

An Efficient Iridium Catalyst for Reduction of Carbon Dioxide to Methane with Trialkylsilanes

Sehoon Park, David Bézier, and Maurice Brookhart*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

S Supporting Information

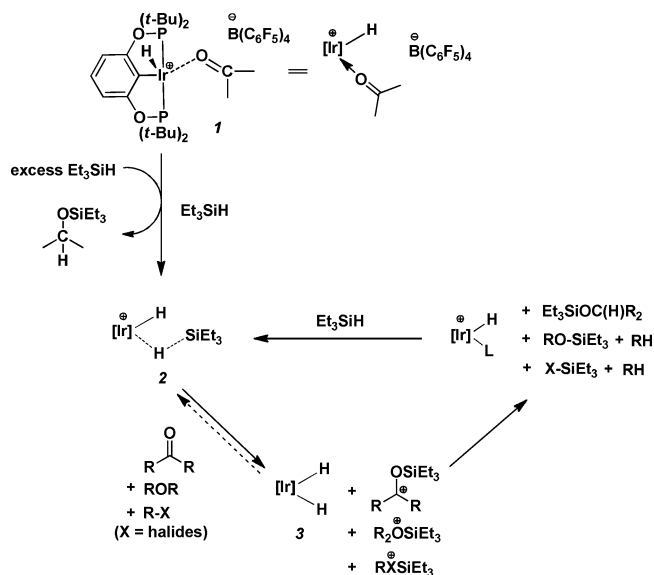
ABSTRACT: Cationic silane complexes of general structure (POCOP)Ir(H)(HSiR₃) {POCOP = 2,6-[OP-(*t*Bu)₂]₂C₆H₃} catalyze hydrosilylations of CO₂. Using bulky silanes results in formation of bis(silyl)acetals and methyl silyl ethers as well as siloxanes and CH₄. Using less bulky silanes such as Me₂EtSiH or Me₂PhSiH results in rapid formation of CH₄ and siloxane with no detection of bis(silyl)acetal and methyl silyl ether intermediates. The catalyst system is long-lived, and 8300 turnovers can be achieved using Me₂PhSiH with a 0.0077 mol % loading of iridium. The proposed mechanism for the conversion of CO₂ to CH₄ involves initial formation of the unobserved HCOOSiR₃. This formate ester is then reduced sequentially to R₃SiOCH₂OSiR₃, then R₃SiOCH₃, and finally to R₃SiOSiR₃ and CH₄.

There has been increasing interest in developing homogeneous catalysts for the reduction of CO₂, an abundant and sustainable C-1 source, under mild conditions to methanol or methane.^{1–7} Sanford has recently reported a cascade system which employs a series of three catalysts and hydrogen as the reductant and involves initial production of formate, catalytic esterification, and finally reduction of methyl formate to methanol.^{2a} A nickel-catalyzed hydroboration of CO₂ with catecholborane (HBcat) which yields CH₃OBCat has been described and proceeds through initial reaction of a nickel(II) hydride complex with CO₂ to yield a nickel formate complex.³ The strong Si–O bond has led to successful reduction of CO₂ using hydrosilylation procedures.^{5–7} Ruthenium and copper complexes have been reported as catalysts for the hydrosilylation of CO₂ to yield formoxysilanes.⁶ Ying reported the first hydrosilylation of CO₂ catalyzed by an *N*-heterocyclic carbene which gives methoxysilanes with a high turnover number and moderate turnover frequency.^{5b}

Two groups have reported catalyst systems employing silanes which reduce CO₂ to methane.^{7a,b} Matsuo and Kawaguchi^{7a} showed that a tandem catalytic system using Zr(IV) bis-benzyl complexes in combination with B(C₆F₅)₃ reduces CO₂ to methane with various silanes. Using PhMe₂SiH, a TOF of 150/h was observed and a total turnover number of 225 was achieved. Piers et al.^{7b} showed that B(C₆F₅)₃ and an ammonium borate work in tandem to achieve catalytic reduction of CO₂ to methane with Et₃SiH at modest rates but with high catalyst stability. Sequential reduction products Et₃SiO₂CH, Et₃SiOCH₂OSiEt₃, and Et₃SiOCH₃ could be observed as intermediates.

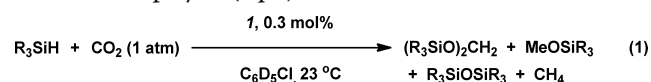
Recently we reported that the highly electrophilic η^1 -silane complex **2**, generated *in situ* from **1** and Et₃SiH, is an efficient catalyst for hydrosilylation of ketones and aldehydes,^{8a} and for reductive cleavage of C–O^{8b,c} and C–X^{8d,e} bonds (X = halides). Complex **2** transfers Et₃Si⁺ to oxygen or halogen atoms of the substrate to form the corresponding cationic species which are then reduced by reaction with the nucleophilic dihydride, **3**. The catalytic cycle is closed by reaction of the resultant cationic monohydride with silane (Scheme 1). Here we describe an efficient catalytic conversion

Scheme 1



of CO₂ to CH₄ via bis(silyl)acetal and methyl silyl ether intermediates using **1** in combination with tertiary silanes. Using PhMe₂SiH, catalyst lifetimes are very long (days) and turnover frequencies of *ca.* 190/h at 23 °C and 660/h at 60 °C were observed.

Several silanes were screened by carrying out reductions in C₆D₅Cl at 23 °C, 1 atm of CO₂ and monitoring reactions by NMR spectroscopy. A catalyst loading of 0.3 mol % relative to silane was employed (eq 1).



Received: June 1, 2012

Published: July 5, 2012

Table 1. Reduction of CO₂ with 1 and Trialkylsilanes^a

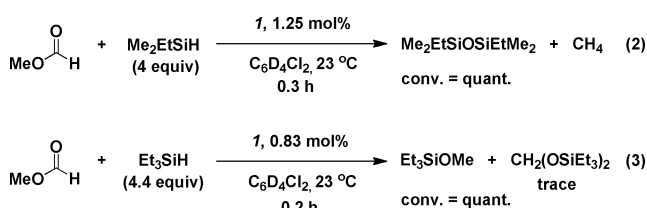
entry	silanes	time (h)	Product ^b			TON ^c	TOF (h ⁻¹) ^c
			(R ₃ SiO) ₂ CH ₂ :	R ₃ SiOMe:	(R ₃ Si) ₂ O		
1 ^d	Et ₃ SiH	2.5	7	1	4	48	19
2	Et ₃ SiH	22	1	2	5	138	6
3 ^{d,e}	Ph ₃ SiH	22.7	100	<1	0	36	2
4	Me ₂ EtSiH	1.7	0	0	1	149	88
5	Me ₂ PhSiH	1.7	0	0	1	119	70
6 ^d	Me ₂ <i>i</i> PrSiH	20	~0	~0	1	105	5
7 ^d	Et ₂ MeSiH	3.8	2	1	178	112	29

^aReaction conditions: 0.0025 mmol of 1, solvent = C₆D₅Cl, 300 equiv of silane, 23 °C. ^bDetermined by ¹H NMR with toluene as an internal standard. ^cDetermined by ¹H NMR based on mol of Si–H bond reacted per mol Ir. ^d[Ir](CO) complex observed in addition to [Ir]H(H₂)⁺ and/or 2 during the reaction. ^eWhite precipitates observed in the NMR tube.

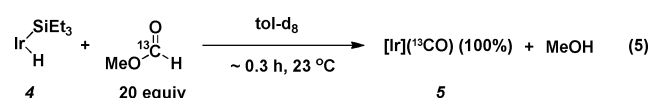
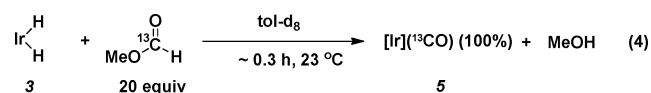
Results of the screening reactions are summarized in Table 1. A turnover number (TON) of 1 is defined as the consumption of 1 equiv of silane. Using Et₃SiH as a reductant, 48 turnovers are achieved in 2.5 h resulting in a mixture of CH₂(OSiEt₃)₂, CH₃OSiEt₃, and (Et₃Si)₂O in a ratio of 7:1:4; after 22 h, 138 turnovers are observed with a product ratio of 1:2:5 (Table 1, entries 1, 2).⁹ The decrease in turnover frequency (TOF) over reaction time is attributed to the reduced concentration of CO₂ in the NMR tube. The ¹H NMR spectrum shows characteristic resonances at δ5.09 and δ3.39 due to the CH₂– of CH₂(OSiEt₃)₂ and the CH₃– of CH₃OSiEt₃, respectively.^{7b} In addition, the ¹³C{¹H} NMR spectrum clearly exhibits signals due to triethylsilyl groups of the products (see Supporting Information). Triphenylsilane reacts slowly with CO₂ to give CH₂(OSiPh₃)₂ and trace amounts of triphenylsilylmethyl ether (entry 3). The GC trace of the gas in the head space of this reaction mixture shows no CH₄.

Use of less bulkier silanes leads to higher activity and selectivity for formation of CH₄ (entries 4–6). CO₂ is readily reduced with Me₂EtSiH and Me₂PhSiH to afford the corresponding siloxanes and CH₄ with TON = 149 and TON = 119 in 1.7 h, respectively. No silyl alkyl ether intermediates are observed by NMR spectroscopy throughout the reaction. Me₂*i*PrSiH reacts selectively to give (Me₂*i*PrSi)₂O and CH₄ with trace amounts of silyl alkyl ethers, although 20 h are required to achieve a TON of 105. Similar to Et₃SiH, the reaction of Et₂MeSiH with CO₂ over 3.8 h affords a mixture of CH₂(OSiMeEt₂)₂, MeOSiMeEt₂, and (Et₂MeSi)₂O in a ratio of 2:1:178 (entry 7). Observation of CH₂(OSiR₃)₂ and MeOSiR₃ intermediates implies that the reduction initially proceeds via hydrosilylation of CO₂ to yield a formoxysilane followed by conversion to the bis(silyl)acetal and then sequential reductive hydrosilylation of the two C–O bonds to form MeOSiR₃ and then the siloxane and CH₄.

To obtain further insight into the mechanism for formation of the silyl alkyl ether intermediates, we examined the hydrosilylation of methyl formate, a model compound for the presumed first-formed formoxysilane intermediate, using both Me₂EtSiH and Et₃SiH at 23 °C (eqs 2, 3).



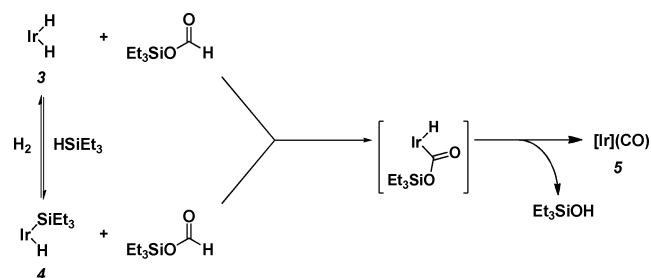
Methyl formate undergoes reductive hydrosilylation with Me₂EtSiH to give Me₂EtSiOSiEtMe₂ and CH₄ in 0.3 h; no intermediates were observed. In contrast, the reaction with Et₃SiH produces CH₃OSiEt₃ (>99%) and traces of the silylmethylacetal (<1%) in 0.2 h. These results are consistent with the proposal that CO₂ is transformed to CH₄ through the formoxysilane and that the C–O bonds of the bis(silyl)acetal and the silyl methyl ether are cleaved more slowly with Et₃SiH than with the less bulky Me₂EtSiH. Monitoring the reaction by ³¹P NMR spectroscopy shows major peaks due to 2 and/or [Ir]H(H₂)⁺ and a minor peak due to the [Ir](CO) complex, 5, when using bulky silanes Et₃SiH, Et₂MeSiH, *i*PrMe₂SiH, or Ph₃SiH as reductants. In order to identify a possible pathway for the formation of 5, we performed reactions of neutral dihydride 3 or [Ir](H)(SiEt₃) 4 with H¹³COOMe (20 equiv) (eqs 4, 5).



Complex 3 quantitatively converts to the [Ir](¹³CO) complex with formation of MeOH in 0.3 h by reaction with excess H¹³COOMe.¹⁰ Similarly, the neutral complex 4 in the presence of H¹³COOMe converts to the [Ir](¹³CO) complex in 0.3 h with formation of MeOH. Based on these results, carbonyl complex 5 is likely formed through the reaction of complex 3 and/or 4 with the formoxysilane, the first formed intermediate in the catalytic cycle (Scheme 2).¹¹

To assess the lifetime of the catalyst system, we first carried out reduction of CO₂ using Me₂PhSiH as a reductant under

Scheme 2



normal conditions (Table 1) and observed a TON of 76 and TOF of 127/h in 0.6 h. This reaction mixture was then allowed to stand at 23 °C for 22.5 h which led to depletion of the CO₂ in the NMR tube. Following the 22.5 h reaction, a fresh charge of CO₂ (1 atm) was introduced into the reaction mixture, whereupon formation of the siloxane (Me₂PhSiOSiPhMe₂) and CH₄ resumes with a TON of 70 and a TOF of 132/h in 0.53 h. This activity is essentially the same as that in the first catalytic cycle and indicates a very long catalyst lifetime.

In view of the high stability of the catalytic system, we examined a large scale reduction of CO₂ with Me₂PhSiH. Results are summarized in Table 2.

Table 2. Results of Large Scale Reduction of CO₂ with Me₂PhSiH^a

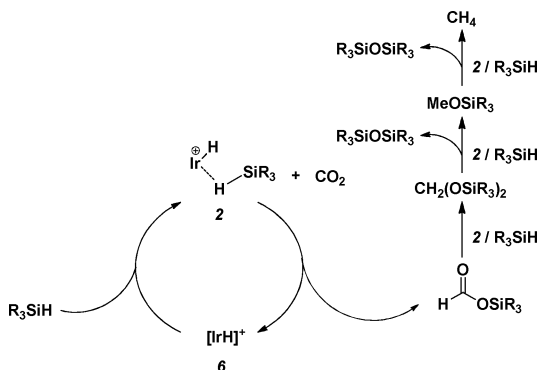
entry	time (h)	TON ^b	TOF (h ⁻¹) ^b	product	isolated yield (g)
1	24	4635	193	Me ₂ PhSiOSiPhMe ₂ + CH ₄	1.66
2	48	7092	148	Me ₂ PhSiOSiPhMe ₂ + CH ₄	2.54
3	72	8293	115	Me ₂ PhSiOSiPhMe ₂ + CH ₄	2.97
4 ^c	3	1982	661	Me ₂ PhSiOSiPhMe ₂ + CH ₄	0.71

^aReaction conditions: 0.0025 mmol of **1**, solvent = C₆H₅Cl (3 mL), Me₂PhSiH (5 mL), CO₂ (1 atm), 23 °C. ^bBased on mol of Si–H bond reacted per mol Ir. ^cReaction at 60 °C.

Complex **1** (0.0077 mol %) together with Me₂PhSiH initiates the reductive hydrosilylation of CO₂ to yield Me₂PhSiOSiPhMe₂ and CH₄ with up to a TON of ~8300 after 72 h. The turnover frequency falls over this period of time due to the consumption of silane. The reaction at 60 °C proceeds more rapidly to achieve TON = 1982 in only 3 h (entry 4), suggesting good thermal stability of the catalytic system.

Results obtained in this study are consistent with the proposed catalytic cycle shown in Scheme 3. Complex **2**,

Scheme 3. Proposed Catalytic Cycle in the CO₂ Reduction to CH₄



generated *in situ* from **1** and R₃SiH, reacts with CO₂ to yield the formoxysilane and [(POCOP)IrH]⁺ **6** which binds silane to regenerate **2**.¹² The formoxysilane rapidly undergoes hydrosilylation catalyzed by **2** to give the bis(silyl)acetal, R₃SiOCH₂OSiR₃. Reductive cleavage of the C–O bonds of the acetal by silanes is highly dependent on the steric bulk of the silanes. R₃SiOCH₂OSiR₃ readily converts to R₃SiOSiR₃ and

CH₄ with less crowded silanes, whereas bulky silanes slowly cleave C–O bonds of the acetal resulting in the observation of a mixture of products.

In summary, we have described a well-defined single iridium pincer catalyst for the reduction of CO₂ to CH₄ with trialkylsilanes under mild conditions. Using Me₂PhSiH as the reductant, more than 8200 turnovers were observed, thus showing this catalyst system is long-lived. The highly electrophilic nature of the iridium silane complex suggests that catalysis is initiated by transfer of R₃Si⁺ to CO₂ to generate a silyloxy carbenium ion.

■ ASSOCIATED CONTENT

Supporting Information

¹H and ¹³C NMR spectroscopic data of reaction mixtures resulted from the reduction of CO₂ with trialkylsilanes, GC traces of the gas in the head space of the reaction mixture, and full ref 2b. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

mbrookhart@unc.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of the National Science Foundation as part of the Center for Enabling New Technologies through Catalysis (CENTC, CHE-0650456). We thank Dr. Peng Kang for help with the GC measurement.

■ REFERENCES

- (1) For reviews of chemical utilization of CO₂, see: (a) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; Verlag Chemie: Weinheim, 1988. (b) Marks, T. J.; et al. *Chem. Rev.* **2001**, *101*, 953–996. (c) Aresta, M.; Dibenedetto, A. *Dalton Trans.* **2007**, 2975–2992. (d) Jessop, P. G.; Joó, F.; Tai, C.-C. *Coord. Chem. Rev.* **2004**, *248*, 2425–2442. (e) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365–2387.
- (2) For homogeneous hydrogenation of CO₂ to CH₃OH, see: (a) Huff, C. A.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18122–18125. (b) Tominaga, K.; Sasaki, Y.; Kawai, M.; Watanabe, T.; Saito, M. *J. Chem. Soc., Chem. Commun.* **1993**, 629–631.
- (3) For catalytic reduction of CO₂ to CH₃OH with borane reducing agents, see: (a) Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J. Am. Chem. Soc.* **2010**, *132*, 8872–8873. (b) Huang, F.; Zhang, C.; Jiang, J.; Wang, Z.; Guan, H. *Inorg. Chem.* **2011**, *50*, 3816–3825.
- (4) For Cu-catalyzed heterogeneous hydrogenation of CO₂ to CH₃OH and H₂O, see: (a) Ushikoshi, K.; Mori, K.; Watanabe, T.; Takeuchi, M.; Saito, M. *Stud. Surf. Sci. Catal.* **1998**, *114*, 357–362. (b) Saito, M. *Catal. Surv. Jpn.* **1998**, 175–184. (c) Grabow, L. C.; Mavrikakis, M. *ACS Catal.* **2011**, *1*, 365–384. (d) Tominaga, K.; Sasaki, Y.; Kawai, M.; Watanabe, T.; Saito, M. *J. Chem. Soc., Chem. Commun.* **1993**, 629–630. (e) Tominaga, K.-I.; Sasaki, Y.; Saito, M.; Hagihara, K.; Watanabe, T. *J. Mol. Catal.* **1994**, *89*, 51–55.
- (5) For catalytic reduction of CO₂ to CH₃OH with silane reducing agents, see: (a) Eisenschmid, T. C.; Eisenberg, R. *Organometallics* **1989**, *8*, 1822–1824. (b) Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 3322–3325. (c) Huang, F.; Lu, G.; Zhao, L.; Li, H.; Wang, Z. *J. Am. Chem. Soc.* **2010**, *132*, 12388–12396.
- (6) For Ru-catalyzed hydrosilylation of CO₂ to give formoxysilanes, see: (a) Koinuma, H.; Kawakami, F.; Kato, H.; Hirai, H. *J. Chem. Soc., Chem. Commun.* **1981**, 213–214. (b) Jansen, A.; Görls, H.; Pitter, S. *Organometallics* **2000**, *19*, 135–138. (c) Jansen, A.; Pitter, S. *J. Mol.*

Catal. A **2004**, 217, 41–45. (d) Deglmann, P.; Ember, E.; Hofmann, P.; Pitter, S.; Walter, O. *Chem.—Eur. J.* **2007**, 13, 2864–2879. For Cu-catalyzed hydrosilylation of CO₂, see: (e) Motokura, K.; Kashiwame, D.; Miyaji, A.; Baba, T. *Org. Lett.* **2012**, 14, 2642–2645.

(7) For catalytic reduction of CO₂ to CH₄ with silanes, see: (a) Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, 128, 12362–12363. (b) Berkefeld, A.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2010**, 132, 10660–10661. (c) Wehmschulte, R. J.; Khandelwal, M. Abstracts of papers, 243rd ACS National Meeting & Exposition, San Diego, March, 2012, SERM-606.

(8) (a) Park, S.; Brookhart, M. *Organometallics* **2010**, 29, 6057–6064. (b) Yang, J.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **2008**, 130, 17509–17518. (c) Park, S.; Brookhart, M. *Chem. Commun.* **2011**, 47, 3643–3645. (d) Yang, J.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, 129, 12656–12657. (e) Yang, J.; Brookhart, M. *Adv. Synth. Catal.* **2009**, 351, 175–187.

(9) A significant amount of CH₄ and excess CO₂ were detected by GC-MS spectroscopy in 22 h.

(10) Even under CO₂ (1 atm) the reaction of **3** with methylformate gives [Ir](CO), **5** in a quantitative yield in 1 h.

(11) It is known that the dihydride complex is a resting state in the cleavage of alkyl ethers with Et₃SiH, and **3** and Et₃SiH are in equilibrium with **4** and H₂.^{8b}

(12) The reaction of **2** with CO₂ may be a concerted process to form the ester or could be a stepwise process via [O=C—OSiR₃]⁺ followed by hydride reduction by (POCOP)IrH₂. Analogues of [O=C—OSiR₃]⁺ are known: [O=C—OMe]⁺ is observed in the electron impact (EI) mass spectrum of methyl acetate: (a) Chen, H.; Zheng, X.; Cooks, R. G. *J. Am. Soc. Mass Spectrom.* **2003**, 14, 182–188. [O=C—CC₆H₄—4-CH₃]⁺ can be formed by the removal of chloride from *p*-toluoyl chloride: (b) Chevrier, B.; Carpentier, J. M.; Weiss, R. *J. Am. Chem. Soc.* **1972**, 94, 5718–5723.