JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

pubs.acs.org/JACS

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

Supporting Information

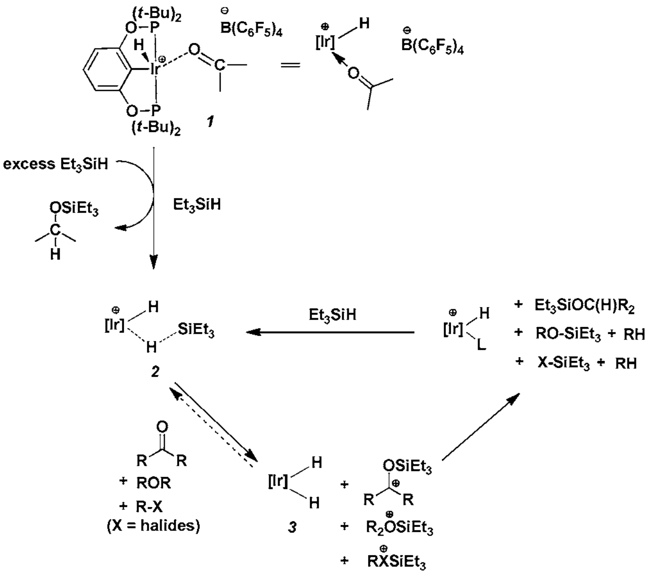
ABSTRACT: Cationic silane complexes of general structure (POCOP)Ir(H)(HSiR$_3$) {POCOP = 2,6-[OP(tBu)$_2$]$_2$C$_6$H$_3$} catalyze hydrosilylations of CO$_2$. Using bulky silanes results in formation of bis(silyl)acetals and methyl silyl ethers as well as siloxanes and CH$_4$. Using less bulky silanes such as Me$_2$EtSiH or Me$_2$PhSiH results in rapid formation of CH$_4$ 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 Me$_2$PhSiH with a 0.0077 mol % loading of iridium. The proposed mechanism for the conversion of CO$_2$ to CH$_4$ involves initial formation of the unobserved HCOOSiR$_3$. This formate ester is then reduced sequentially to R$_3$SiOCH$_2$OSiR$_3$, then R$_3$SiOCH$_3$, and finally to R$_3$SiOSiR$_3$ and CH$_4$.

There has been increasing interest in developing homogeneous catalysts for the reduction of CO$_2$, 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 CO$_2$ with catecholborane (HBcat) which yields CH$_3$OBCat has been described and proceeds through initial reaction of a nickel(II) hydride complex with CO$_2$ to yield a nickel formate complex.[3] The strong Si−O bond has led to successful reduction of CO$_2$ using hydrosilylation procedures.[5−7] Ruthenium and copper complexes have been reported as catalysts for the hydrosilylation of CO$_2$ to yield formoxysilanes.[6] Ying reported the first hydrosilylation of CO$_2$ 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 CO$_2$ to methane.[7a,b] Matsuo and Kawaguchi[7a] showed that a tandem catalytic system using Zr(IV) bis-benzyl complexes in combination with B(C$_6$F$_5$)$_3$ reduces CO$_2$ to methane with various silanes. Using PhMe$_2$SiH, a TOF of 150/h was observed and a total turnover number of 225 was achieved. Piers et al.[7b] showed that B(C$_6$F$_5$)$_3$ and an ammonium borate work in tandem to achieve catalytic reduction of CO$_2$ to methane with Et$_3$SiH at modest rates but with high catalyst stability. Sequential reduction products Et$_3$SiO$_2$CH, Et$_3$SiOCH$_2$OSiEt$_3$, and Et$_3$SiOCH$_3$ could be observed as intermediates.

Recently we reported that the highly electrophilic η^1-silane complex **2**, generated *in situ* from **1** and Et$_3$SiH, 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 Et$_3$Si$^+$ 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 of CO$_2$ to CH$_4$ via bis(silyl)acetal and methyl silyl ether intermediates using **1** in combination with tertiary silanes. Using PhMe$_2$SiH, catalyst lifetimes are very long (days) and turnover frequencies of *ca.* 190/h at 23 °C and 660/h at 60 °C were observed.

Scheme 1



Several silanes were screened by carrying out reductions in C$_6$D$_5$Cl at 23 °C, 1 atm of CO$_2$ and monitoring reactions by NMR spectroscopy. A catalyst loading of 0.3 mol % relative to silane was employed (eq 1).

$$R_3SiH + CO_2\ (1\ atm) \xrightarrow[C_6D_5Cl,\ 23\ ^{\circ}C]{\mathbf{1},\ 0.3\ mol\%} \begin{array}{l}(R_3SiO)_2CH_2 + MeOSiR_3 \\ + R_3SiOSiR_3 + CH_4\end{array} \qquad (1)$$

Received: June 1, 2012
Published: July 5, 2012

Table 1. Reduction of CO_2 with **1** and Trialkylsilanes[a]

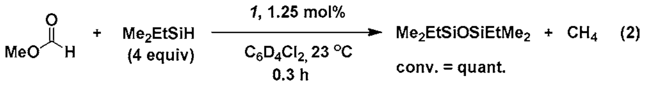
entry	silanes	time (h)	Product[b] $(R_3SiO)_2CH_2$:	R_3SiOMe:	$(R_3Si)_2O$	TON[c]	TOF (h^{-1})[c]
1[d]	Et_3SiH	2.5	7	1	4	48	19
2	Et_3SiH	22	1	2	5	138	6
3[d,e]	Ph_3SiH	22.7	100	<1	0	36	2
4	Me_2EtSiH	1.7	0	0	1	149	88
5	Me_2PhSiH	1.7	0	0	1	119	70
6[d]	$Me_2\textit{i}PrSiH$	20	~0	~0	1	105	5
7[d]	Et_2MeSiH	3.8	2	1	178	112	29

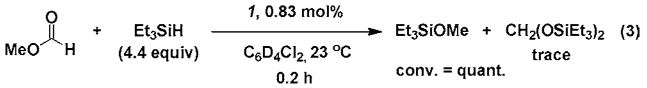
[a] Reaction conditions: 0.0025 mmol of **1**, solvent = C_6D_5Cl, 300 equiv of silane, 23 °C. [b] Determined by ^1H NMR with toluene as an internal standard. [c] Determined by ^1H NMR based on mol of Si−H bond reacted per mol Ir. [d] [Ir](CO) complex observed in addition to $[Ir]H(H_2)^+$ and/or **2** during the reaction. [e] White 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 Et_3SiH as a reductant, 48 turnovers are achieved in 2.5 h resulting in a mixture of $CH_2(OSiEt_3)_2$, CH_3OSiEt_3, and $(Et_3Si)_2O$ 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 CO_2 in the NMR tube. The ^1H NMR spectrum shows characteristic resonances at $\delta 5.09$ and $\delta 3.39$ due to the CH_2- of $CH_2(OSiEt_3)_2$ and the CH_3- of CH_3OSiEt_3, respectively.[7b] In addition, the $^{13}C\{^1H\}$ NMR spectrum clearly exhibits signals due to triethylsilyl groups of the products (see Supporting Information). Triphenylsilane reacts slowly with CO_2 to give $CH_2(OSiPh_3)_2$ and trace amounts of triphenylsilylmethyl ether (entry 3). The GC trace of the gas in the head space of this reaction mixture shows no CH_4.

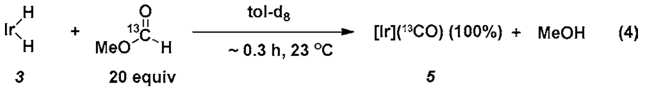
Use of less bulkier silanes leads to higher activity and selectivity for formation of CH_4 (entries 4−6). CO_2 is readily reduced with Me_2EtSiH and Me_2PhSiH to afford the corresponding siloxanes and CH_4 with TON = 149 and TON = 119 in 1.7 h, respectively. No silyl alkyl ether intermediates are observed by NMR spectroscopy throughout the reaction. $Me_2\textit{i}PrSiH$ reacts selectively to give $(Me_2\textit{i}PrSi)_2O$ and CH_4 with trace amounts of silyl alkyl ethers, although 20 h are required to achieve a TON of 105. Similar to Et_3SiH, the reaction of Et_2MeSiH with CO_2 over 3.8 h affords a mixture of $CH_2(OSiMeEt_2)_2$, $MeOSiMeEt_2$, and $(Et_2MeSi)_2O$ in a ratio of 2:1:178 (entry 7). Observation of $CH_2(OSiR_3)_2$ and $MeOSiR_3$ intermediates implies that the reduction initially proceeds via hydrosilylation of CO_2 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 $MeOSiR_3$ and then the siloxane and CH_4.

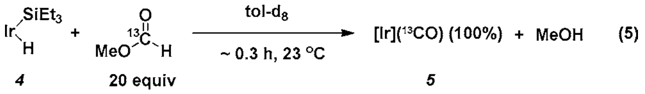
To obtain further insight into the mechanism for formation of the silyl alkyl ether intermediates, we examined the hydrosilylation of methyl formate, a model compound for the presumed first-formed formoxysilane intermediate, using both Me_2EtSiH and Et_3SiH at 23 °C (eqs 2, 3).





Methyl formate undergoes reductive hydrosilylation with Me_2EtSiH to give $Me_2EtSiOSiEtMe_2$ and CH_4 in 0.3 h; no intermediates were observed. In contrast, the reaction with Et_3SiH produces CH_3OSiEt_3 (>99%) and traces of the silylmethylacetal (<1%) in 0.2 h. These results are consistent with the proposal that CO_2 is transformed to CH_4 through the formoxysilane and that the C−O bonds of the bis(silyl)acetal and the silyl methyl ether are cleaved more slowly with Et_3SiH than with the less bulky Me_2EtSiH. Monitoring the reaction by ^{31}P NMR spectroscopy shows major peaks due to **2** and/or $[Ir]H(H_2)^+$ and a minor peak due to the [Ir](CO) complex, **5**, when using bulky silanes Et_3SiH, Et_2MeSiH, $\textit{i}PrMe_2SiH$, or Ph_3SiH as reductants. In order to identify a possible pathway for the formation of **5**, we performed reactions of neutral dihydride **3** or [Ir](H)($SiEt_3$) **4** with $H^{13}COOMe$ (20 equiv) (eqs 4, 5).

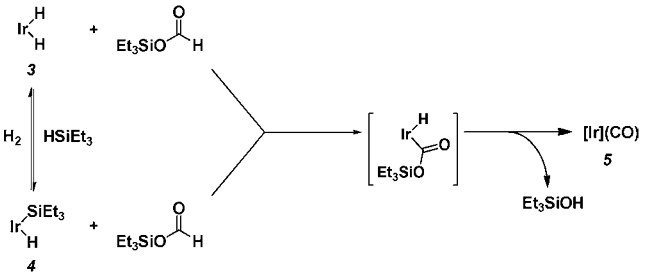




Complex **3** quantitatively converts to the [Ir](^{13}CO) complex with formation of MeOH in 0.3 h by reaction with excess $H^{13}COOMe$.[10] Similarly, the neutral complex **4** in the presence of $H^{13}COOMe$ converts to the [Ir](^{13}CO) complex in 0.3 h with formation of MeOH. Based on these results, 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 CO_2 using Me_2PhSiH 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 CO_2 in the NMR tube. Following the 22.5 h reaction, a fresh charge of CO_2 (1 atm) was introduced into the reaction mixture, whereupon formation of the siloxane ($Me_2PhSiOSiPhMe_2$) and CH_4 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 CO_2 with Me_2PhSiH. Results are summarized in Table 2.

Table 2. Results of Large Scale Reduction of CO_2 with Me_2PhSiH[a]

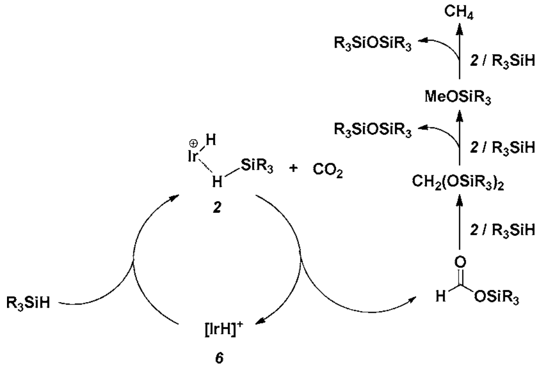
entry	time (h)	TON[b]	TOF (h^{-1})[b]	product	isolated yield (g)
1	24	4635	193	$Me_2PhSiOSiPhMe_2$ + CH_4	1.66
2	48	7092	148	$Me_2PhSiOSiPhMe_2$ + CH_4	2.54
3	72	8293	115	$Me_2PhSiOSiPhMe_2$ + CH_4	2.97
4[c]	3	1982	661	$Me_2PhSiOSiPhMe_2$ + CH_4	0.71

[a] Reaction conditions: 0.0025 mmol of **1**, solvent = C_6H_5Cl (3 mL), Me_2PhSiH (5 mL), CO_2 (1 atm), 23 °C. [b] Based on mol of Si−H bond reacted per mol Ir. [c] Reaction at 60 °C.

Complex **1** (0.0077 mol %) together with Me_2PhSiH initiates the reductive hydrosilylation of CO_2 to yield $Me_2PhSiOSiPhMe_2$ and CH_4 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**, generated *in situ* from **1** and R_3SiH, reacts with CO_2 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, $R_3SiOCH_2OSiR_3$. Reductive cleavage of the C−O bonds of the acetal by silanes is highly dependent on the steric bulk of the silanes. $R_3SiOCH_2OSiR_3$ readily converts to $R_3SiOSiR_3$ and CH_4 with less crowded silanes, whereas bulky silanes slowly cleave C−O bonds of the acetal resulting in the observation of a mixture of products.

Scheme 3. Proposed Catalytic Cycle in the CO_2 Reduction to CH_4



In summary, we have described a well-defined single iridium pincer catalyst for the reduction of CO_2 to CH_4 with trialkylsilanes under mild conditions. Using Me_2PhSiH 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 R_3Si^+ to CO_2 to generate a silyloxy carbenium ion.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR spectroscopic data of reaction mixtures resulted from the reduction of CO_2 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 CO_2, 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 CO_2 to CH_3OH, 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 CO_2 to CH_3OH 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 CO_2 to CH_3OH and H_2O, 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 CO_2 to CH_3OH 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 CO_2 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 CO_2, see: (e) Motokura, K.; Kashiwame, D.; Miyaji, A.; Baba, T. *Org. Lett.* **2012**, *14*, 2642−2645.

(7) For catalytic reduction of CO_2 to CH_4 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 CH_4 and excess CO_2 were detected by GC-MS spectroscopy in 22 h.

(10) Even under CO_2 (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 Et_3SiH, and **3** and Et_3SiH are in equilibrium with **4** and H_2.[8b]

(12) The reaction of **2** with CO_2 may be a concerted process to form the ester or could be a stepwise process via $[O{=}C{-}OSiR_3]^+$ followed by hydride reduction by $(POCOP)IrH_2$. Analogues of $[O{=}C{-}OSiR_3]^+$ 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. $[O{=}CC_6H_4\text{-}4\text{-}CH_3]^+$ 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.