Chem. Appl.* **2018**, #2379141.

(7) In view of the unfavorable thermodynamics for the addition of H_2 to CO_2, the reverse reaction is of relevance to the use of formic acid in hydrogen storage. See, for example:

(a) Sordakis, K.; Tang, C. H.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. *Chem. Rev.* **2018**, *118*, 372-433.

(b) Müller, K.; Brooks, K.; Autrey, T. *Energy Fuels* **2017**, *31*, 12603-12611.

(c) Onishi, N.; Laurenczy, G.; Beller, M.; Himeda, Y. *Coord. Chem. Rev.* **2018**, *373*, 317-332.

(d) Zell, T.; Langer, R. *Phys. Sci. Rev.* **2018**, #20170012.

(e) Loges, B.; Boddien, A.; Gartner, F.; Junge, H.; Beller, M. *Top. Catal.* **2010**, *53*, 902-914.

(8) (a) Chen, J.; McGraw, M.; Chen, E. Y,-X. *ChemSusChem* **2019**, *12*, 4543-4569.

(b) Ghosh, D.; Kumar, G. R.; Subramanian, S.; Tanaka, K. *ChemSusChem* **2021**, *14*, 824-841.

(c) Zhang, Y.; Zhang, T.; Das, S. *Green Chem.* **2020**, *22*, 1800-1820.

(d) Pramuditaa, R. A.; Motokura, K. *Green Chem.* **2018**, 20, 4834-4843.

(e) Fernandez-Alvarez, F. J.; Oro, L. A. *ChemCatChem* **2018**, *10*, 4783-4796.

(f) Iglesias, M.; Fernandez-Alvarez, F. J.; Oro, L. A. *Coord. Chem. Rev.* **2019**, *386*, 240-266.

(g) Fernandez-Alvarez, F. J.; Aitani, A. M.; Oro, L. A. *Catal. Sci. Tech.* **2014**, *4*, 611-624.

(h) Fernandez-Alvarez, F. J.; Iglesias, M.; Oro, L. A.; Polo, V. *ChemCatChem* **2013**, *5*, 3481-3494.

(i) Manaka, Y. *J. Jpn. Pet. Inst* **2021**, *64*, 172-177.

(j) Pramudita, R. A.; Motokura, K. *ChemSusChem* **2021**, *14*, 281-292.

(k) Pramudita, R. A.; Manaka, Y.; Motokura, K. *Chem.Eur. J.* **2020**, *26*, 7937-7945.

(l) Motokura, K.; Nakagawa, C.; Pramudita, R. A.; Manaka, Y. *ACS Sustain. Chem. Eng.* **2019**, *7*, 11056-11061.

(m) Motokura, K.; Naijo, M.; Yamaguchi, S.; Miyaji, A.; Baba, T. *Chem. Lett.* **2015**, *44*, 1217-1219.

(n) Liu, X.-F.; Li, X.-Y.; He, L.-N. *Eur. J. Org. Chem.* **2019**, 2437-2447.

(o) Jacquet, O.; Das Neves Gomes, C.; Ephritikhine, M.; Cantat, T. *J. Am. Chem. Soc.* **2012**, *134*, 2934-2937.

(p) Kraushaar, K.; Schmidt, D.; Schwarzer, A.; Kroke, E. *Adv. Inorg. Chem.* **2014**, *66*, 117-162.

(9) (a) Bontemps, S. *Coord. Chem. Rev.* **2016**, *308*, 117-130.

(b) Liu, M.; Qin, T.; Zhang, Q.; Fang, C.; Fu, Y.; Lin, B.-L. *Sci. China Chem.* **2015**, *58*, 1524-1531.

(c) Wang, X.; Xia, C.; Wu, L. *Green Chem.* **2018**, *20*, 5415-5426.

(10) (a) Lawrence, N. J.; Drew, M. D.; Bushell, S. M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3381-3391.

(b) Senapati, K. K. *Synlett* **2005**, 1960-1961.

(11) Cramer, H. H.; Chatterjee, B.; Weyhermuller, T.; Werle, C.; Leitner, W. *Angew. Chem. Int. Edit.* **2020**, *59*, 15674-15681.

(12) (a) Olah, G. A. *Angew. Chem. Int. Edit.* **2005**, *44*, 2636-2639.

(b) Olah, G. A.; Goeppert, A.; Prakash, G. K. S. *J. Org. Chem.* **2009**, *74*, 487-498.

(c) Guil-Lopez, R.; Mota, N.; Llorente, J.; Millan, E.; Pawelec, B.; Fierro, J. L. G.; Navarro, R. M. *Materials* **2019**, *12*, 3902.

(13) Shimbayashi, T.; Fujita, K. *Tetrahedron* **2020**, *76*, 130946.

(14) Gianotti, E.; Taillades-Jacquin, M.; Roziere, J.; Jones, D. J. *ACS Catal.* **2018**, *8*, 4660-4680.

(15) Kumar, A.; Daw, P.; Milstein, D. *Chem. Rev.* **2022**, *122*, 385–441.

(16) (a) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2012**, *134*, 17462-17465.

(b) Sattler, W.; Shlian, D. G.; Sambade, D.; Parkin, G. *Polyhedron* **2020**, *187*, 114542.

(c) Rauch, M.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139*, 18162-18165.

(d) Ruccolo, S.; Amemiya, E.; Shlian, D. G.; Parkin, G. *Can. J. Chem.* **2021**, *99*, 259-267.

(17) (a) Tüchler, M.; Gärtner, L.; Fischer, S.; Boese, A. D.; Belaj, F.; Mösch-Zanetti, N. C. *Angew. Chem. Int. Edit.* **2018**, *57*, 6906-6909.

(b) Feng, G.; Du, C.; Xiang, L.; del Rosal, I.; Li, G.; Leng, X.; Chen, E.-X.; Maron, L.; Chen, Y. *ACS Catal.* **2018**, *8*, 4710-4718.

(c) Ballmann, G.; Grams, S.; Elsen, H.; Harder, S. *Organometallics* **2019**, *38*, 2824-2833.

(d) Chambenahalli, R.; Bhargav, R. M.; McCabe, K. N.; Andrews, A. P.; Ritter, F.; Okuda, J.; Maron, L.; Venugopal, A. *Chem. Eur. J.* **2021**, *27*, 7391-7401.

(18) For non-metal catalyzed hydrosilylation of CO_2, see reference 8m, 8o and

(a) Janes, T.; Yang, Y.; Song, D. *Chem. Commun.* **2017**, *53*, 11390-11398.

(b) Das Neves Gomes, C.; Jacquet, O.; Villiers, C.; Thuéry, P.; Ephritikhine, M.; Cantat, T. *Angew. Chem. Int. Edit.* **2012**, *51*, 187-190.

(c) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, *132*, 10660-10661.

(d) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Edit.* **2009**, *48*, 3322-3325.

(e) Riduan, S. N.; Ying, J. Y.; Zhang, Y. *ChemCatChem* **2013**, *5*, 1490-1496.

(f) Motokura, K.; Naijo, M.; Yamaguchi, S.; Miyaji, A.; Baba, T. *Chem. Lett.* **2015**, *44*, 1464-1466.

(g) Motokura, K.; Naijo, M.; Yamaguchi, S.; Miyaji, A.; Baba, T. *Chin. J. Catal.* **2017**, *38*, 434-439.

(h) Lang, X.-D.; He, L.-N. *ChemSusChem* **2018**, *11*, 2062-2067.

(i) Mukherjee, D.; Sauer, D. F.; Zanardi, A.; Okuda, J. *Chem. Eur. J.* **2016**, *22*, 7730-7733.

(19) Sattler, W.; Parkin, G. *J. Am. Chem. Soc.* **2011**, *133*, 9708-9711.

(20) A closely related zinc hydride compound, [Tntm]ZnH, which features thiopyridazine donors, has also been recently shown to catalyze the hydrosilylation of CO_2 by $(MeO)_3SiH$ to afford $HCO_2Si(OMe_3)_3$. See reference 17a.

(21) For recent reviews of the reactivity of CO_2 towards metal complexes, see:

(a) Grice, K. A. *Coord. Chem. Rev.* **2017**, *336*, 78-95.

(b) Paparo, A.; Okuda, J. *Coord. Chem. Rev.* **2017**, *334*, 136-149.

(c) Fan, T.; Chen, X.; Lin, Z. *Chem. Commun.* **2012**, *48*, 10808-10828.

(22) We have also observed that $PhSiH_3$ can reduce bicarbonate and carbonate to formate in molecular zinc complexes, but the reaction occurs *via* the insertion of CO_2 into a Zn–H bond. See: Sattler, W.; Parkin, G. *Catal. Sci. Tech.* **2014**, *4*, 1578–1584.

(23) (a) Deshmukh, M. M.; Sakaki, S. *Inorg. Chem.* **2014**, *53*, 8485-8493.

(b) Singh, V.; Sakaki, S.; Deshmukh, M. M. *Organometallics* **2018**, *37*, 1258-1270.

(c) Takagi, N.; Sakaki, S. *J. Am. Chem. Soc.* **2013**, *135*, 8955-8965).

(24) See references 8a, 9h and 10b.

(25) (a) Itagaki, S.; Yamaguchi, K.; Mizuno, N. *J. Mol. Catal. A: Chem.* **2013**, *366*, 347-352.

(b) Chauvier, C.; Thuery, P.; Cantat, T. *Angew. Chem. Int. Edit.* **2016**, *55*, 14096-14100.

(c) Chauvier, C.; Godou, T.; Cantat, T. *Chem. Commun.* **2017**, *53*, 11697-11700.

(d) Godou, T.; Chauvier, C.; Thuery, P.; Cantat, T. *Synlett* **2017**, *28*, 2473-2477.

(g) Motokura, K.; Kashiwame, D.; Miyaji, A.; Baba, R. *Org. Lett.* **2012**, *14*, 2642-2645.

(h) Koo, J.; Kim, S. H.; Hong, S. H. *Chem. Commun.* **2018**, *54*, 4995-4998.

(26) Lalrempuia, R.; Iglesias, M.; Polo, V.; Miguel, P. J. S.; Fernandez-Alvarez, F. J.; Perez-Torrente, J. J.; Oro, L. A. *Angew. Chem. Int. Edit.* **2012**, *51*, 12824-12827.

(27) (a) Singh, M. S.; Chowdhury, S. *RSC Adv.* **2012**, *2*, 4547-4592.

(b) Martins, M. A. P.; Frizzo, C. P.; Moreira, D. N.; Buriol, L.; Machado, P. *Chem. Rev.* **2009**, *109*, 4140-4182.

(c) Walsh, P. J.; Li, H. M.; de Parrodi, C. A. " *Chem. Rev.* **2007**, *107*, 2503-2545.

(28) Sheldon, R. A. *Green Chem.* **2005**, *7*, 267-278.

(29) For other examples, see reference 17b and

(a) Jaseer, E. A.; Akhtar, M. N.; Osman, M.; Al-Shammari, A.; Oladipo, H. B.; Garces, K.; Fernandez-Alvarez, F. J.; Al-Khattaf, S.; Oro, L. A. *Catal. Sci. Technol.* **2015**, *5*, 274-279.

(b) Azpeitia, S.; Garralda, M. A.; Huertos, M. A. *ChemCatChem* **2017**, *9*, 1901-1905.

(c) Szewczyk, M.; Bezlada, A.; Mlynarski, J. *ChemCatChem* **2016**, *8*, 3575-3579.

(d) Wekesa, F. S.; Arias-Ugarte, R.; Kong, L.; Sumner, Z.; McGovern, G. P.; Findlater, M. *Organometallics* **2015**, *34*, 5051-5056.

(e) Chen, C.; Hecht, M. B.; Kavara, A.; Brennessel, W. W.; Mercado, B. Q.; Weix, D. J.; Holland, P. L. *J. Am. Chem. Soc.* **2015**, *137*, 13244-13247.

(f) Conifer, C.; Gunanathan, C.; Rinesch, T.; Hölscher, M.; Leitner, W. *Eur. J. Inorg. Chem.* **2015**, 333-339.

(g) Zhao, M.; Xie, W.; Cui, C. *Chem.-Eur. J.* **2014**, *20*, 9259-9262.

(h) Bézier, D.; Jiang, F.; Roisnel, T.; Sortais, J. B.; Darcel, C. *Eur. J. Inorg. Chem.* **2012**, 1333-1337.

(i) Egbert, J. D.; Nolan, S. P. *Chem. Commun.* **2012**, *48*, 2794-2796.

(j) Wang, J.; Zhu, Z.; Huang, W.; Deng, M.; Zhou, X. *J. Organomet. Chem.* **2008**, *693*, 2188-2192.

(k) Murata, T.; Hiyoshi, M.; Ratanasak, M.; Hasegawa, J.; Ema, T. *Chem. Commun.* **2020,** *56*, 5783-5786.

(l) Julián, A.; Polo, V.; Jaseer, E. A.; Fernández-Alvarez, F. J.; Oro, L. A. *ChemCatChem* **2015**, *7*, 3895-3902.

(30) Sattler, W.; Ruccolo, S.; Chaijan, M. R.; Allah, T. N.; Parkin, G. *Organometallics* **2015**, *34*, 4717-4731.

(31) It is pertinent to note that a variety of other mechanisms for hydrosilylation of carbonyl compounds have been discussed in the literature. See, for example, reference 30 and

(a) Iglesias, M.; Fernandez-Alvarez, F. J.; Oro, L. A. *ChemCatChem* **2014**, *6*, 2486-2489.

(b) Chakraborty, S.; Guan, H. *Dalton Trans.* **2010**, *39*, 7427–7436.

(32) For another example of this transformation, see reference 17b.

(33) In addition to the reduction of the direct reduction of formate to methoxy species, it is pertinent to note that formic acid can also be converted to methanol

via disproportionation. See, for example reference 3 and:

(a) Neary, M. C.; Parkin, G. *Chem. Sci.* **2015**, *6*, 1859-1865.

(b) Miller, A. J. M.; Heinekey, D. M.; Mayer, J. M.; Goldberg, K. I. *Angew. Chem. Int. Edit.* **2013**, *52*, 3981-3984.

(c) Chauvier, C.; Imberdis, A.; Thuery, P.; Cantat, T. *Angew. Chem. Int. Edit.* **2020**, *59*, 14019-14023.

(d) Savourey, S.; Lefèvre, G.; Berthet, J. C.; Thuery, P.; Genre, C.; Cantat, T. *Angew. Chem.-Int. Edit.* **2014**, *53*, 10466-10470.

(e) Alberico, E.; Leischner, T.; Junge, H.; Kammer, A.; Sang, R.; Seifert, J.; Baumann, W.; Spannenberg, A.; Junge, K.; Beller, M. *Chem. Sci.* **2021**, *12*, 13101-13119.

(34) The formation of methoxy species $MeOSiR_3$ upon reaction of CO_2 with R_3SiH is accompanied by the siloxane, $R_3SiOSiR_3$, which provides the driving force for removing the oxygen from the formate moiety. See, for example, reference 8a and Du, C.; Chen, Y. *Acta Chim. Sin.* **2020**, *78*, 938-944.

(35) (a) Rit, A.; Zanardi, A.; Spaniol, T. P.; Maron, L.; Okuda, J. *Angew. Chem. Int. Edit.* **2014**, *53*, 13273-13277.

(b) Peterson, E.; Khalimon, A. Y.; Sirnionescu, R.; Kuzmina, L. G.; Howard, J. A. K.; Nikonov, G. I. *J. Am. Chem. Soc.* **2009**, *131*, 908-909.

(c) Boone, C.; Korobkov, I.; Nikonov, G. I. *ACS Catal.* **2013**, *3*, 2336-2340.

(36) For other reports of redistribution reactions of silanes, see reference 17b and

(a) Ryan, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 4730-4734.

(b) Buchwald, S. L. *Chem. Eng. News* **1993**, *71*, 2.

(37) For examples of hydrosilylation of CO_2 to the methanol level catalyzed by zinc compounds, see: 17b, 17c, 34 and

(a) Zhang, Q.; Fukaya, N.; Fujitani, T.; Choi, J.-C. "Carbon dioxide hydrosilylation to methane catalyzed by zinc and other first-row transition metal salts" *Bull. Chem. Soc. Jpn.* **2019**, *92*, 1945-1949.

(b) Specklin, D.; Hild, F.; Fliedel, C.; Gourlaouen, C.; Veiros, L. F.; Dagorne, S. *Chem. Eur. J.* **2017**, *23*, 15908-15912.

(c) Ritter, F.; Spaniol, T. P.; Douair, I.; Maron, L.; Okuda, J. *Angew. Chem. Int. Edit.* **2020**, *59*, 23335-23342.

(38) For other examples of hydrosilylation to the methanol level, see reference 11, 18e,f and:

(a) Eisenschmid T. C.; Eisenberg, R. *Organometallics* **1989**, *8*, 1822-1824.

(b) Metsanen, T. T.; Oestreich, M. *Organometallics* **2015**, *34*, 543-546.

(c) Morris, D. S.; Weetman, C.; Wennmacher, J. T. C.; Cokoja, M.; Drees, M.; Kuhn, F. E.; Love, J. B. *Catal. Sci. Technol.* **2017**, *7*, 2838-2845.

(d) Khandelwal, M.; Wehmschulte, R. J. *Angew. Chem. Int. Edit.* **2012**, *51*, 7323-7326.

(e) Saleh, M.; Powell, D. R.; Wehmschulte, R. J. *Organometallics* **2017**, *36*, 4810-4815.

(39) In addition to the experimental evidence for the catalytic cycle, the reaction has also been addressed theoretically, which provides additional support for the proposed mechanism. See reference 23a.

(40) (a) Sadow, A. D. *Comp. Coord. Chem. III*, Chapter 3.06; Constable, E. C.; Parkin, G.; Que, L., Jr. (Eds.) Elsevier, 2021.

(b) Wiegand, A. K.; Rit, A.; Okuda, J. *Coord. Chem. Rev.* **2016**, *314*, 71-82.

(c) Roy, M. M. D.; Omana, A. A.; Wilson, A. S. S.; Hill, M. S.; Aldridge, S.; Rivard, E. *Chem. Rev.* **2021,** *121*, 12784-12965.

(41) Other types of mechanisms are also possible. See, for example, reference 8.

(42) See references 8e, 8g, 16c,18k, 38b and

(a) Park, S.; Bézier, D.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 11404-11407.

(b) Chen, J.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y. X. *J. Am. Chem.*

Soc. **2016**, *138*, 5321-5333.

(d) Mitton, S. J.; Turculet, L. *Chem. Eur. J.* **2012**, *18*, 15258-15262.

(e) Jiang, Y.; Blacque, O.; Fox, T.; Berke, H. *J. Am. Chem. Soc.* **2013**, *135*, 7751-7760.

(f) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, *128*, 12362-12363.

(g) LeBlanc, F. A.; Piers, W. E.; Parvez, M. *Angew. Chem. Int. Ed.* **2014**, *53*, 789-792.

(h) Rios, P.; Curado, N.; Lopez-Serrano, J.; Rodriguez, A. *Chem. Commun.* **2016**, 52, 2114-2117.

(i) Rios, P.; Rodriguez, A.; Lopez-Serrano, J. *ACS Catal.* **2016**, *6*, 5715-5723.

(j) Scheuermann, M. L.; Semproni, S. P.; Pappas, I.; Chirik, P. J. *Inorg. Chem.* **2014**, *53*, 9463-9465.

(k) Del Rio, N.; Lopez-Reyes, M.; Baceiredo, A.; Saffon-Merceron, N.; Lutters, D.; Muller, T.; Kato, T. *Angew. Chem. Int. Edit.* **2017**, *56*, 1365-1370.

(l) Lu, Z.; Hausmann, H.; Becker, S.; Wegner, H. A. *J. Am. Chem. Soc.* **2015**, *137*, 5332-5335.

(m) Berkefeld, A.; Piers, W. E.; Parvez, M.; Castro, L.; Maron, L.; Eisenstein, O. *Chem. Sci.* **2013**, *4*, 2152-2162.

(n) Mu, Z.-J.; Ding, X.; Chen, Z.-Y.; Han, B.-H. *ACS Appl. Mater. Interfaces* **2018**, *10*, 41350-41358.

(o) Huang, F.; Lu, G.; Zhao, L.; Li, H.; Wang, Z.-X. *J. Am. Chem. Soc.* **2010**, *132*, 12388-12396.

(p) Huang, W. H.; Roisnel, T.; Dorcet, V.; Orione, C.; Kirillov, E. *Organometallics* **2020**, *39*, 698-710.

(q) Jansen, A.; Pitter, S. *J. Mol. Catal. A: Chem.* **2004**, *217*, 41-45.

(43) A trinuclear zinc hydride complex, $[(IMes)_3Zn_3H_4(THF)]\}^{2+}$, has also been shown to catalyze the hydrosilylation of CO_2 be $(EtO)_3SiH$ to afford $HCO_2Si(OEt)_3$ and $H_2C[OSi(OEt)_3]_2$. See reference 35a.

(44) (a) Ruccolo, S.; Rauch, M.; Parkin, G. *Chem. Sci.* **2017**, *8*, 4465-4474.

(b) Rauch, M.; Ruccolo, S.; Parkin, G. *J. Am. Chem. Soc.* **2017**, *139*, 13264-13267.

(45) See reference 16c and Rauch, M.; Strater, Z.; Parkin, G. *J. Am. Chem. Soc.* **2019**, *141*, 17754-17762.

(46) See, for example references 18e,f, 42b, 42o, 45 and

(a) Zhu, D.-Y.; Fang, L.; Han, H.; Wang, Y.; Xia, J.-B. *Organic Letters* **2017**, *19*, 4259-4262.

(b) Zhu, D.-Y.; Li, W.-D.; Yang, C.; Chen, J.; Xia, J.-B. *Org. Lett.* **2018**, *20*, 3282-3285.

(47) For further reference, dissociation of formaldehyde from $H_2C(OSiH_2Ph)_2$ to afford $O(SiH_2Ph)_2$ has been calculated to have an activation barrier of 26.7 kcal mol^{-1}. See reference 42o.

(48) Huang, F.; Zhang, C.; Jiang, J.; Wang, Z.-X.; Guan, H. *Inorg. Chem.* **2011**, *50*, 3816-3825.

(49) Caise, A.; Hicks, J.; Fuentes, M. A.; Goicoechea, J. M.; Aldridge, S. *Chem. Eur. J.* **2021**, *27*, 2138-2148.

(50) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic Chemistry*, Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 2, pp 6-23.

(b) Burger, B.J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98.

(c) Shriver, D. F.; Drezdzon, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2nd Edition; Wiley-Interscience: New York, 1986.

(51) (a) Jaguar, version 8.9, Schrodinger, Inc., New York, NY, 2015.

(b) Bochevarov, A. D.; Harder, E.; Hughes, T. F.; Greenwood, J. R.; Braden, D. A.; Philipp, D. M.; Rinaldo, D.; Halls, M. D.; Zhang, J.; Friesner, R. A. *Int. J. Quantum Chem.* **2013**, *113*, 2110–2142.