

Carbon Dioxide Hydrosilylation to Methane Catalyzed by Zinc and Other First-Row Transition Metal Salts

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Abstract

We accomplished zinc catalyzed hydrosilylation of carbon dioxide (CO₂) to silyl formate (C^{+II}), bis(silyl)acetal (C⁰), methoxysilane (C^{-II}), and finally methane (C^{-IV}). Among several zinc salts, we found that Zn(OAc)₂ with ligand 1,10phenanthroline was the best. A turnover number of 815000 was achieved using the zinc catalyst to yield C^{+II}. Unexpectedly, we observed the generation of CO from CO₂ and hydrosilane for the first time. In addition to Zn, other first-row transition metals (Mn, Fe, Co, Ni, and Cu) also served as Lewis acid catalysts for CO₂ hydrosilylation, regardless of the nature of the metal.

Keywords: Carbon dioxide | Hydrosilylation | Zinc

1. Introduction

Carbon dioxide (CO₂) is a non-toxic, non-flammable, and inexpensive gas, and it can be applied as a C1 synthon for the preparation of a range of valuable chemicals.^{1–5} Although the synthesis of organic carbonate, urea, or carbamate from CO₂ does not involve changes in the oxidation state of carbon, the transformation of CO₂ to formic acid, formaldehyde, methanol, and methane requires the reduction of carbon to C^{+II}, C⁰, C^{-II}, and C^{-IV}, respectively. For such processes, hydrosilanes, hydroboranes, and H₂ can be employed as reductants for CO₂.^{6–13} With hydrosilane, the reduction of CO₂ is facile, as this process involves the cleavage of a weak Si–H bond, followed by the formation of a stronger Si–O bond.

As indicated in Scheme 1, the products of CO_2 hydrosilylation contain four different oxidation states, including C^{+II} , C^0 , C^{-II} , and C^{-IV} . During this process, the reduction of CO_2



Scheme 1. Catalytic CO₂ hydrosilylation.

to formic acid level is the most facile, yielding silyl formate (HCOOSiR₃, **C**^{+II}) when noble,^{14–26} non-noble metal,^{27–36} and organocatalysts³⁷ are employed. The further reduction of CO₂ to yield bis(silyl)acetal (CH₂(OSiR₃)₂, **C**⁰),^{22–24,38–44} methoxy-silane (CH₃OSiR₃, **C**^{-II}),^{22–24,34,39,41,45–51} or methane (CH₄, **C**^{-IV})^{22,39,41,43,47,48,52–59} has also been reported, in addition to mechanistic studies into CO₂ hydrosilylation.^{60–67}

In the context of previous work carried out in this area, we considered a number of issues that required addressing. For example, although all CO₂ hydrosilylations reported to date require a catalyst, a number also require the use of noble metals^{14–19,21–26} and both the ligands and organocatalysts employed tend to be complicated. The use of a non-precious catalyst based on readily available ligands is therefore desirable. In addition, only 25% of studies in this field reported full hydrosilylation of CO₂ to CH₄. Furthermore, although the properties of the catalyst metal cations have been examined, the interactions between counteranions and hydrosilanes received little attention.

We previously reported CO_2 as a C1 building block in organic synthesis^{68–72} based on a catalytic combination of $Zn(OAc)_2$ and ligand 1,10-phenanthroline (phen).⁶⁸ In this system, carboxylate-assisted proton abstraction from the amine was the key step in the catalytic cycle.^{68,69,71} Encouraged by these results, we herein report the use of a $Zn(OAc)_2$ /phen

catalyst (1, Zn(OAc)₂:phen = 1:3) for the hydrosilylation of CO₂. This strategy is particularly desirable as both Zn(OAc)₂ and phen are commercially available. Thus, we attempted the step-by-step reduction of CO₂ to CH₄ with the characterization of ¹H, ¹³C{¹H}, and ¹³C NMR spectra. Furthermore, we examined the use of other first-row transition metal acetates as catalysts (M(OAc)₂, M = Mn, Fe, Co, Ni, and Cu).

2. Experimental

Materials. Unless stated otherwise, all of the chemicals were purchased from Sigma-Aldrich, Tokyo Chemical Industry (TCI), or Wako Chemicals in the best grade, and they were stored under N_2 in a glovebox. Ph_2SiD_2 was purchased from Santa Cruz Biotechnology. CO_2 was purchased from Showa Tansan. ¹³CO₂ was purchased from Sigma-Aldrich (99.9% atom ¹³C).

Instruments. The catalytic hydrosilylation reactions were carried out in a 10 mL stainless-steel autoclave with a gaspressure monitor (max. 25 MPa), or in a valved NMR tube (V = 1 mL) produced by Norell Inc. All of the operations were carried out in a glovebox under N₂. ¹H, ¹³C{¹H}, and ¹³C NMR spectra were recorded on a 400 MHz Bruker NMR spectrometer at 25 °C.

Identifying CO₂ Reduction Products. (1) Silyl Formate (C^{+II}): Zn(OAc)₂ (0.02 mmol, 3.7 mg), phen (0.06 mmol, 10.8 mg), CD₃CN (1 mL), Ph₂SiH₂ (1 mmol, 184 mg) were added to an autoclave. The autoclave was sealed tightly, and filled with CO₂ to 1 MPa (initial pressure). After 24 h reaction at room temperature, CO₂ was released gently, and mesitylene was added as an internal standard. The solution was then transferred to a J. Young NMR tube for analysis. ¹H NMR (400 MHz): 8.3 ppm for *H*COOSiR₃; ¹³C{¹H} NMR (100 MHz): 160 ppm for HCOOSiR₃.

(2) Bis(silyl)acetal (C⁰): $Zn(OAc)_2$ (0.02 mmol, 3.7 mg), phen (0.06 mmol, 10.8 mg), CD₃CN (1 mL), Ph₂SiH₂ (2 mmol, 368 mg) were added to an autoclave. The autoclave was sealed tightly, and filled with CO₂ to 0.25 MPa (initial pressure). After 24 h reaction at room temperature, CO₂ was released gently, and mesitylene was added as an internal standard. The solution was then transferred to a J. Young NMR tube for NMR analysis. ¹H NMR (400 MHz): 5.8 ppm for CH₂(OSiR₃); ¹³C{¹H} NMR (100 MHz): 83 ppm for CH₂(OSiR₃).

(3) Methoxysilane (C^{-II}): $Zn(OAc)_2$ (0.02 mmol, 3.7 mg), phen (0.06 mmol, 10.8 mg), CD₃CN (1 mL), Ph₂SiH₂ (3 mmol, 552 mg) were added to an autoclave. The autoclave was sealed tightly, and filled with CO₂ to 0.25 MPa (initial pressure). After 24 h reaction at 80 °C, CO₂ was released gently, and mesitylene was added as an internal standard. The solution was then transferred to a J. Young NMR tube for NMR analysis. ¹H NMR (400 MHz): 3.6 ppm for CH₃OSiR₃; ¹³C{¹H} NMR (100 MHz): 52 ppm for CH₃OSiR₃.

(4) ¹³CH₄ (C^{-IV}): Zn(OAc)₂ (0.01 mmol, 1.8 mg), phen (0.03 mmol, 5.4 mg), B(C₆F₅)₃ (0.01 mmol, 5.1 mg), C₆D₆ (0.15 mL), Ph₂SiH₂ (0.5 mmol, 92 mg) were added to a valved NMR tube, and filled with ¹³CO₂ to 0.25 MPa (initial pressure). Then the NMR tube was heated to 80 °C for 24 h reaction. ¹H NMR (400 MHz): 0.16 ppm (d, J = 125 Hz). ¹³C NMR (100 MHz): -4.57 ppm (q, J = 125 Hz). ¹³C{¹H} NMR (100 MHz): -4.57 ppm (s). (5) Detection of ¹³CO: $Zn(OAc)_2$ (0.01 mmol, 1.8 mg), phen (0.03 mmol, 5.4 mg), CD_3CN (0.15 mL), Ph_2SiH_2 (0.2 mmol, 36.8 mg) were added to a valved NMR tube, and filled with ¹³CO₂ to 0.25 MPa (initial pressure) at room temperature. ¹³C NMR (100 MHz): 184 ppm (s). ¹³C{¹H} NMR (100 MHz): 184 ppm (s).

3. Results and Discussion

Initially, the catalytic ability of 1 (1:3 mixture of $Zn(OAc)_2$) and phen) in the activation of hydrosilane was investigated. According to the transformation indicated in Scheme 2, rapid H/D exchange was observed between Ph₂SiD₂ and PhSiH₃ at 25 °C over 0.5 h (Figure S1, supporting information), thereby suggesting the formation of a Zn-H(D) intermediate. The obtained results appeared to confirm that 1 promoted both the rapid activation of hydrosilane and hydride exchange. Furthermore, in the presence of 1, bubbles were observed immediately in a mixture of Ph₂SiD₂ and MeOH, which suggested the formation of deuterated hydrogen gas (HD). Indeed, in the ¹HNMR spectrum recorded in a valved NMR tube, a triplet with a J value of 42.6 Hz was observed at 4.4 ppm in C_6D_6 , which confirmed the formation of HD gas (Figure S2, supporting information). These results suggested that 1 was an efficient catalyst for activating hydrosilanes.

Encouraged by the efficient catalytic performance of 1, we carried out an initial investigation into the hydrosilvlation of CO₂ using an autoclave containing a solution of Ph₂SiH₂ in CD_3CN . In the presence of 2 mol% 1, silvl formate was formed at 25 °C under a CO₂ pressure of 1 MPa (initial pressure), as confirmed by ¹H and ¹³CNMR measurements (i.e., signals at 8.3 and 160 ppm, respectively). With excess CO₂, both Si-H bonds could be activated to yield (HCOO)₂SiPh₂ with m/z =272 (Figure S7, supporting information). In the presence of phen and other zinc salts, such as $ZnBr_2$, ZnI_2 , and $Zn(ClO_4)_2$, the catalytic reactivities were poor, while in the presence of $ZnCl_2$, $ZnSO_4$, and $Zn(OTf)_2$ (OTf = trifluoromethanesulfonate), the reduction of CO2 to silyl formate was observed in moderate to good yields. Polar solvent was good media while non-polar solvent (e.g. toluene) was not preferred (Table 1). In addition to Ph₂SiH₂, we found that PhSiH₃ was also a good source for CO₂ hydrosilylation, however, Ph₃SiH, Et₃SiH, and (EtO)₃SiH had poor reactivities (Table S1).

We therefore considered that the catalyst efficiency was determined by interactions between hydrosilane and the counteranion of the zinc salt (i.e., an O or Cl donor). The influence of the acetate anion on activation of the Si–H bond was therefore monitored by ¹H NMR spectroscopy. Thus, in the



Scheme 2. H/D exchange and neutralization.

Entry	Catalyst	Yield
1	Zn(OAc) ₂ /phen	99%
2	ZnCl ₂ /phen	78%
3	ZnBr ₂ /phen	trace
4	ZnI ₂ /phen	16%
5	ZnSO ₄ /phen	95%
6	Zn(ClO ₄) ₂ /phen	trace
7	Zn(OTf) ₂ /phen	53%
8	$Zn(OAc)_2/phen^b$	99%
9	Zn(OAc) ₂ /phen ^c	7%
10	none	trace

Table 1. Catalyst and solvent screening for CO_2 hydrosilylation to silyl formate (C^{+II}).^{*a*}

^{*a*}Reaction conditions: Ph₂SiH₂ (1 mmol), Zn salt (0.02 mmol), phen (0.06 mmol), CD₃CN (1 mL), CO₂ (1 MPa), 24 h, 25 °C. Yields were determined by ¹H NMR (400 MHz) using mesitylene as the internal standard. ^{*b*}Solvent = DMF. ^{*c*}Solvent = toluene.



Figure 1. ¹H NMR shifts (CD₃CN, 400 MHz) of Ph₂SiH₂ and **1** mixture at 25 °C. Tetramethylsilane (TMS) was added as an internal standard (0.0000 ppm).



Scheme 3. Proposed interactions between the hydrosilane and 1 (L = 1,10-phenanthroline).

presence of 0.1 equiv. **1**, the position of the Si–H signal of Ph₂SiH₂ was shifted upfield from 4.8887 to 4.8678 ppm. Moreover, in the presence of 0.2 and 0.3 equiv. of **1**, more significant shifts to 4.8586 and 4.8461 ppm were observed (Figure 1). It therefore appeared that a six-member ring was formed with the interaction between Zn(OAc)₂ and Si–H thereby activating the Si–H bond for the subsequent CO₂ insertion (Scheme 3). With Zn(ClO₄)₂, there was almost no NMR shift. Eyring analysis of CO₂ hydrosilylation to C^{+II} from 25 to 55 °C (Figure 2) resulted $\Delta H^{\ddagger} = 19.3$ kJ mol⁻¹, $\Delta S^{\ddagger} = -249$ J mol⁻¹ K⁻¹, and $\Delta G^{\ddagger_{298}} = 93.5$ kJ mol⁻¹. The large negative entropy of activation is in agreement with an association mechanism.

As the CO₂ hydrosilylation could be carried out with decreased loadings of 1, we moved on to examine the efficiency of 1 in the hydrosilylation of CO₂ to C^{+II} , as summarized in



Figure 2. Eyring plot of CO₂ hydrosilylation to C^{+II} from 25 to 55 °C. Reaction conditions: Ph₂SiH₂ (0.1 mmol), Zn(OAc)₂ (0.002 mmol), phen (0.006 mmol), MeCN (1 mL), CO₂ (1 MPa), 15 min. Yield of C^{+II} was determined by ¹H NMR using mesitylene as the internal standard.

Table S3. We found that at 125 °C, the turnover number (TON) reached 815000 (81.5% yield) with high thermostability and a catalyst loading of 1 ppm. To the best of our knowledge, no TON $>10^5$ has been reported for the catalytic CO₂ hydrosilylation to C^{+II}. Other outstanding examples include a copper *N*-heterocyclic carbene complex (TON = 7500),²⁹ Ru₃(CO)₁₂ (TON = 9000),²² and a copper diphosphine complex (TON = 70000).²⁸

Further reduction of CO₂ with hydrosilane was found to yield C^{0} . However, tuning the selectivity of this step was challenging, as a precise 2:1 molar ratio of hydrosilane to CO₂ must be employed. Interestingly, in the presence of greater quantities of CO_2 , the formation of C^{+II} was preferred, while with higher hydrosilane contents, methoxysilane C^{-II} was formed preferentially. The amount of CO₂ in the autoclave was calculated using the ideal gas equation. At 25 °C, 1 mmol CO₂ was reduced in the presence of 2 mmol Ph₂SiH₂ and 1 in CD₃CN to give 0.40 mmol bis(silyl)acetal C^0 , as confirmed by the observation of ¹H and ¹³C{¹H} NMR signals at 5.8 and 83 ppm, respectively. In addition, the reduction of CO_2 to C^0 was disfavored at high temperatures. More specifically, upon increasing the temperature to 80 °C, the preferred product was C^{-II} (methoxysilane, CH₃OSiR₃), which represents the same oxidation state as methanol. Longer reaction times led to over-reduction and the formation of $\tilde{C^{-II}}$ (Figure S12, supporting information). The product C^{-II} was confirmed by the observation of ¹H and ¹³C{¹H} NMR signals at 3.6 and 52 ppm, respectively.

Unexpectedly, upon the attempted preparation of a \mathbb{C}^{0} product from ¹³CO₂, the formation of ¹³CO was observed, which was catalyzed by **1** in a valved NMR tube at 25 °C in CD₃CN (Figure 3) confirmed by the observation of a signal at 184 ppm in the ¹³C NMR spectrum. Although catalytic reduction of CO₂ to CO has been documented with electro- and photo-catalytic processes,⁷ the characterization of CO from CO₂ hydrosilylation was challenging.⁷³ However, upon attempting the preparation of silyl formate, only traces of ¹³CO were detected, illustrating that no competing reaction existed between silyl formate (**C**^{+II}) and CO. Nevertheless, it appeared that a competing reaction existed between CO and bis(silyl)acetal (**C**⁰) due to the relatively low yield of **C**⁰.

The full reduction of CO_2 by hydrosilane resulted in the production of CH_4 . Theoretically, the reduction of CO_2 to CH_4 (C^{-IV}) requires at least 4 equiv. of hydrosilane. However, we



Figure 3. Confirmation of ¹³CO formation by ¹³C NMR spectroscopy (100 MHz, CD₃CN) at 25 °C. Reaction conditions: 0.4 mmol Ph₂SiH₂, 0.2 mmol ¹³CO₂, 2 mol% **1**, 25 °C. (A) 10 min and (B) 2 h.



Figure 4. Confirmation of ${}^{13}CH_4$ formation in C_6D_6 at 25 °C: (A) ${}^{1}H$ NMR (400 MHz), (B) ${}^{13}C$ NMR (100 MHz), (C) ${}^{13}C{}^{1}H$ NMR (100 MHz) after 5 h reaction, and (D) ${}^{13}C{}^{1}H$ NMR (100 MHz) after 24 h reaction.

found that CH₄ formation was not observed at 80 °C, with C^{-II} being observed instead. Fortunately, the addition of tris(pentafluorophenyl)borane (B(C₆F₅)₃) assisted hydride transfer,⁵³ acting as a hydride shuttle between Si–H and [HB(C₆F₅)₃]^{-,74} where the latter species reduced C^{-II} to CH₄, a process which required a greater energy input.⁶¹ We also observed that the hydrosilylation of CO₂ to CH₄ was carried out preferentially in a non-polar solvent such as benzene. Thus, the formation of ¹³CH₄ from Ph₂SiH₂ and ¹³CO₂ catalyzed by 1 and B(C₆F₅)₃ at 80 °C over 16 h was confirmed by ¹H NMR (0.16 ppm, doublet, J = 125 Hz) and ¹³C NMR (-4.57 ppm, quintet, J = 125 Hz) (Figure 4). Note that the use of B(C₆F₅)₃ as a co-catalyst was not required for the preparation of C^{+II}, C⁰, and C^{-II} products.

It was therefore apparent from our results that the described $Zn(OAc)_2$ -based catalyst (1) could successfully transform CO_2 to C^{+II} , C^0 , C^{-II} , and C^{-IV} (with $B(C_6F_5)_3$) products in the presence of Ph₂SiH₂. In addition, our results confirmed that the identity of the counteranion was key in activating the Si–H bond, while the metal took part in Lewis acid binding with CO_2 . We were therefore curious to examine the use of other first-row transition metal acetates (M(OAc)₂, M = Mn, Fe, Co, Ni, and Cu) as catalysts for this reaction, as all metals between Mn and Zn exhibit Lewis acidity. Indeed, we found that all metal acetates examined catalyzed the hydrosilylation of CO_2 to C^{+II} , C^0 , C^{-II} , and C^{-IV} under identical conditions to those employed for 1 (Tables S4–S6 and Figure S15, supporting

information, except Ni(OAc)₂ for CO₂ hydrosilylation to C^{-II}). These observations therefore removed the limitation of the metal employed in the CO₂ hydrosilylation process, with metals from different periodic groups being suitable. However, we did note that the selection of an appropriate counteranion was necessary for this process.

4. Conclusion

In summary, we successfully employed Zn(OAc)₂/phen catalyst (1) for the step-by-step hydrosilylation of CO₂ to CH₄ through silvl formate (C^{+II}) , bis(silvl)acetal (C^{0}) , methoxysilane (C^{-II}). With ¹³CO₂, the final reduction product ¹³CH₄ was fully characterized by ¹H, ¹³C{¹H}, and ¹³C NMR, cocatalyzed by $B(C_6F_5)_3$. The reaction conditions and selectivity were summarized in Table S7 and Table S8. Unusually, we accomplished the catalytic ¹³CO₂ hydrosilylation to yield ¹³CO. In addition to zinc-based catalyst 1, other metal acetate catalysts $(M(OAc)_2, M = Mn, Fe, Co, Ni, or Cu)$ also served as catalysts for the CO₂ hydrosilylation. We therefore expect that our described process can be applicable in the area of organic and green synthesis for the transformation of amines (RR'NH) to N-formamides (RR'N-CHO) and N-methylamines (RR'N-CH₃) using CO₂ as the C1 building block.⁷⁵⁻⁷⁸ Studies are currently ongoing in our laboratory into the above method.

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Supporting Information

Detailed NMR spectra, silane screening, and the summary of reaction conditions and selectivity. This material is available on https://doi.org/10.1246/bcsj.20190203.

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