View Article Online
View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: J. Koo, S. H. Kim and S. H. Hong, *Chem. Commun.*, 2018, DOI: 10.1039/C8CC02276C.

View Article Online
DOI: 10.1039/C8CC02276C

Journal Name

COMMUNICATION

Hydrogenation of Silyl Formate: Sustainable Production of Silanol and Methanol from Hydrosilane and Carbon Dioxide

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

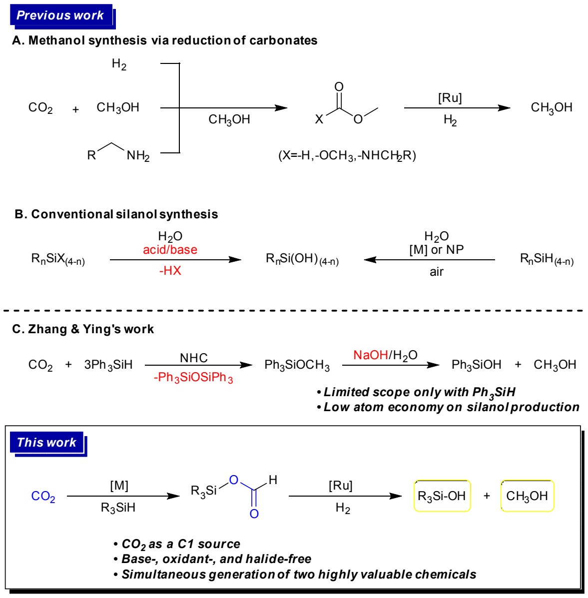
www.rsc.org/

Jangwoo Koo, Seung Hyo Kim, and Soon Hyeok Hong*

A new process for simultaneously obtaining two chemical building blocks, methanol and silanol, was realized starting from silyl formates which can be derived from silane and carbon dioxide. Understanding the reaction mechanism enabled us to improve the reaction efficiency by the addition of small amount of methanol.

Selective reduction of carbon dioxide (CO_2) is a fascinating approach for the production of methanol,[1] which is a versatile commodity chemical[2] and a future energy source.[3] Methanol is commercially produced from fossil-fuel-based syngas at high temperatures and pressures.[4] Research on the catalytic hydrogenation of carbon dioxide[5] and alternative approaches such as reduction of carbonates[6] and formic acid[7] is being pursued to realize a highly efficient and economically viable conversion of carbon dioxide to methanol (Scheme 1A). In heterogeneous catalysis, Cu-based catalysts have been actively investigated for the industrial scale production of methanol by the hydrogenation of CO_2.[8] In homogeneous catalysis, improvement of the overall catalytic efficiency for the selective production of methanol from CO_2 is a current challenge.

Silanol is widely utilized in industry as a monomer for polysiloxane synthesis,[9] precursor for cross-coupling reactions,[10] and key functional group on silicon surfaces.[11] Silanol can be produced by the hydrolysis of silyl halides (Scheme 1B),[12] however in this case, toxicological and environmental problems may arise because of the toxic reagents required for the process, i.e., acid, or base and the generated halide waste. To address this issue, catalytic oxidation of hydrosilanes with water producing silanols has been developed using homogeneous[13] and heterogeneous[14] catalysts (Scheme 1B).



Scheme 1 Synthesis of methanol and silanols.

The use of silane derivatives to fixate CO_2 has been actively investigated.[15, 16] In 2009, the Zhang and Ying group[15a] reported N-heterocyclic carbene (NHC)-catalyzed reduction of CO_2 to methanol using hydrosilane, where silanol was generated as a coproduct (Scheme 1C). However, the major silicon product was siloxane (two-third molar equiv of [Si]), the competitive side product in NHC-catalyzed reaction; consequently, the atom economy for the production of silanol was reduced. Besides, the direct catalytic Si-H oxidation is only applicable to diphenylsilane, and this limits the utility of the method.

Inspired by the recent development of readily available silyl formate synthesis from CO_2[16] and the Ru-catalyzed hydrogenation of carbonates,[6] we envisioned a new process for the simultaneous production of highly valuable silanol and methanol via the reduction of silyl formates, which can serve

---

Department of Chemistry, College of Natural Sciences, Seoul National University, 1 Gwanak-ro, Seoul 08826, South Korea. E-mail: soonhong@snu.ac.kr

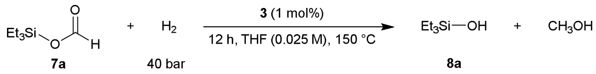
Electronic Supplementary Information (ESI) available: [Experimental details, TON test, Mechanistic investigation, NMR spectras and HRMS data]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C8CC02276C

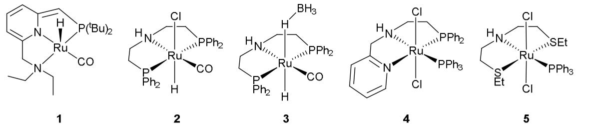
as a novel process for the concurrent production of the value-added products from economical and sustainable hydrosilane and CO_2. Additionally, our developed reaction does not generate waste and requires no additive such as base, oxidant, or halide.

To realize the aforesaid goal, hydrogenation of triethylsilyl formate **7a** was first investigated with ruthenium complexes, and excellent activity for the hydrogenation of carbonyl compounds was observed.[17] Milstein catalyst **1**[18] was not effective for this reaction (entry 1). Ru-MACHO catalyst **2**[19] did not show any notable reactivity in the presence of a base (entry 2). When Ru-MACHO-BH **3** was used as the precatalyst, the two desired products were obtained in quantitative amounts without the need of any base or additive (entry 3). Complexes **4** and **5**, which showed better performance in the hydrogenation of ester derivatives[20] were further tested, but they were not active for this reaction (entries 4 and 5). Among the tested solvents, THF showed the highest yields for both products (entries 3, 6–9). When we decreased the H_2 pressure to 10 bar, the product was isolated in excellent yield (entry 10).

Table 1 Optimization of reaction conditions.[a]



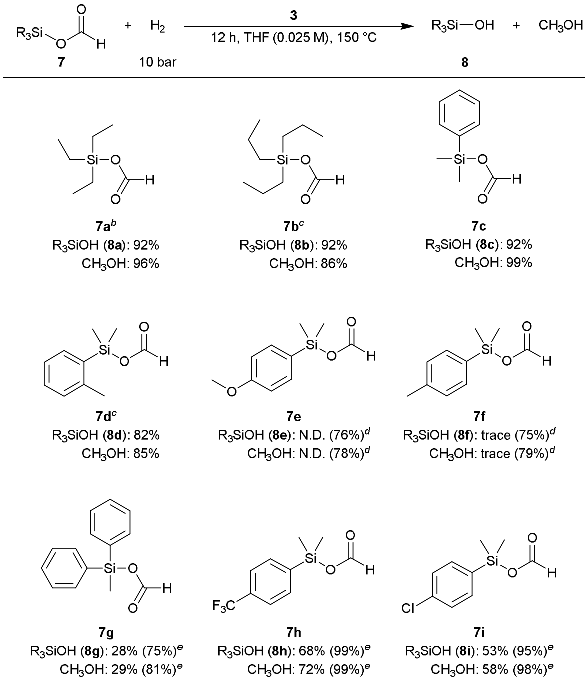
entry	[Ru]	base	solvent	H_2 (bar)	yield (%) 8a	yield (%) CH_3OH
1	**1**	-	THF	40	56	75
2	**2**	KOtBu	THF	40	11	50
3	**3**	-	THF	40	99	99
4	**4**	KOtBu	THF	40	16	43
5	**5**	KOtBu	THF	40	11	54
6	**3**	-	toluene	40	79	99
7	**3**	-	ethanol	40	0	0
8	**3**	-	dioxane	40	68	81
9	**3**	-	hexane	40	46	92
10	**3**	-	THF	10	90	91



[a] Reaction conditions: triethylsilyl formate **7a** (0.5 mmol), [Ru] (1 mol%), base (1 mol%), THF (20 mL), 150 °C, 12 h, H_2 (40 bar). Yields were determined by GC analysis using *p*-xylene as an internal standard. THF = tetrahydrofuran.

Various silyl formates, which were synthesized from silane and carbon dioxide (Scheme S1 and S2),[16a, 16c] were hydrogenated to silanol and methanol in good to excellent yields under the optimized conditions (Table 2). Triethylsilyl formate **7a** was efficiently reduced in excellent yield even with reduced loading of the catalyst (0.1 mol%). Additionally, **7a** exhibited good turnover numbers (**8a**: 1680, CH_3OH: 1900, see Table S1 in the Supporting Information) under 500 ppm catalyst loading. Tri-n-propylsilyl formate **7b** and dimethyl(2-methylphenyl)silyl formate **7d** required a higher catalyst loading (2 mol%) to provide good yields, presumably due to the steric hindrance at the silicon center. Aryl-substituted compounds such as dimethylphenylsilyl formate **7c** reacted smoothly to produce methanol and silanol in good yields. To investigate electronic effects, silyl formates with electron-withdrawing or electron-donating groups at the *para*-position of the phenyl group were prepared. Electron-rich compounds, methoxyphenyl- and tolyl- substituted silyl formates (**7e** and **7f**), exhibited limited reactivity for the desired products, generating byproducts such as methoxysilane (22%, **7e**; 42%, **7f**) and dimerized siloxanes (10%, **7e**; 24%, **7f**). A further increase in H_2 pressure to 80 bar enabled the selective reduction of **7e** and **7f** in good yields. Reduction of methyldiphenylsilyl formate **7g** required an elevated pressure of 40 bar H_2 to achieve good yields of the products. Relatively electron-deficient substrates with *para* trifluoromethyl- or chloro- substituted phenyl groups (**7h** and **7i**) showed fair to good yields under 10 bar H_2. When the H_2 pressure was increased to 40 bar, nearly quantitative yields of both methanol and silanol were obtained.

Table 2 Hydrogenation of silyl formate to silanol and methanol catalyzed by **3**.[a]

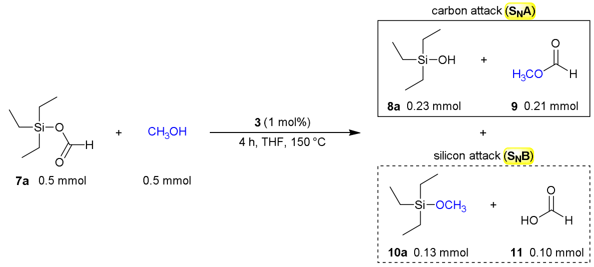


[a] Reaction conditions: silyl formate **7** (0.5 mmol), **3** (1 mol%), THF (20 mL), 150 °C, 12 h, H_2 (10 bar). Methanol was checked by GC analysis using *p*-xylene as an internal standard. Silanol was isolated by silica column chromatography. [b] **3** (0.1 mol%). [c] **3** (2 mol%). [d] **3** (5 mol%), H_2 (80 bar). [e] H_2 (40 bar). N.D.=not detected.

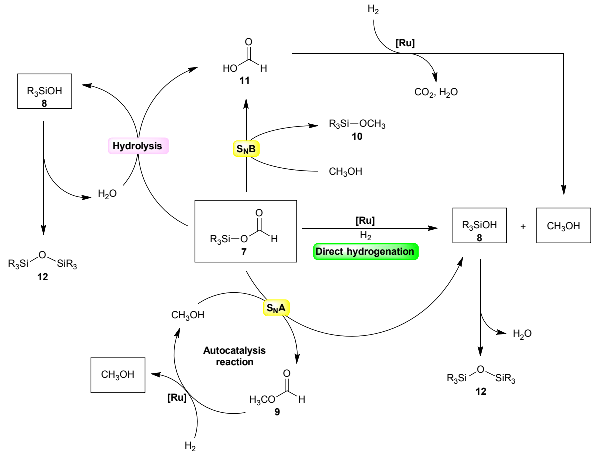
During the reactions depicted in Table 2, a small amount of methyl formate **9** was observed in the case of **7b**, **7d**, **7f**, **7g**,

View Article Online
DOI: 10.1039/C8CC02276C

and **7i**. Under the reaction conditions, **9** could be generated via a simple nucleophilic substitution (S_N) to silyl formate **7** with methanol, which is initially obtained from the direct hydrogenation of **7**. To demonstrate the postulation, a stoichiometric reaction between **7a** and methanol was conducted (Scheme 2). The reaction proceeded via two pathways—one involving carbon attack (S_NA) to produce triethylsilanol **8a** and **9**, and the other involved silicon attack (S_NB) pathway to produce triethyl(methoxy)silane **10a** (Table S2 and Figure S1). The results indicated that the initially formed methanol can react with the starting silyl formate, leading to divergent pathways.

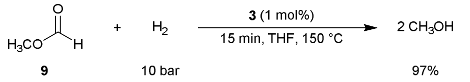


Scheme 2 Reaction of silyl formate **7a** with methanol.

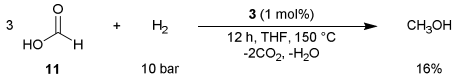


Scheme 3 Proposed mechanism for hydrogenation of silyl formate.

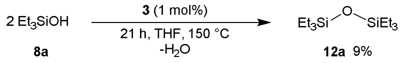
Based on this observation, we propose a plausible reaction mechanism (Scheme 3). The initially postulated direct hydrogenation (DH) of silyl formate **7** can generate methanol and silanol **8** simultaneously. The initially formed methanol can react with **7** via nucleophilic substitution (S_N). If methanol attacks the carbon center of **7** (S_NA), methyl formate **9** and silanol **8** can be generated. Then, **9** can be reduced to methanol under our catalytic conditions. A control experiment confirms that reduction of **9** is efficient under our catalytic conditions (eq 1). Instead of S_NA, if methanol reacts with the silicon center of **7** (S_NB), methoxysilane **10** and formic acid **11** can be formed. Although **11** can be hydrogenated to methanol,[7b] lower efficiency is observed under the conditions with two-third of the molar equivalents of carbon being consumed to afford CO_2, suggesting that this is a minor and undesirable pathway (eq 2). Additionally, hydrolysis of **7** by water[16b] generated from the dimerization of silanol **8** (eq 3) or disproportionation of formic acid **11**[7b] (eq 2) may occur, inducing the regeneration of **11** and **8**. Thus, it is essential to control the reaction pathway preferably to DH and S_NA for a more efficient production of the desired silanol and methanol.



(1)

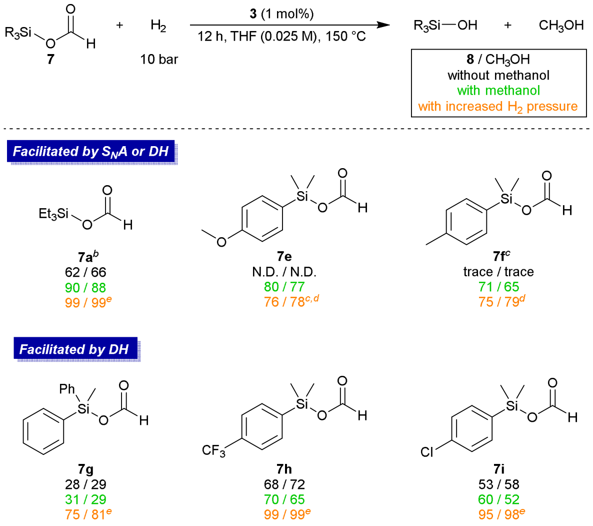


(2)



(3)

Table 3 Improvement of reactivity by the addition of methanol[a]



[a] Reaction conditions: **7** (0.5 mmol, 1.0 equiv.), **3** (1 mol%), THF (20 mL), 150 °C, 12 h, H_2 (10 bar), CH_3OH (0.1 equiv.). Yields were determined by GC analysis using *p*-xylene as an internal standard. [b] **3** (0.1 mol%), 4 h. [c] **3** (5 mol%). [d] H_2 (80 bar). [e] H_2 (40 bar). N.D. = not detected.

Inspired by the investigated positive S_NA pathway, we suspect that methanol as an additive could aid the catalysis. In a preliminary test with **7a**, methanol was found to accelerate the production of both methanol and silanol **8a** (Table 3). Upon the addition of 0.1 equiv methanol to the reaction of **7e** and **7f**, which required a high H_2 pressure of 80 bar to obtain acceptable yields, silanol and methanol were furnished in about 70% yield even at 10 bar H_2 pressure, which is typically ineffective for product formation. However, no significant

View Article Online
DOI: 10.1039/C8CC02276C

improvement was observed with silyl formates **7g–7i** that work reasonably at 10 bar (Table 2). We believe that the relatively electron-deficient **7g**–**7i** prefer DH as the major pathway. At reduced H_2 pressure, the silicon attack S_NB pathway is preferred over the S_NA pathway with the electron-deficient silyl formates, thereby limiting the overall reaction efficiency.

In summary, a new atom-economical catalytic process was developed to produce highly valuable chemical feedstocks, silanol and methanol, from silyl formate, which is readily obtained from carbon dioxide and silane. In addition to the direct hydrogenation of silyl formate, generation of methyl formate via the reaction of silyl formate and the initially formed methanol was identified as a positive pathway. The mechanistic understanding of autocatalysis enabled us to improve the reaction efficiency for less reactive silyl formates using methanol as the additive.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the National Research Foundation of Korea (NRF-2014R1A2A1A11050028; NRF-2015M3D3A1A01065480; NRF-2014R1A5A1011165).

Notes and references

1 (a) G. A. Olah, *Angew. Chem. Int. Ed.*, 2013, **52**, 104-107; (b) J. Klankermayer, S. Wesselbaum, K. Beydoun and W. Leitner, *Angew. Chem. Int. Ed.*, 2016, **55**, 7296-7343.

2 (a) N. Ortega, C. Richter and F. Glorius, *Org. Lett.*, 2013, **15**, 1776-1779; (b) T. T. Dang, B. Ramalingam and A. M. Seayad, *ACS Catal.*, 2015, **5**, 4082-4088; (c) S. H. Kim and S. H. Hong, *Org. Lett.*, 2016, **18**, 212-215.

3 (a) T. B. Reed and R. M. Lerner, *Science*, 1973, **182**, 1299-1304; (b) J. S. Lee, J. C. Kim and Y. G. Kim, *Appl. Catal.*, 1990, **57**, 1-30.

4 (a) K. C. Waugh, *Catal. Today*, 1992, **15**, 51-75; (b) M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Kniep, M. Tovar, R. W. Fischer, J. K. Nørskov and R. Schlögl, *Science*, 2012, **336**, 893-897.

5 (a) C. A. Huff and M. S. Sanford, *J. Am. Chem. Soc.*, 2011, **133**, 18122-18125; (b) S. Wesselbaum, T. vom Stein, J. Klankermayer and W. Leitner, *Angew. Chem. Int. Ed.*, 2012, **51**, 7499-7502; (c) N. M. Rezayee, C. A. Huff and M. S. Sanford, *J. Am. Chem. Soc.*, 2015, **137**, 1028-1031; (d) S. Wesselbaum, V. Moha, M. Meuresch, S. Brosinski, K. M. Thenert, J. Kothe, T. v. Stein, U. Englert, M. Holscher, J. Klankermayer and W. Leitner, *Chem. Sci.*, 2015, **6**, 693-704; (e) J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah and G. K. S. Prakash, *J. Am. Chem. Soc.*, 2016, **138**, 778-781; (f) J. Schneidewind, R. Adam, W. Baumann, R. Jackstell and M. Beller, *Angew. Chem. Int. Ed.*, 2017, **56**, 1890-1893.

6 (a) E. Balaraman, C. Gunanathan, J. Zhang, L. J. W. Shimon and D. Milstein, *Nat. Chem.*, 2011, **3**, 609-614; (b) Z. Han, L. Rong, J. Wu, L. Zhang, Z. Wang and K. Ding, *Angew. Chem. Int. Ed.*, 2012, **51**, 13041-13045; (c) J. R. Khusnutdinova, J. A. Garg and D. Milstein, *ACS Catal.*, 2015, **5**, 2416-2422.

7 (a) A. J. M. Miller, D. M. Heinekey, J. M. Mayer and K. I. Goldberg, *Angew. Chem. Int. Ed.*, 2013, **52**, 3981-3984; (b) S. Savourey, G. Lefèvre, J.-C. Berthet, P. Thuéry, C. Genre and T. Cantat, *Angew. Chem. Int. Ed.*, 2014, **53**, 10466-10470; (c) M. C. Neary and G. Parkin, *Chem. Sci.*, 2015, **6**, 1859-1865.

8 (a) Y. Zhang, J. Fei, Y. Yu and X. Zheng, *Energy Convers. Manage.*, 2006, **47**, 3360-3367; (b) J. Graciani, K. Mudiyanselage, F. Xu, A. E. Baber, J. Evans, S. D. Senanayake, D. J. Stacchiola, P. Liu, J. Hrbek, J. F. Sanz and J. A. Rodriguez, *Science*, 2014, **345**, 546-550; (c) C. Liu, B. Yang, E. Tyo, S. Seifert, J. DeBartolo, B. von Issendorff, P. Zapol, S. Vajda and L. A. Curtiss, *J. Am. Chem. Soc.*, 2015, **137**, 8676-8679.

9 P. D. Lickiss, *Adv. Inorg. Chem.*, 1995, **42**, 147-262.

10 (a) K. Hirabayashi, J. Kawashima, Y. Nishihara, A. Mori and T. Hiyama, *Org. Lett.*, 1999, **1**, 299-302; (b) S. E. Denmark and R. F. Sweis, *Chem. Pharm. Bull.*, 2002, **50**, 1531-1541; (c) D. G. Chan, D. J. Winternheimer and C. A. Merlic, *Org. Lett.*, 2011, **13**, 2778-2781.

11 (a) X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. M. Kemner, *Science*, 1997, **276**, 923-926; (b) P. K. Jal, S. Patel and B. K. Mishra, *Talanta*, 2004, **62**, 1005-1028.

12 (a) A. Yoshimoto and K. Ichiro, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1118-1123; (b) J. Beckmann, D. Dakternieks, A. Duthie, M. L. Larchin and E. R. T. Tiekink, *Appl. Organomet. Chem.*, 2003, **17**, 52-62.

13 (a) M. Lee, S. Ko and S. Chang, *J. Am. Chem. Soc.*, 2000, **122**, 12011-12012; (b) Y. Lee, D. Seomoon, S. Kim, H. Han, S. Chang and P. H. Lee, *J. Org. Chem.*, 2004, **69**, 1741-1743.

14 (a) E. Choi, C. Lee, Y. Na and S. Chang, *Org. Lett.*, 2002, **4**, 2369-2371; (b) T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Commun.*, 2009, **0**, 5302-5304; (c) N. Asao, Y. Ishikawa, N. Hatakeyama, Menggenbateer, Y. Yamamoto, M. Chen, W. Zhang and A. Inoue, *Angew. Chem.*, 2010, **122**, 10291-10293; (d) J. John, E. Gravel, A. Hagège, H. Li, T. Gacoin and E. Doris, *Angew. Chem. Int. Ed.*, 2011, **50**, 7533-7536; (e) M. Jeon, J. Han and J. Park, *ACS Catal.*, 2012, **2**, 1539-1549.

15 (a) S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem. Int. Ed.*, 2009, **48**, 3322-3325; (b) M.-A. Courtemanche, M.-A. Legare, E. Rochette and F.-G. Fontaine, *Chem. Commun.*, 2015, **51**, 6858-6861; (c) T. T. Metsänen and M. Oestreich, *Organometallics*, 2015, **34**, 543-546; (d) Q. Zhou and Y. Li, *J. Am. Chem. Soc.*, 2015, **137**, 10182-10189; (e) S. Zhang, Q. Mei, H. Liu, H. Liu, Z. Zhang and B. Han, *RSC Adv.*, 2016, **6**, 32370-32373.

16 (a) A. Jansen and S. Pitter, *J. Mol. Catal. A: Chem.*, 2004, **217**, 41-45; (b) K. Motokura, D. Kashiwame, A. Miyaji and T. Baba, *Org. Lett.*, 2012, **14**, 2642-2645; (c) S. Itagaki, K. Yamaguchi and N. Mizuno, *J. Mol. Catal. A: Chem.*, 2013, **366**, 347-352; (d) L. Zhang, J. Cheng and Z. Hou, *Chem. Commun.*, 2013, **49**, 4782-4784; (e) K. Motokura, M. Naijo, S. Yamaguchi, A. Miyaji and T. Baba, *Chem. Lett.*, 2015, **44**, 1217-1219; (f) J. Takaya and N. Iwasawa, *J. Am. Chem. Soc.*, 2017, **139**, 6074-6077; (g) P. Deglmann, E. Ember, P. Hofmann, S. Pitter, and O. Walter, *Chem. Eur. J.*, 2007, **13**, 2864-2879.

17 P. A. Dub and T. Ikariya, *ACS Catal.*, 2012, **2**, 1718-1741.r

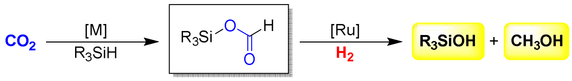
18 C. Gunanathan, Y. Ben-David and D. Milstein, *Science*, 2007, **317**, 790-792.

19 (a) W. Kuriyama, T. Matsumoto, O. Ogata, Y. Ino, K. Aoki, S. Tanaka, K. Ishida, T. Kobayashi, N. Sayo and T. Saito, *Org. Process Res. Dev.*, 2012, **16**, 166-171; (b) M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali and M. Beller, *Nature*, 2013, **495**, 85-89.

20 (a) D. Spasyuk, S. Smith and D. G. Gusev, *Angew. Chem. Int. Ed.*, 2013, **52**, 2538-2542; (b) J. R. Cabrero-Antonino, E. Alberico, H.-J. Drexler, W. Baumann, K. Junge, H. Junge and M. Beller, *ACS Catal.*, 2016, **6**, 47-54.

View Article Online
DOI: 10.1039/C8CC02276C

Table of Contents Entry



- ***Yields up to >99%***
- ***Abundant and eco-friendly C1 source***
- ***No external additive***
- ***No byproduct***
- ***Simultaneous generation of two valuable products***

Simultaneous production of methanol and silanols was achieved by hydrogenation of silyl formates readily obtained from silanes and CO_2.