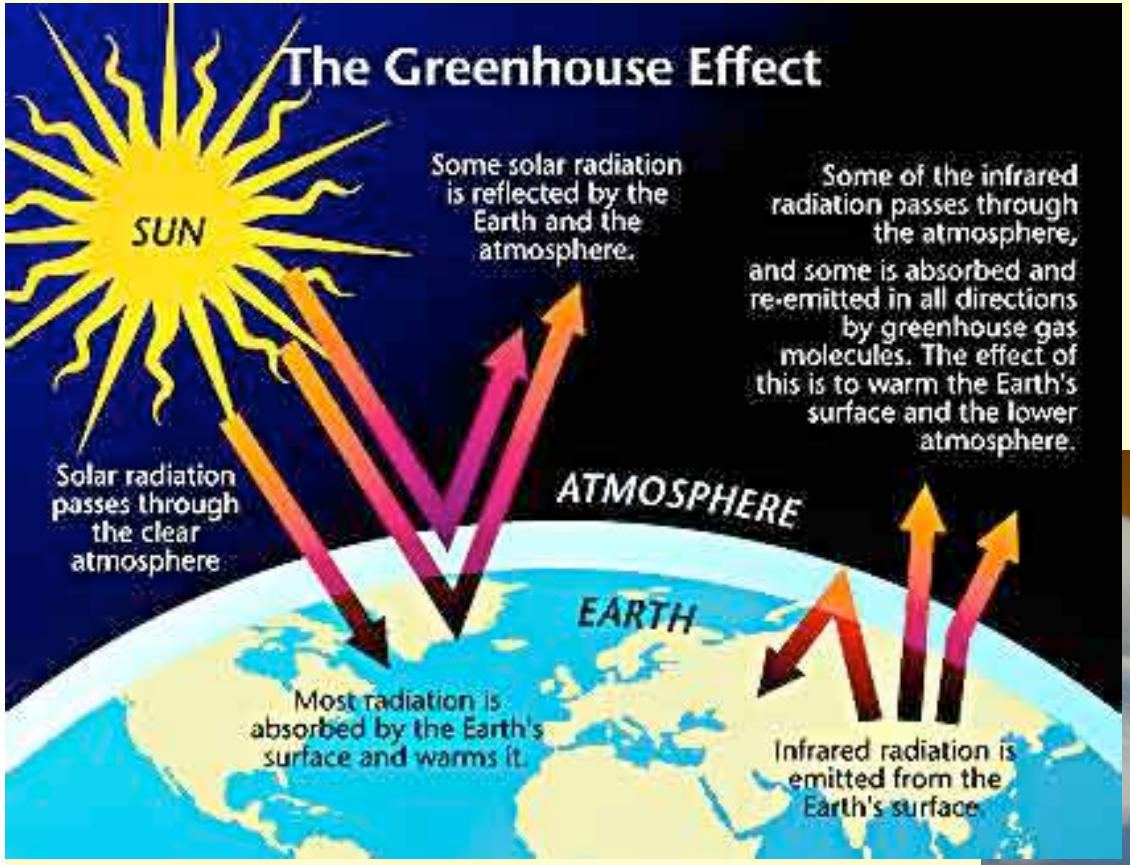
A New Method in Conversion of CO_2 into Methanol

Wynter Gilson

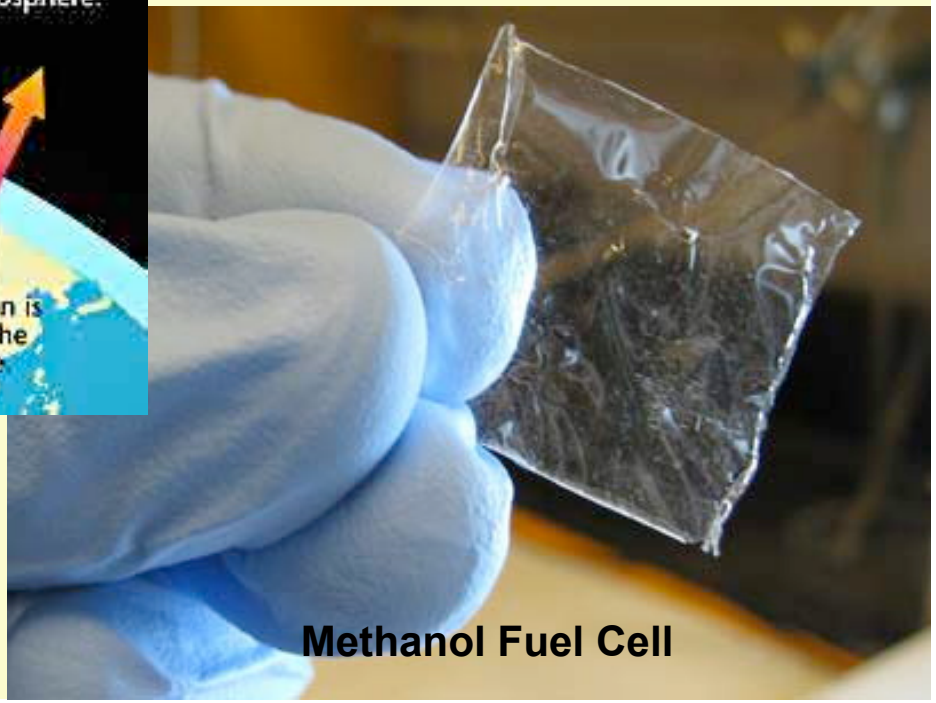
April 24, 2009

Disadvantages of CO_2 and Advantages of CH_3OH



Harmful Effects of Carbon Dioxide

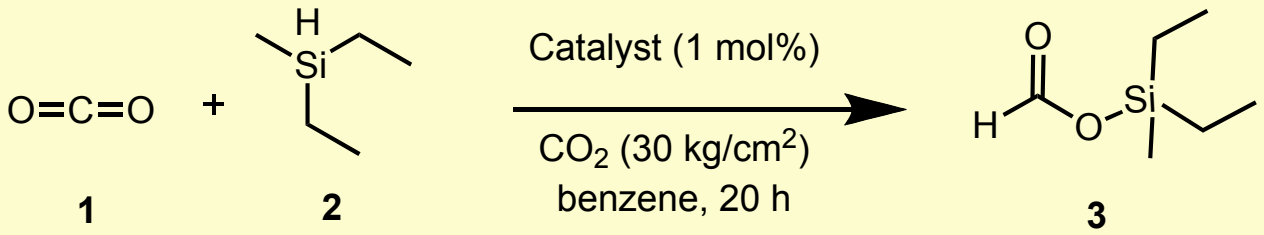
- ♦Rising sea levels
- ♦Increased drought and wild fires
- ♦Stress on forests
- ♦Disruption of agriculture



http://students.washington.edu/nofrills/phil.htm

http://web.mit.edu/newsoffice/2008/fuel-cell-0516.html

Hydrosilylation of CO_2 Catalysed by Ru Complexes

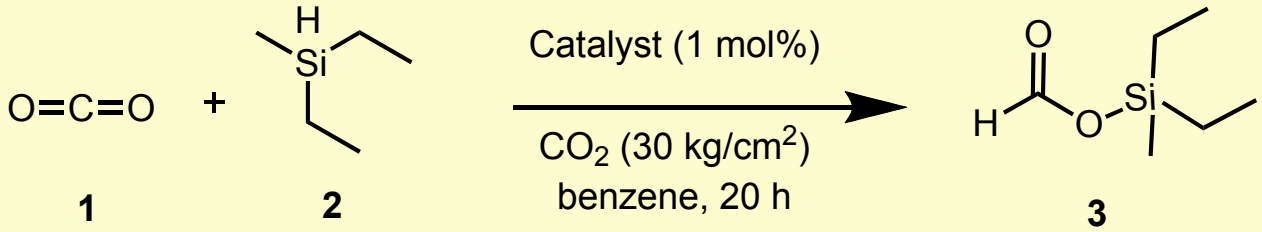


1 **2** **3**

$HSiR_3$	Catalyst	T (°C)	**3** (mol %)
$HSiMeEt_2$	$RuCl_2(PPh_3)_3$	100	14
"	"	80	1
"	"	120	4
"	$RuH_2(PPh_3)_4$	100	6
"	$Pd(PPh_3)_4$	100	1
$HSiMe(OMe)_2$	$RuCl_2(PPh_3)_3$	100	1

Koinuma, H.; Kawakami, F.; Kato, G.; Hirai, H. J.C.S. *Chem. Comm.* **1981**, 213-214.

Hydrosilylation of CO_2 Catalysed by Ru Complexes



1 **2** **3**

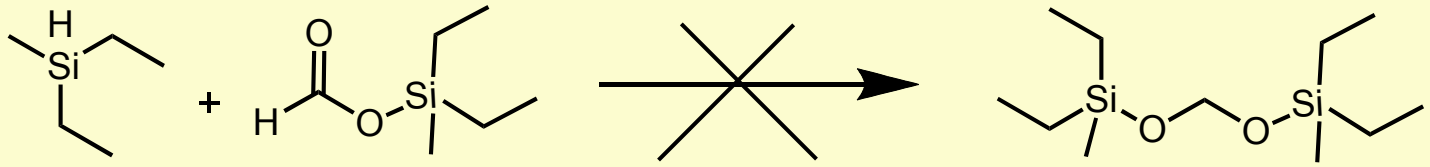
Inactive Catalyst

$RhCl(PPh_3)_3$

$Rh(CO)Cl(PPh_3)_2$

$PdCl_2$

Indication of higher reactivity of **2** towards CO_2 than towards **3.**



2 **3**

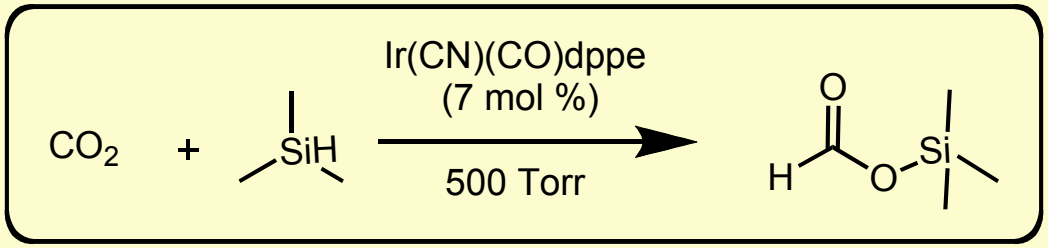
Koinuma, H.; Kawakami, F.; Kato, G.; Hirai, H. J.C.S. *Chem. Comm.* **1981**, 213-214.

Pros and Cons of Ru Complexes for Hydrosilylation of CO_2

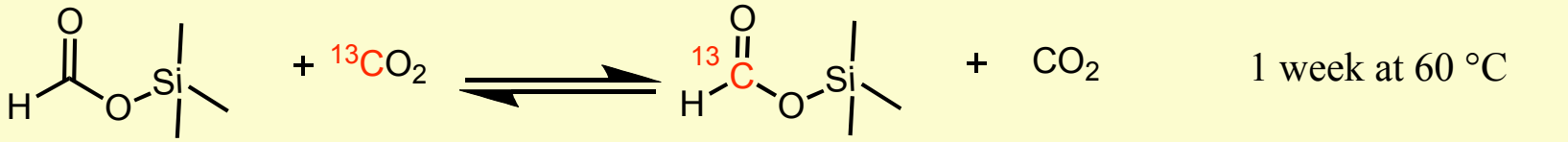
Pros	Cons
♦First insertion of Si-H bond into C=O bond	♦Use of pressure 30 Kg/cm^2 = 29 psi
♦Some catalytic activity seen	♦Use of heat
	♦Catalysts not efficient

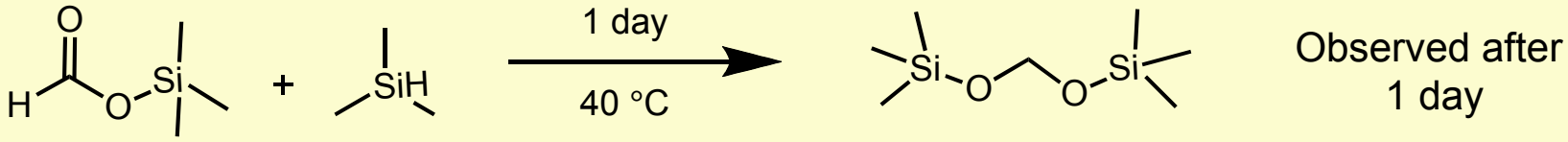
Koinuma, H.; Kawakami, F.; Kato, G.; Hirai, H. J.C.S. *Chem. Comm.* **1981**, 213-214.

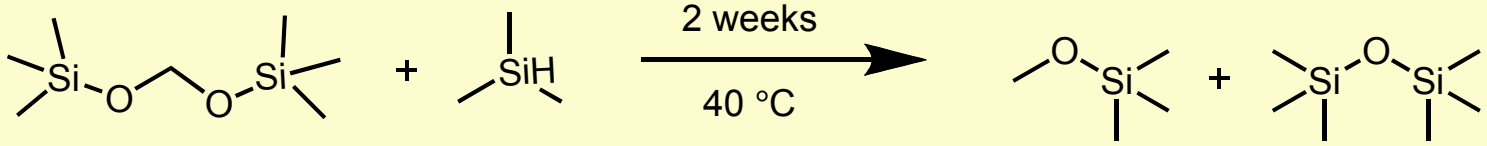
Hydrosilylation of CO_2 by Iridium Complex



Dppe = 1,2-bis(diphenylphosphino)ethane







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

Pros and Cons of Hydrosilylation of CO_2 by Iridium Complex

Pros

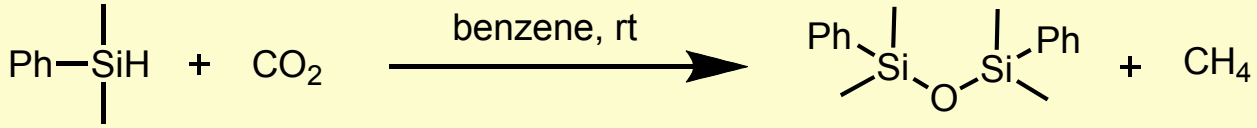
- Identified carbon transfer by ^{13}C labeling
- Identified the precursor later used to make methanol

Cons

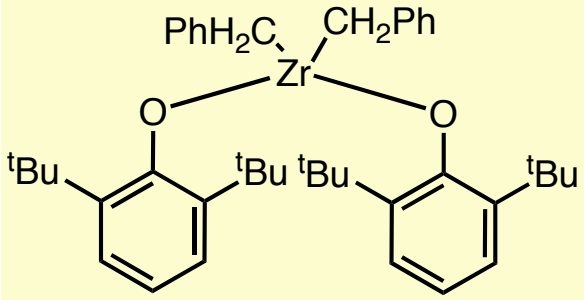
- Long reaction times of up to 2 weeks
- Requires temperature and pressure

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

Transforming CO_2 to Methane



entry	catalyst (mol %)	TOF (h^{-1})	TON	Yield (%)	time (h)
1	**1**/$B(C_6F_5)_3$ (0.45)	23	34	15	1.5
2	**2**/$B(C_6F_5)_3$ (0.42)	31	46	19	1.5
3	**3**/$B(C_6F_5)_3$ (0.44)	150	225	98	1.5
4	**3**/$[Ph_3C][B(C_6F_5)_4]$ (1.8)			0	1.5
5	$B(C_6F_5)_3$ (1.9)			0	3 days



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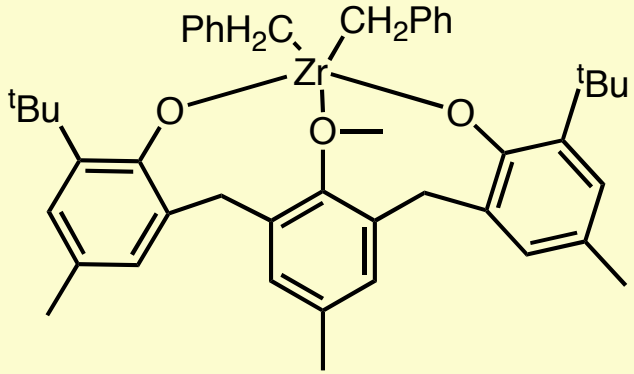

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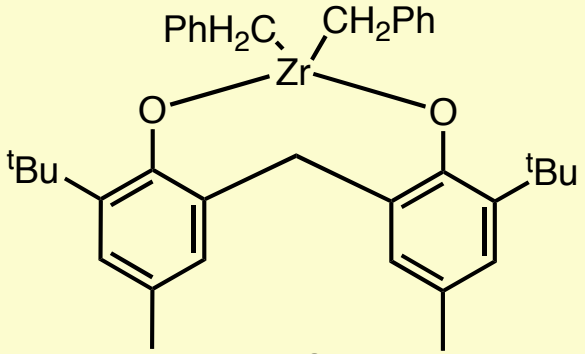
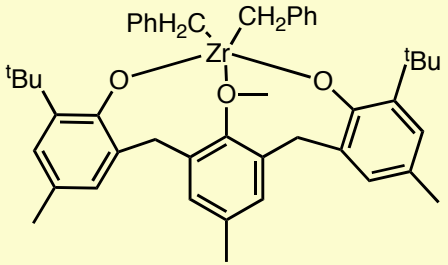


2

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

Silane Variation



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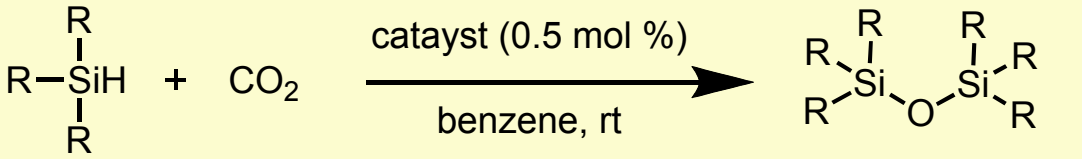
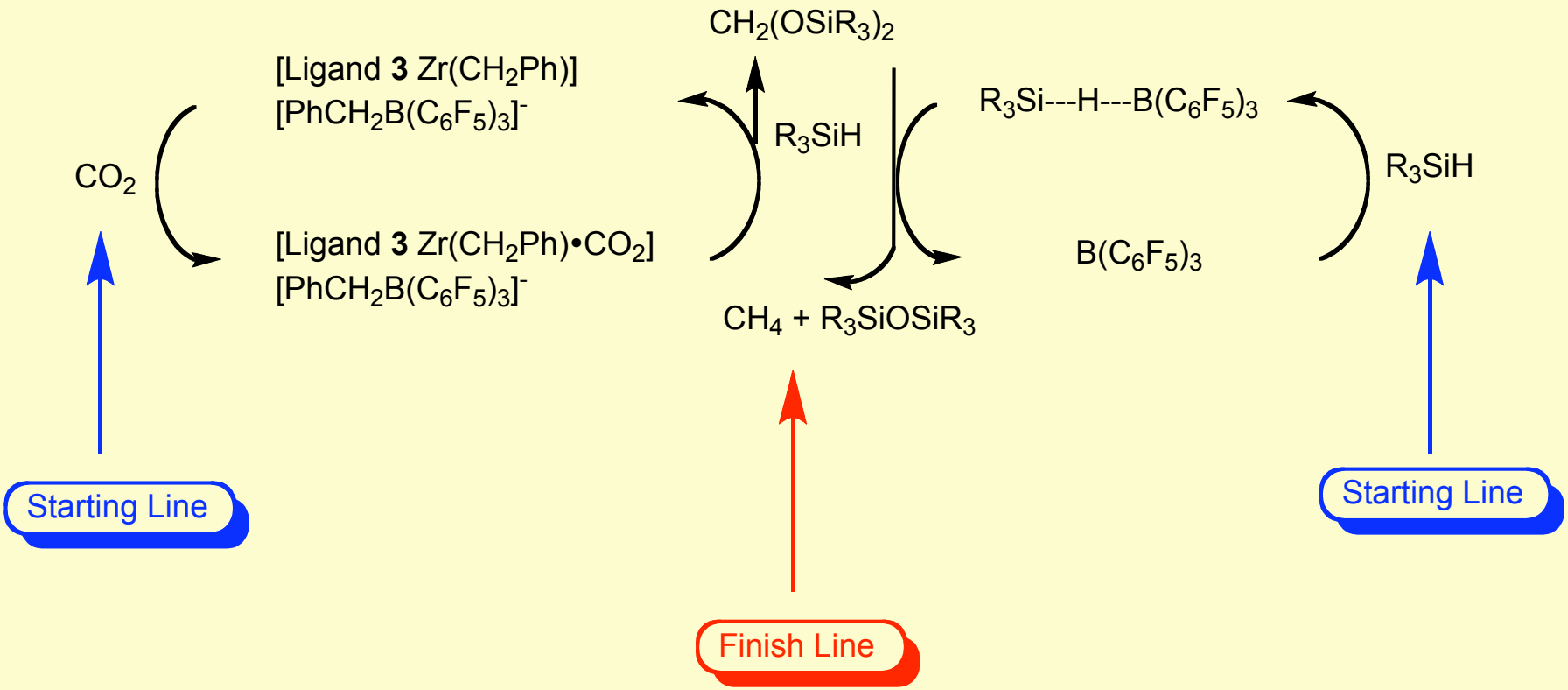


Catalyst = **3**/$B(C_6F_5)_3$ (0.44)

Entry	Substrate	Product	TOF (h^{-1})	TON	Yield (%)	time (h)
1	Et_2MeSiH	$(Et_2MeSi)_2O$	7.3	211	93	29
2	Et_3SiH	$(Et_3Si)_2O$	1.1	180	93	162
3	Ph_3SiH	$(Ph_3SiO)_2CH_2$ $(Ph_3Si)_2O$	0.13	50	64 28	384
4	Et_2SiH_2	$(Et_2Si)_nO$	0.57	108	45	189
5	Ph_2SiH_2	$(Ph_2HSi)_2O$	0.29	49	46	168
6	$PhSiH_3$	$(PhSiO_{1.5})_n$	1.1	162	74	145

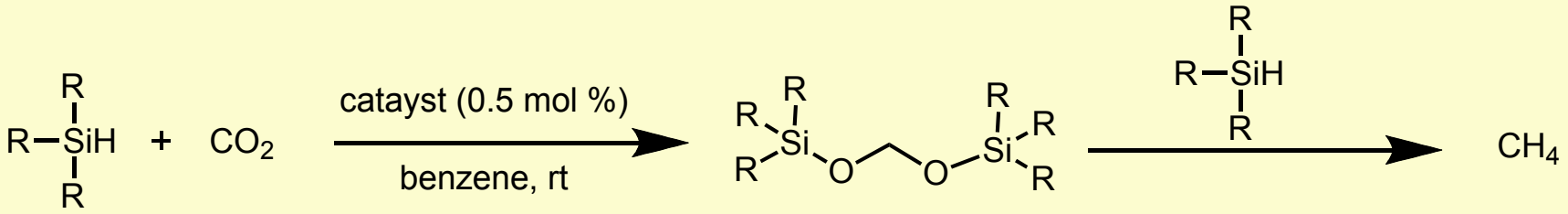
Matsuo, T.; Kawaguchi, H. *J. Am. Chem. Soc.* **2006**, *128*, 12362-12363.

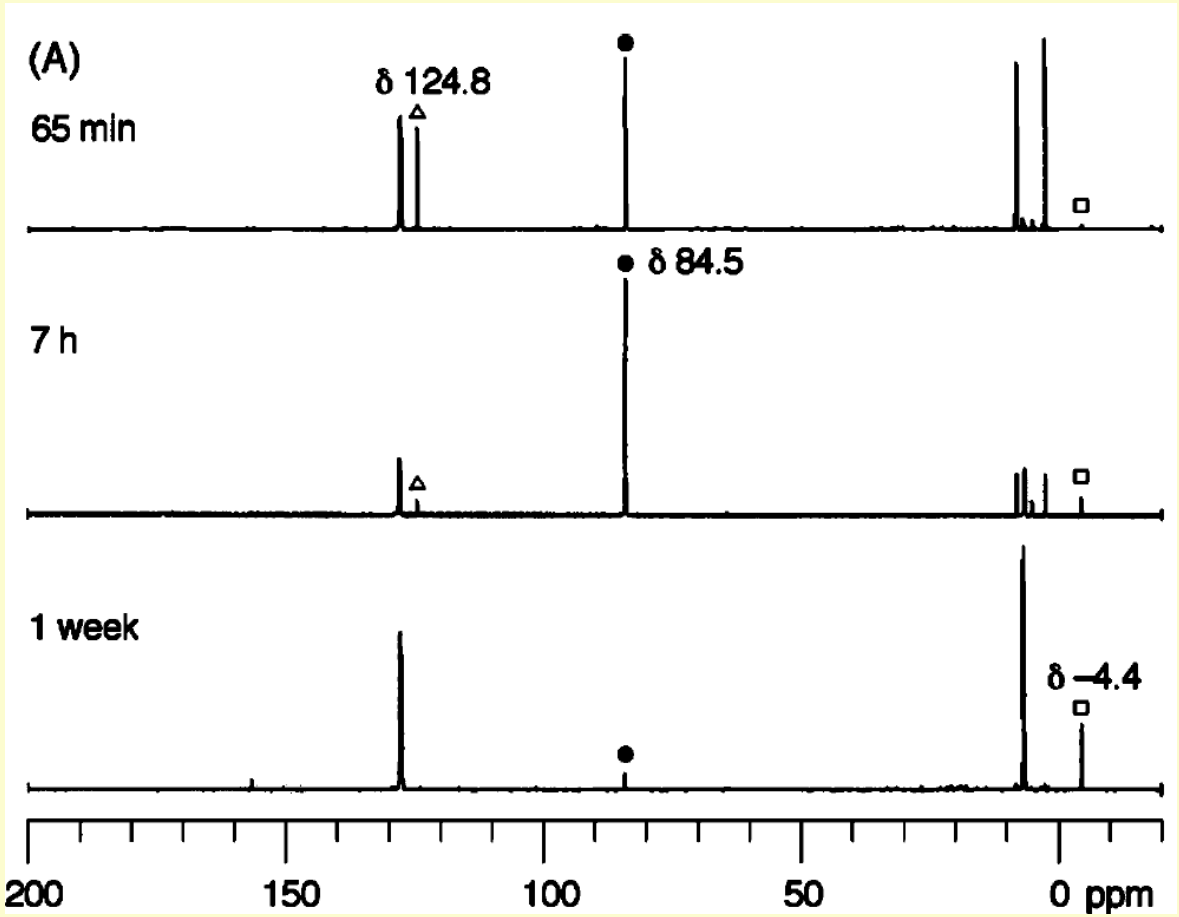
Proposed Mechansim



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

NMR Study of Methane Formation





□ Methane

△ CO_2

● $CH_2(OSiEt_3)_2$

Pros and Cons of Zr Complex

Pros

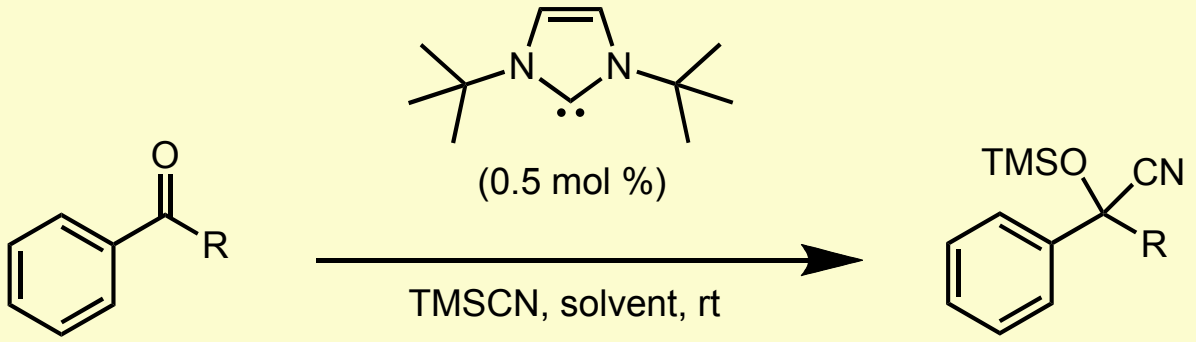
- Production of methane
- Good yields
- Decent Time

Cons

- Transition metal catalyst

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

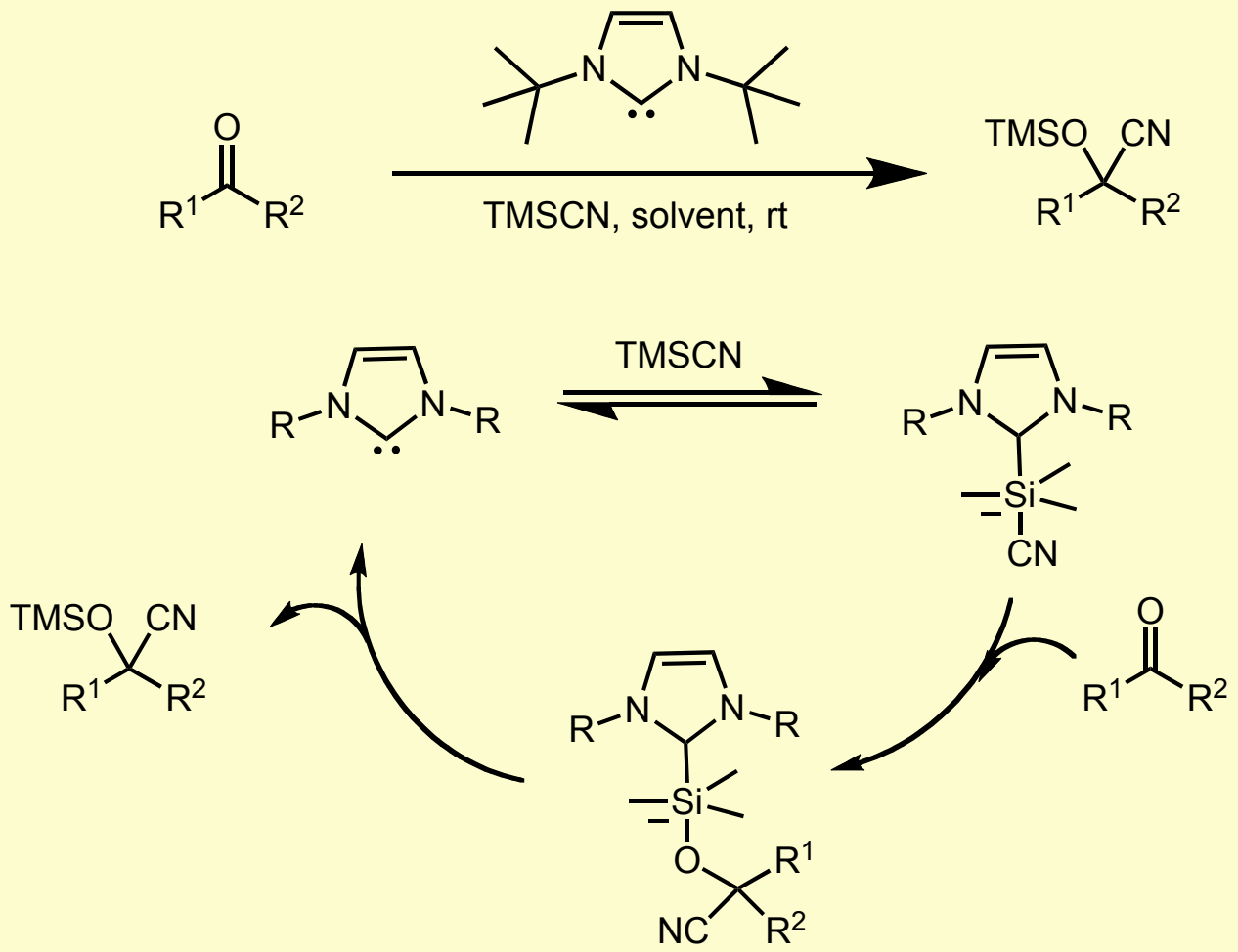
Activation of TMSCN by N-Heterocyclic Carbenes (NHC) for Cyanosilylation of Carbonyl Compounds



Entry	R	Solvent	Catalyst (mol%)	time	% conversion (% isolated yield)
1	H	THF	0.5	10 min	99 (91)
2	H	THF	0.01	4 h	97 (83)
3	Me	DMF	0.5	1 h	95 (80)
4	Me	DMF	0.1	16 h	95 (74)

Song, J. J.; Gallou, F.; Reeves, J. R.; Tan, Z.; Yee, N. K.; Senanayake, C. H. *J. Org. Chem.* **2006**, *71*, 1273-1276.

Proposed Mechanism



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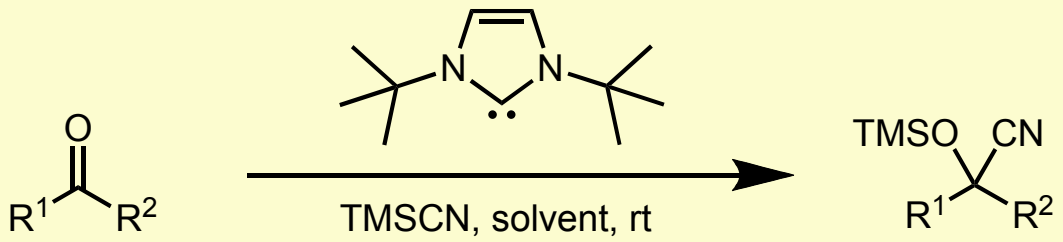
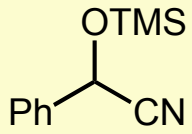
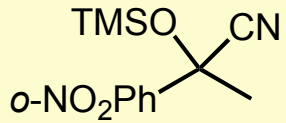
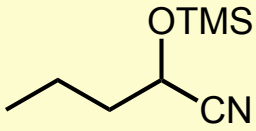
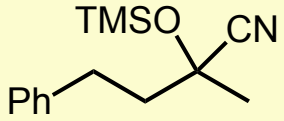
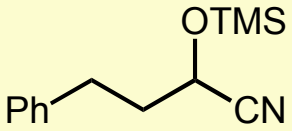
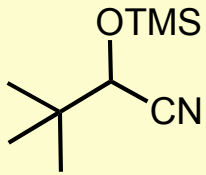
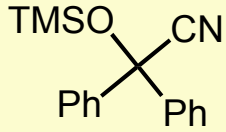
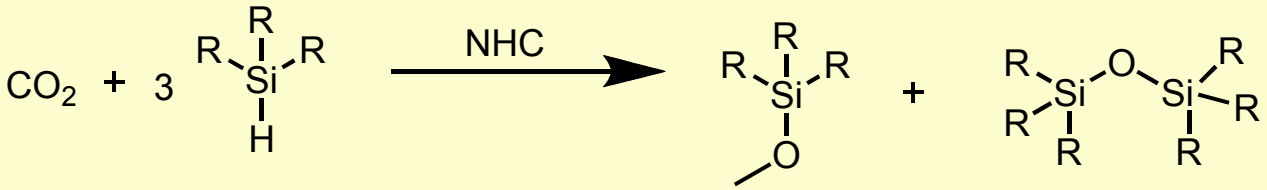
NCH for Cyanosilylation

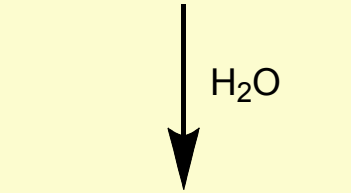


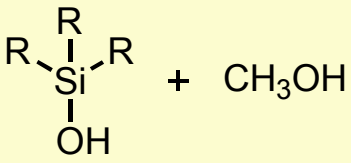
THF, 10 min	Yield (%)	DMF, 2 h	Yield (%)
	91		81
	95		84
	93		83
	87		83

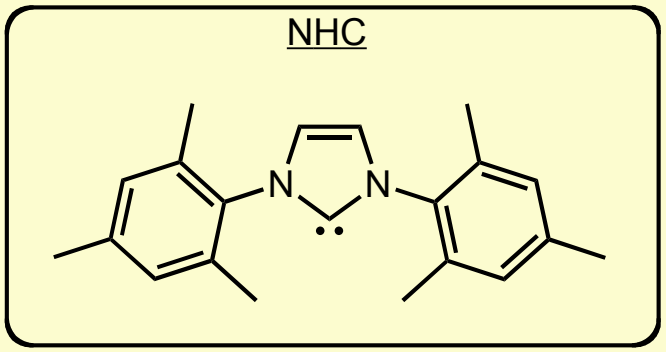
Song, J. J.; Gallou, F.; Reeves, J. R.; Tan, Z.; Yee, N. K.; Senanayake, C. H. *J. Org. Chem.* **2006**, *71*, 1273-1276.

NHC Utilized in CO_2 Transformation to CH_3OH



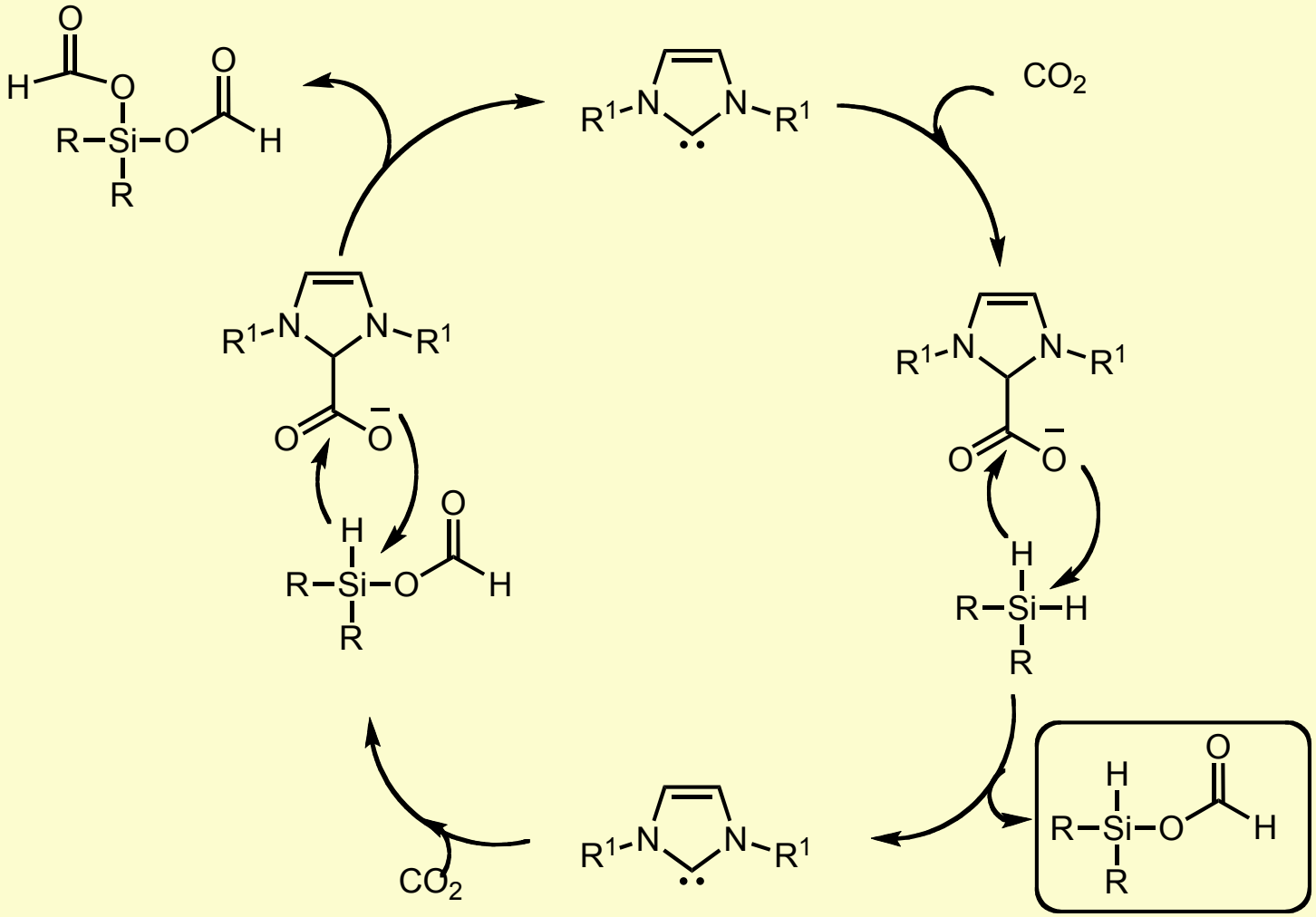






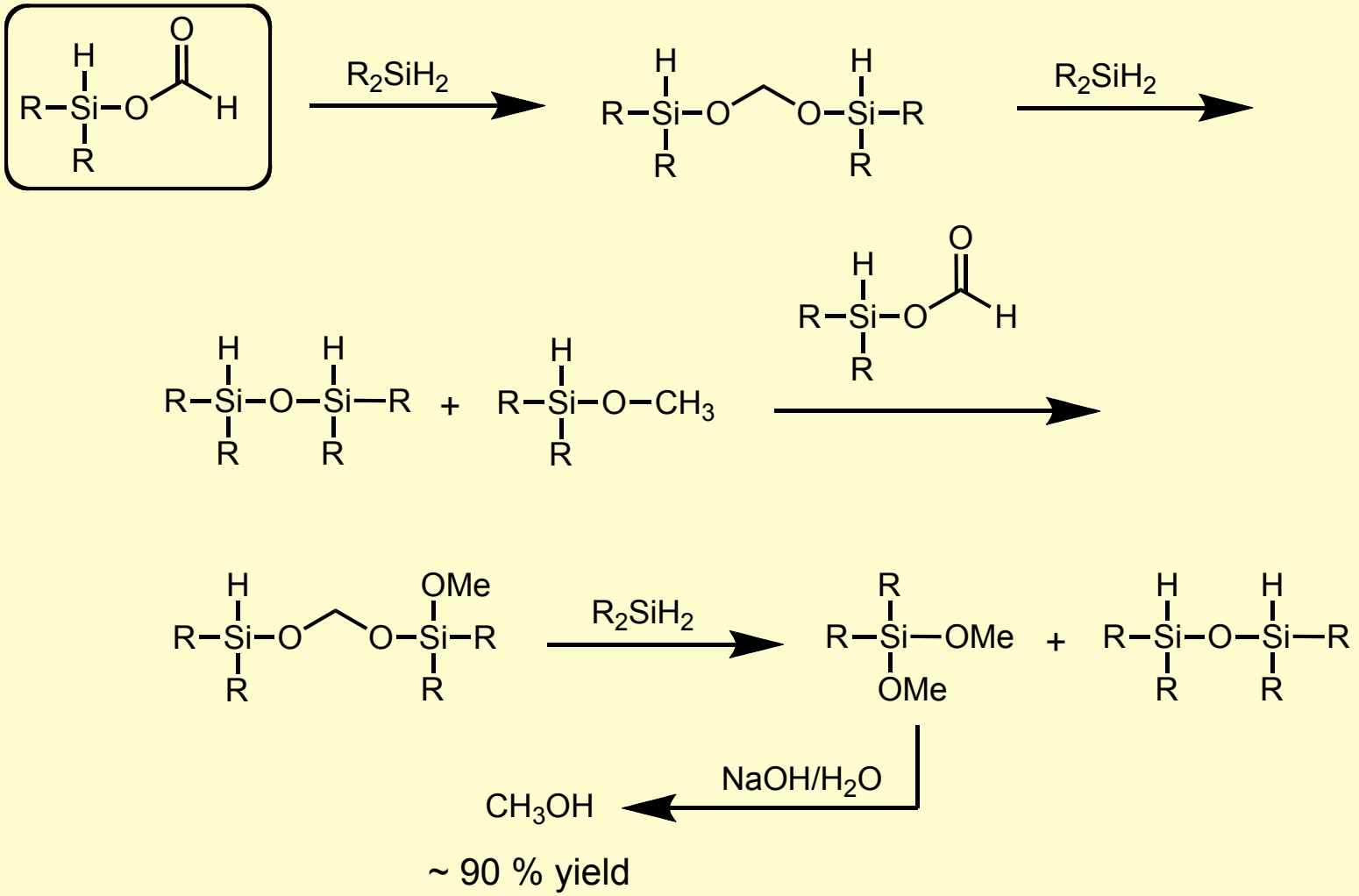
Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 3322-3325.

Proposed Mechanism



Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 3322-3325.

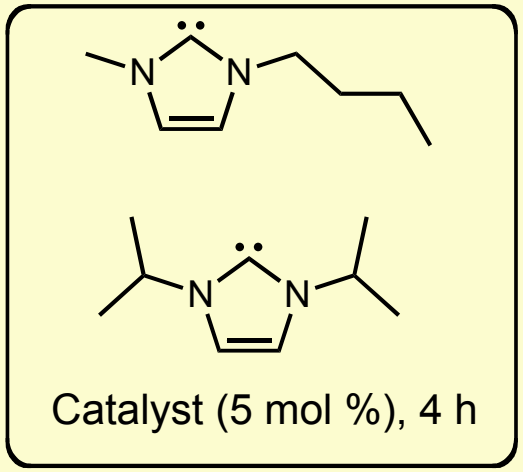
Formation of Methanol



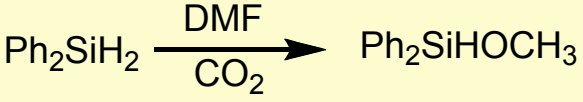
~ 90 % yield

Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 3322-3325.

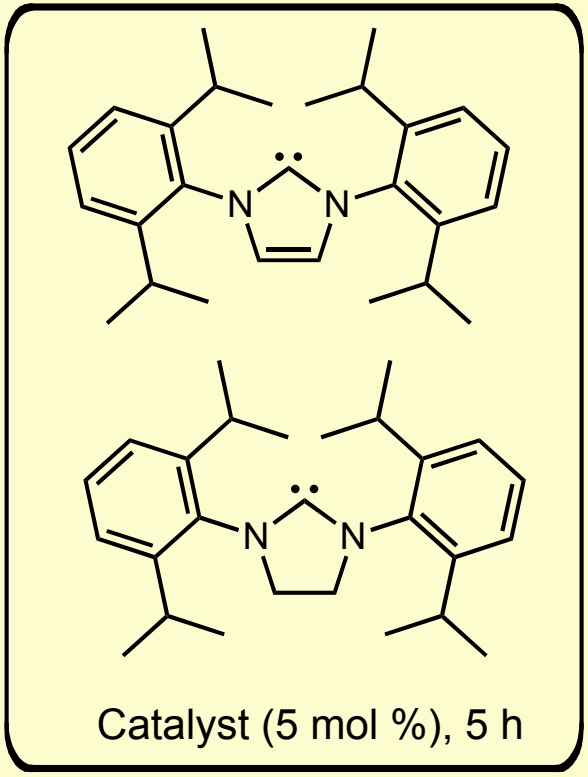
NHC Catalysts Variation



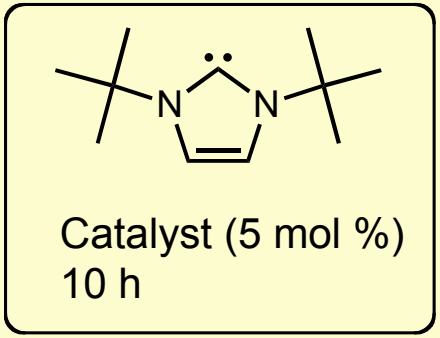
Catalyst (5 mol %), 4 h



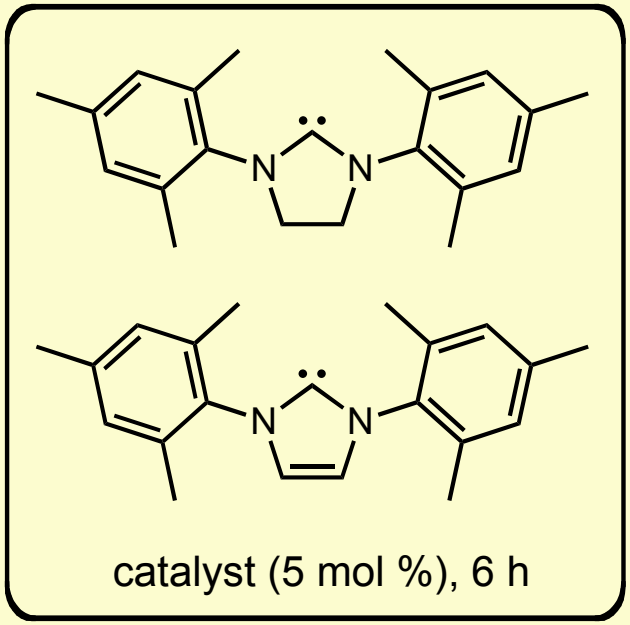
Time = Full Conversion of Silane



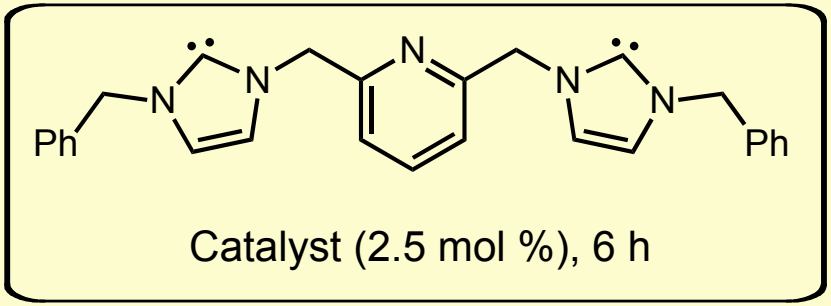
Catalyst (5 mol %), 5 h



Catalyst (5 mol %) 10 h



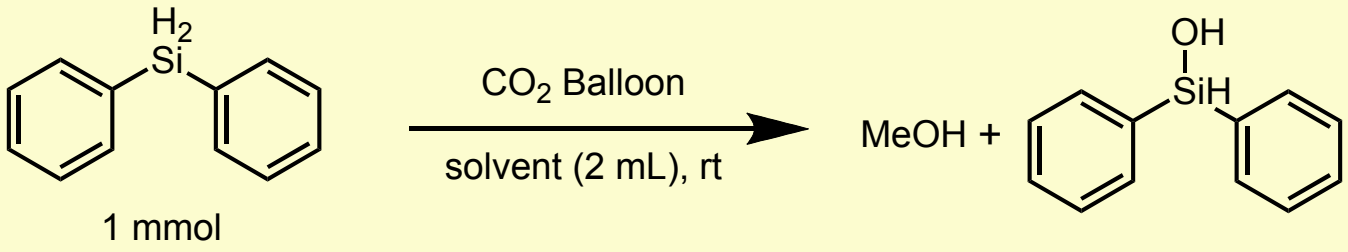
catalyst (5 mol %), 6 h



Catalyst (2.5 mol %), 6 h

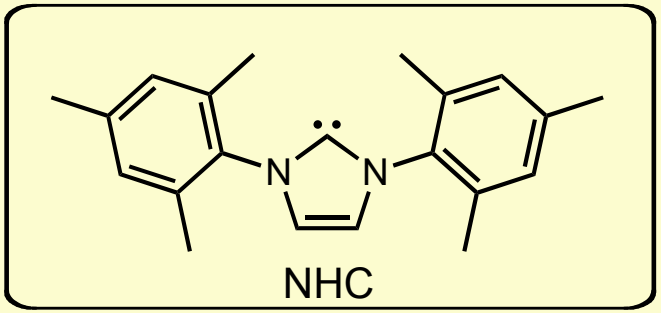
Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 3322-3325.

Solvent Variation



Entry	Catalyst (mol % Si-H)	Solvent	Time (h) [a]
1	1.25	DMF	24
2	1.25	THF	30
3	1.25	MeCN	88
4	1.25	CH_2Cl_2	No Rxn
5	5.00	DMF	6
6	0.50	DMF	30
7	0.25	DMF	40
8	0.05	DMF	72

[a] Time required for the full consumption of silane



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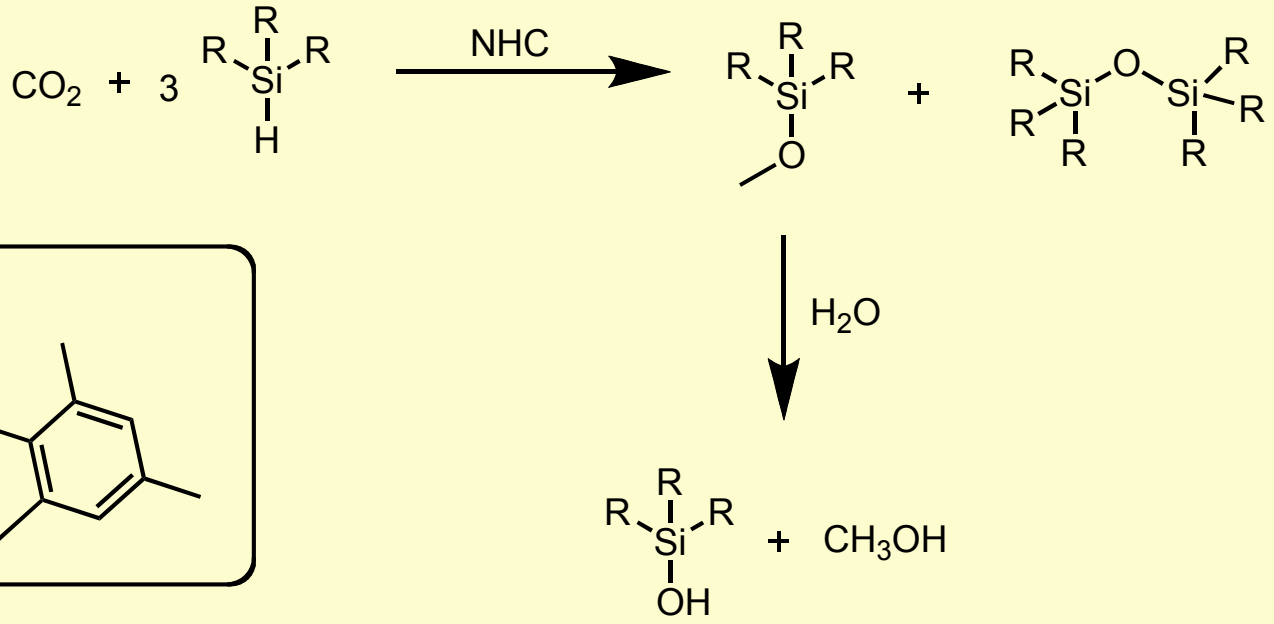
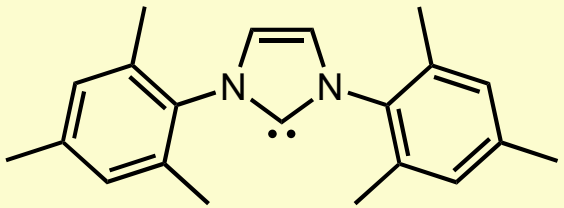
Silane Variation



NHC



Activity of Silane

$PhSiH_3$ >> Ph_2SiH_2 >> $PhSiHMe_2$ > Et_2SiHMe > Et_3SiH, Ph_2SiHMe, Ph_3SiH

No Reaction: Ph_3SiH and Ph_2SiHMe

Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 3322-3325.

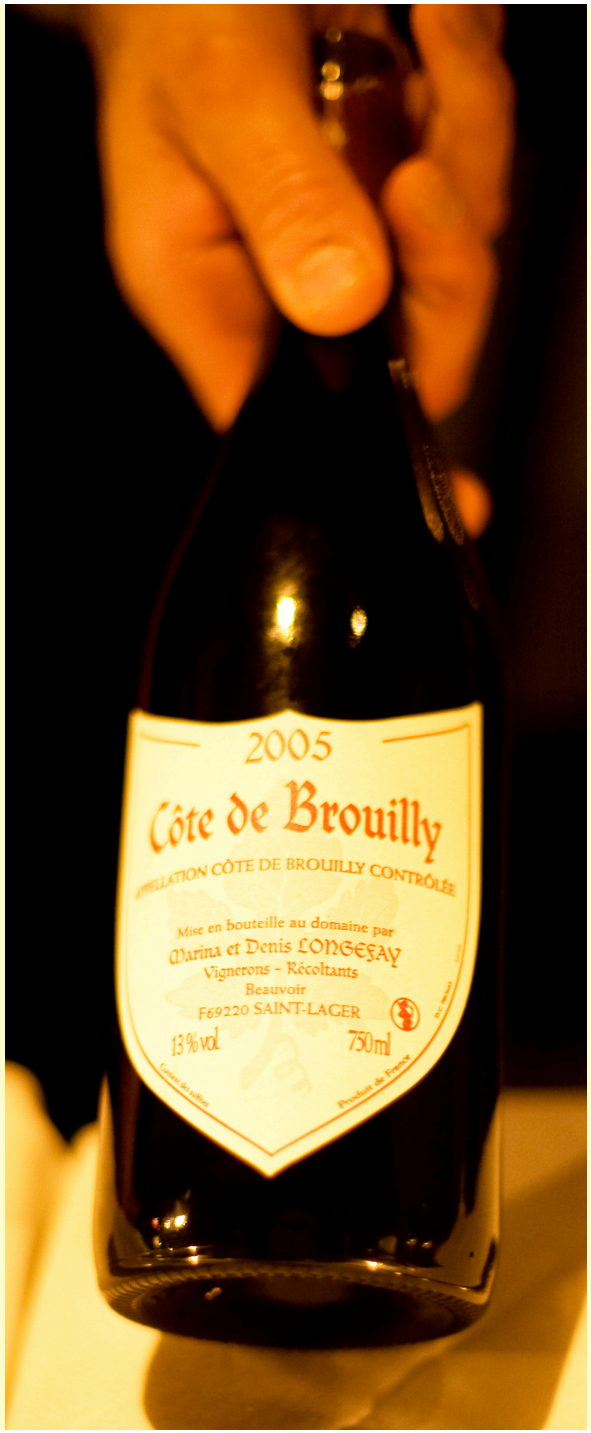
Practicality of the NHC Assisted CO_2 Transformation

NHC

Silane

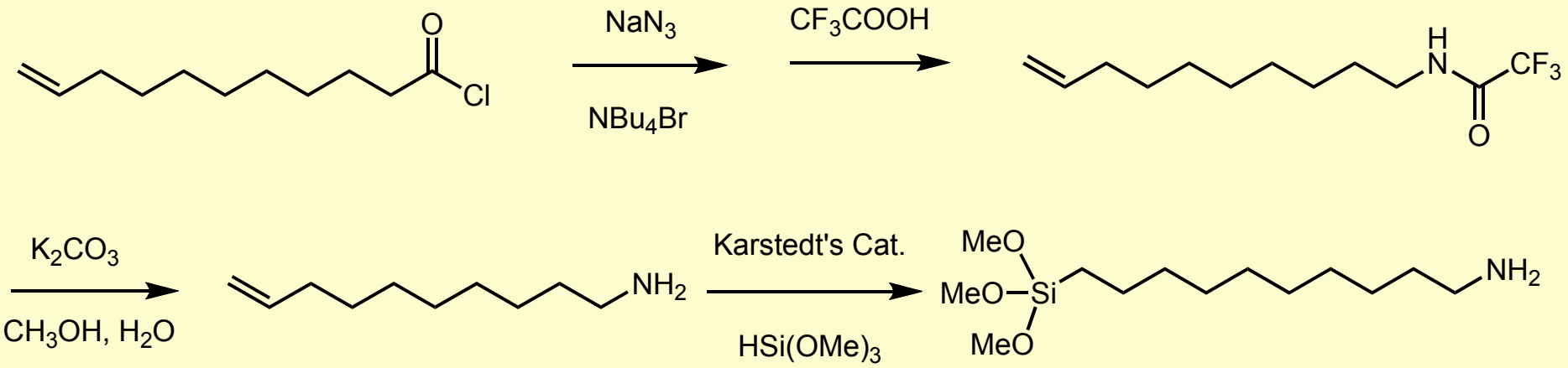
CO_2 is still converted to MeOH
Therefore, catalyst is stable in oxygen conditions.

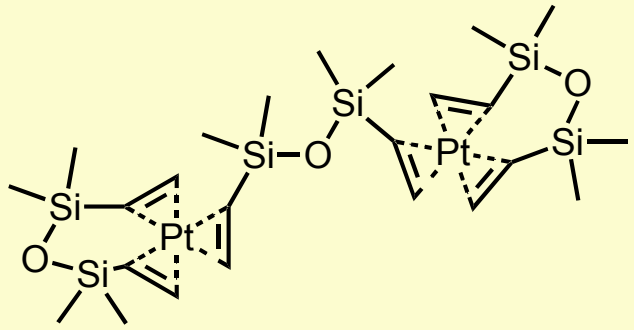
So, why do we need Carbon Dioxide?



A rhetorical figure in which an epigrammatic effect is created by the conjunction of incongruous or contradictory terms.

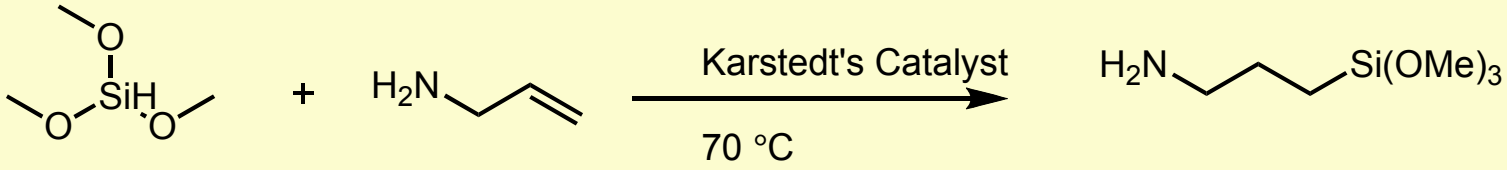
Why I Like This Topic

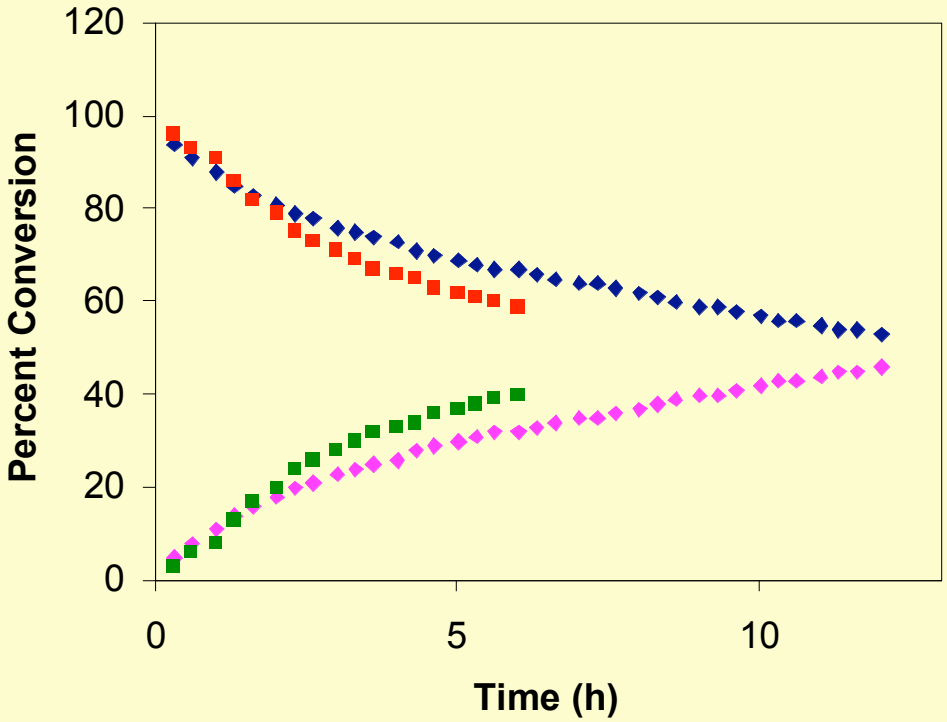




Karstedt's Catalyst

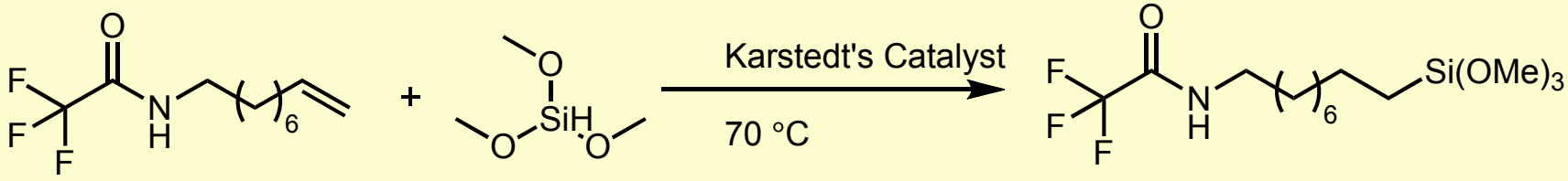
Hydrosilylation of Allylamine

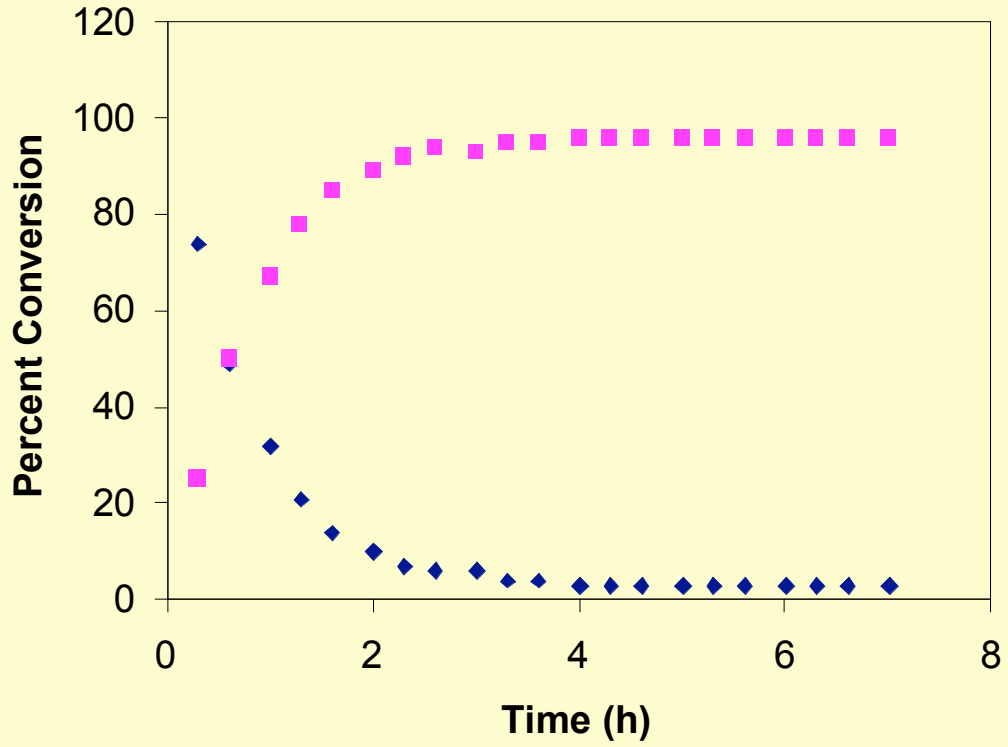




Square/Diamonds = separate runs
Red/Blue = alkene
Purple/Green = silane product

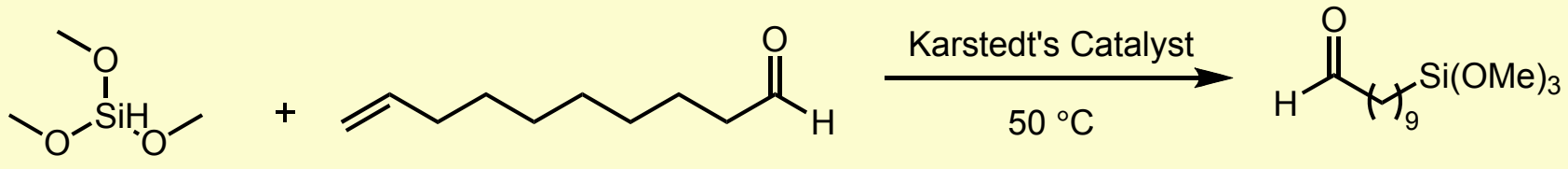
Hydrosilylation of Amides

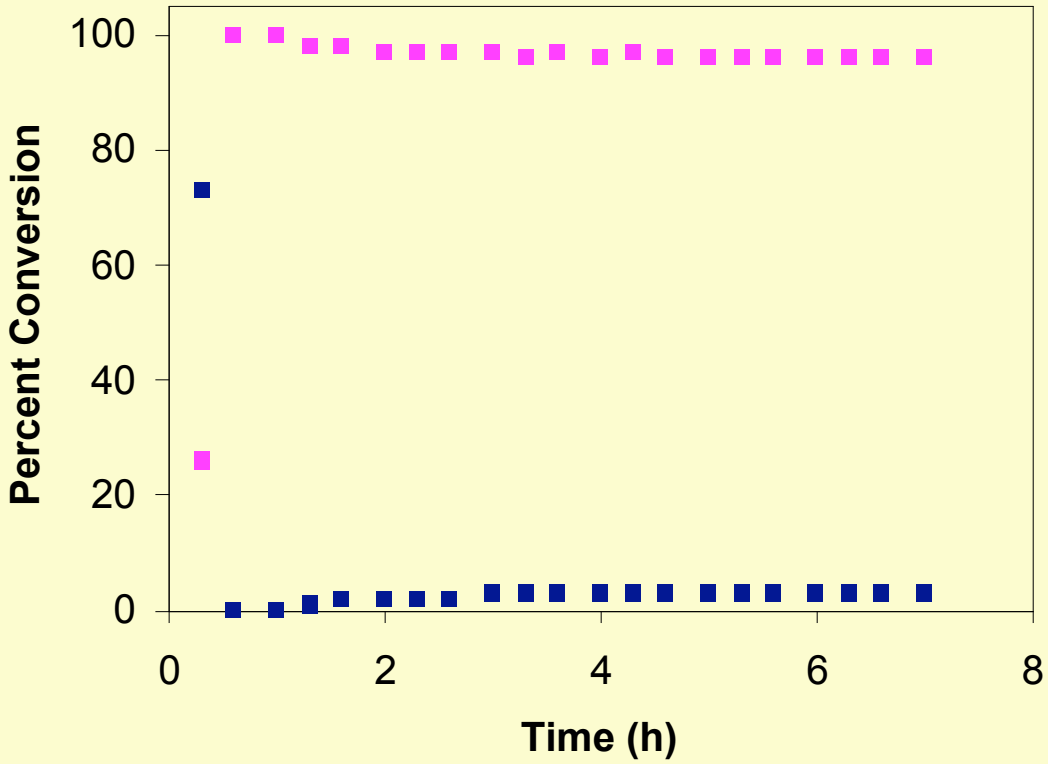




Blue = alkene
Purple = silane product

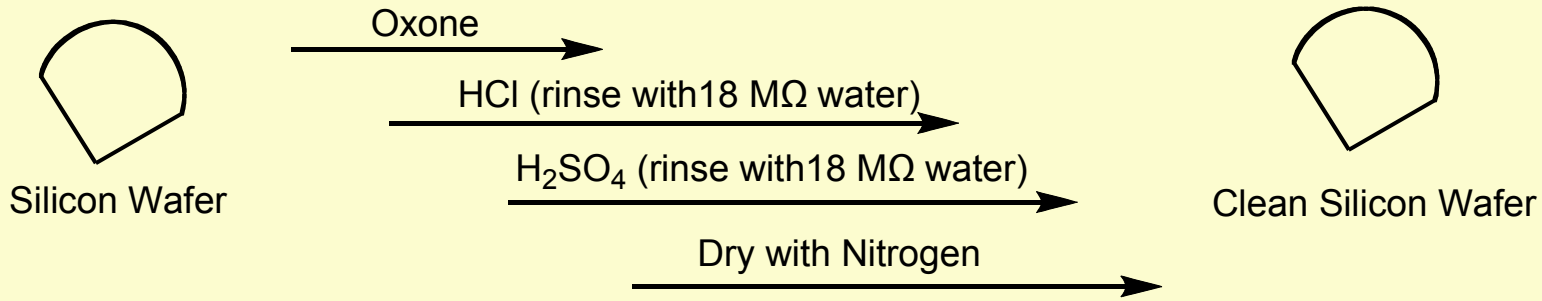
Hydrosilylation of Aldehydes





Blue = alkene
Purple = silane product

Biosensor Formation



Glassware cleaned in base bath
and rinsed with 18 MΩ water.
Dried for 3 h in oven.