Career Review: Prof. Maurice Brookhart

A selection of nearly 280 papers

Dong group at UT Austin
Fanyang Mo
April 24, 2013

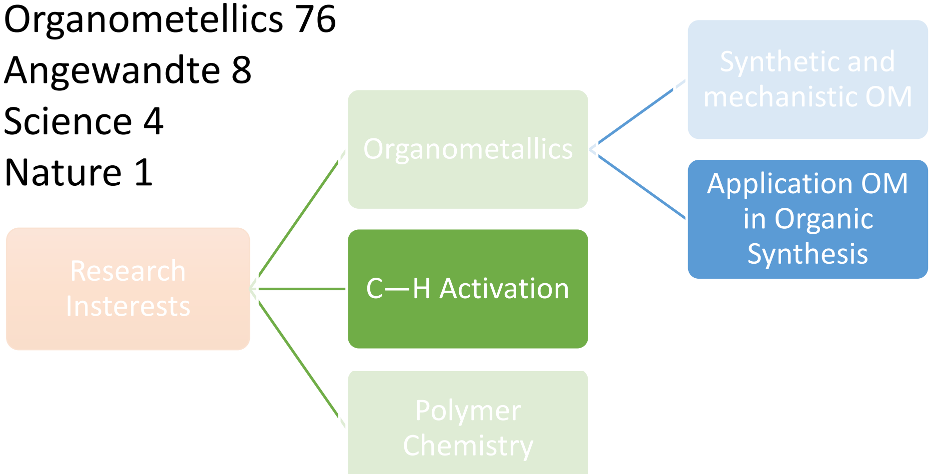
Maurice Brookhart (Organometallic Chemist)

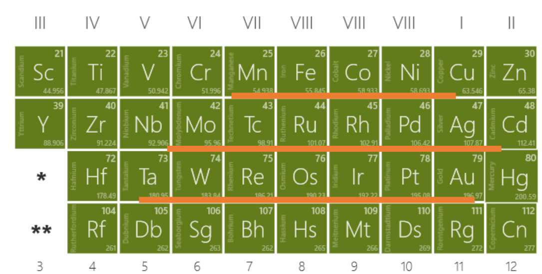
William R. Kenan, Jr. Professor of Chemistry
Department of Chemistry
University of North Carolina at Chapel Hill (**1969**-present)

Born: 1943, North Carolina

Education:
Johns Hopkins University (B. S., **1964**)
University of California, Los Angeles (Ph. D, **1968**)
Southampton University, England (Postdoc, **1969**)

Publications: 274 papers (**1964**-present)
JACS 106
Organometellics 76
Angewandte 8
Science 4
Nature 1



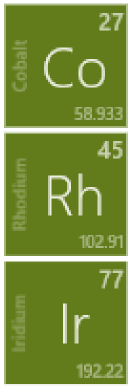


Latest 15 years (Since 1998)

Contents

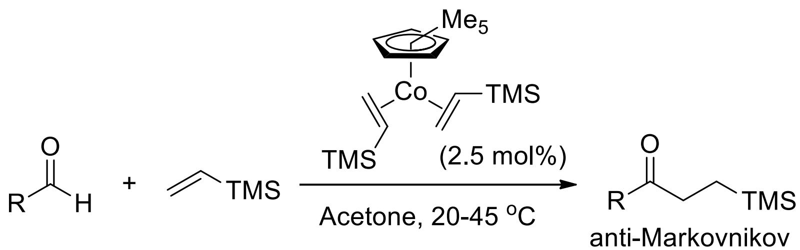
1. Inert Bond Activation (Co, Rh)
    - C—H Activation
    - C—C Activation
2. Dehydrogenation (Ir)
3. Reduction of Alkyl Halides and Carbonyl compounds (Ir)
4. Miscellaneous
5. Acknowledgement

VIII

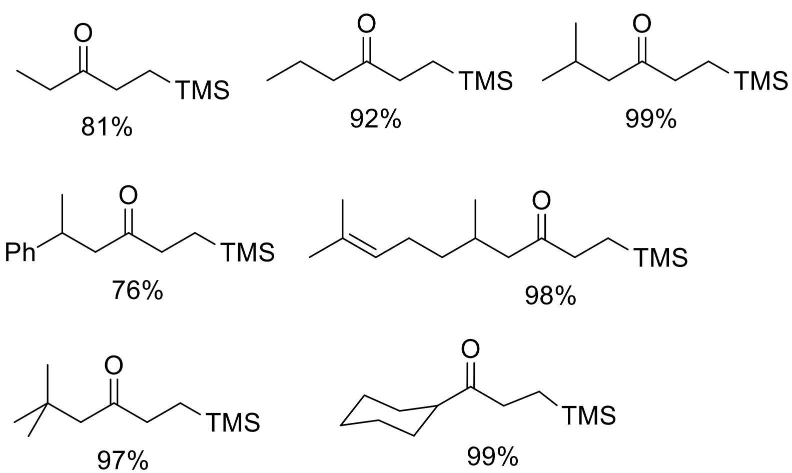


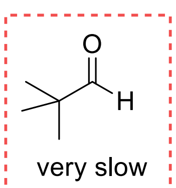
1. Inert Bond Activation *C—H bond*

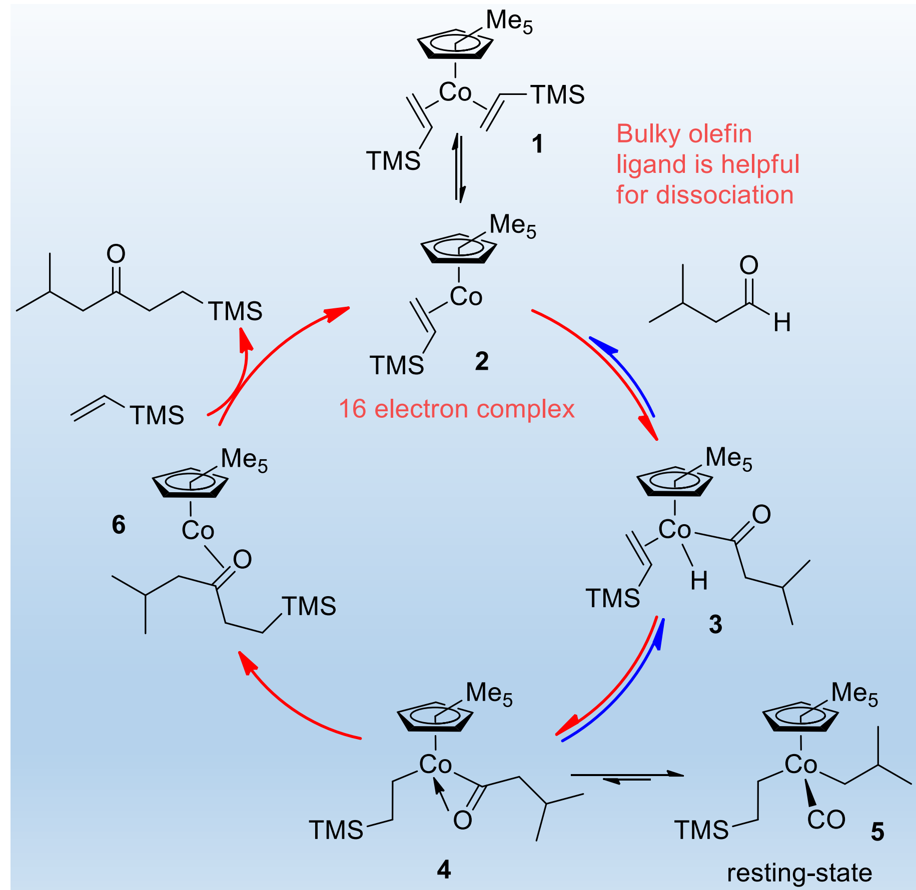
1) Co(I) catalyzed addition of Aliphatic Aldehyde to Vinyl Silanes

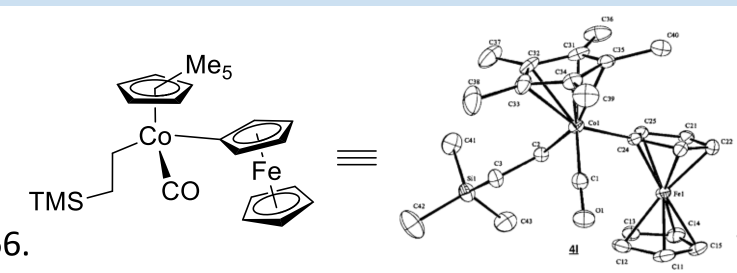


Selected examples:





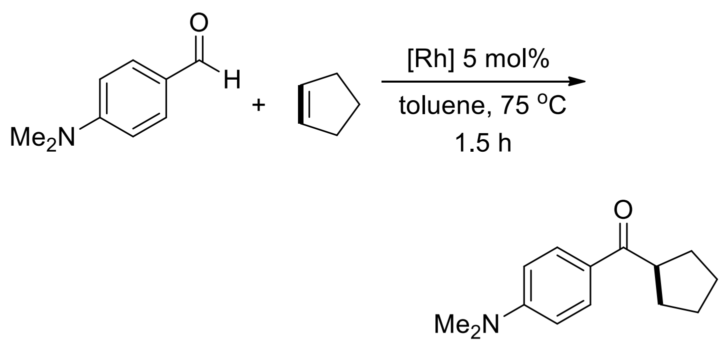


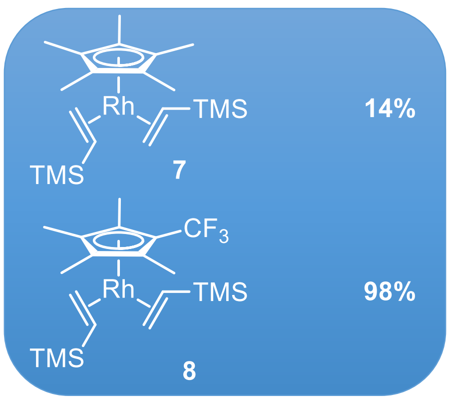


Lenges, C. P., *et. al. J. Am. Chem. Soc.* **1998**, *120*, 6965-6979.
Aromatic version, see: *J. Am. Chem. Soc.* **1997**, *119*, 3165-3166.

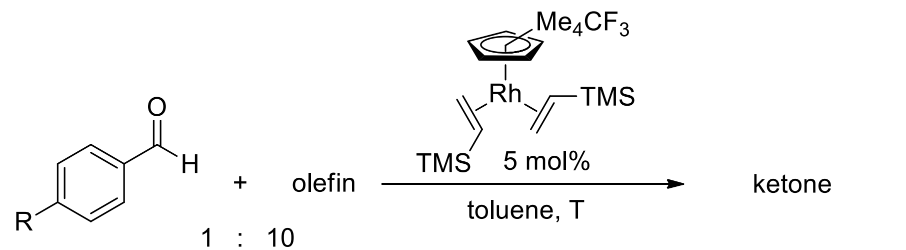
1. Inert Bond Activation *C—H bond*

2) Rh(I) catalyzed addition of Aromatic Aldehyde to Olefins





*Reductive elimination would increase for a more electron deficient metal center.



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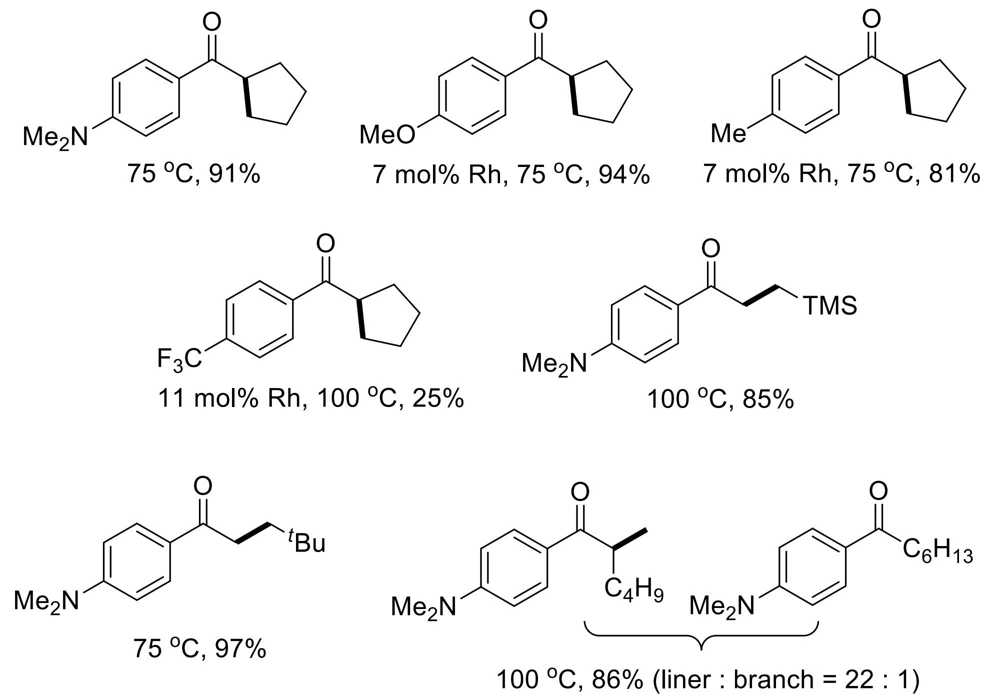
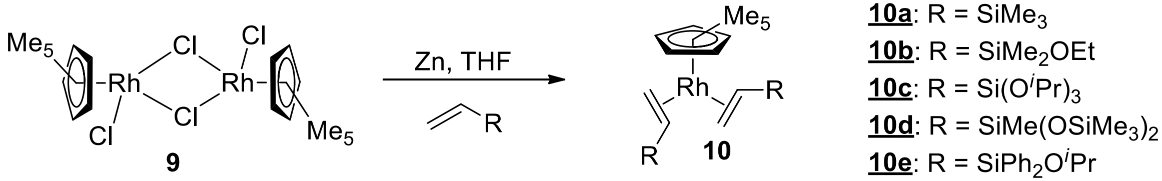


Roy, A. H. *et. al., J. Am. Chem. Soc.* **2007**, *129*, 2082-2093.

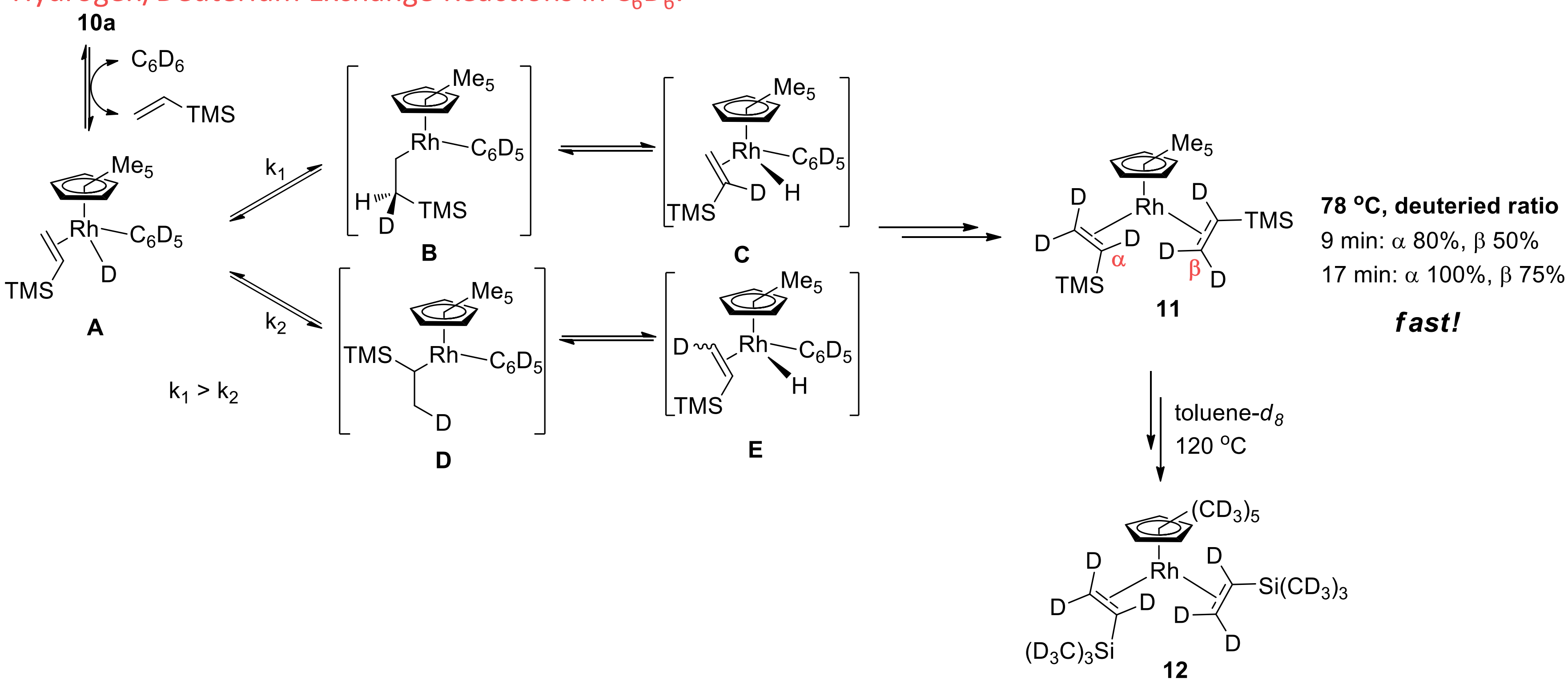
1. Inert Bond Activation *C—H bond*

3) $[C_5Me_5Rh(olefin)_2]$ catalyzed Hydrogen/Deuterium Exchange Reactions

Synthesis of $[C_5Me_5Rh(olefin)_2]$:



Hydrogen/Deuterium Exchange Reactions in C_6D_6:

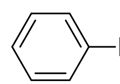
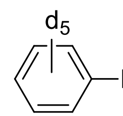
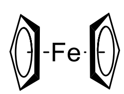
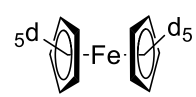
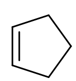
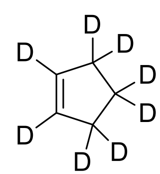
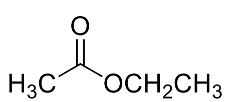
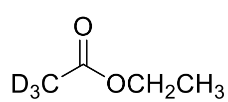


Lenges, C. P., *et. al. J. Am. Chem. Soc*. **1999**, *121*, 4385-4396;
Seiwell, L. P. *J. Am. Chem. Soc*. **1974**, *96*, 7134-7135.

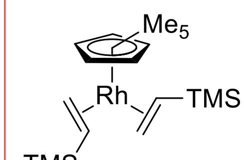
1. Inert Bond Activation *C—H bond*

3) $[C_5Me_5Rh(olefin)_2]$ catalyzed Hydrogen/Deuterium Exchange Reactions

Table 1. H/D Exchange between Benzene-d_6 to Other Substrates Catalyzed by **10a**[a]

entry	substrate	product	%deuteration[b] 5h	24h
1			*ortho*: 76 *meta*: 94 *para*: 93	91 97 97
2	$H_3C{-}O{-}^tBu$	$D_3C{-}O{-}^tBu$	31	44
3	$H_3C{-}O{-}TMS$	$D_3C{-}O{-}TMS$	46	62
4			93	-
5			49	46
6			61	80

[a] **8a** (0.01 g, 2.3×10^{-5} mol), substrate (4.6×10^{-4} mol) in C_6D_6 at 110 °C.
[b] %deuteration estimated from residual 1H NMR signal intensities.



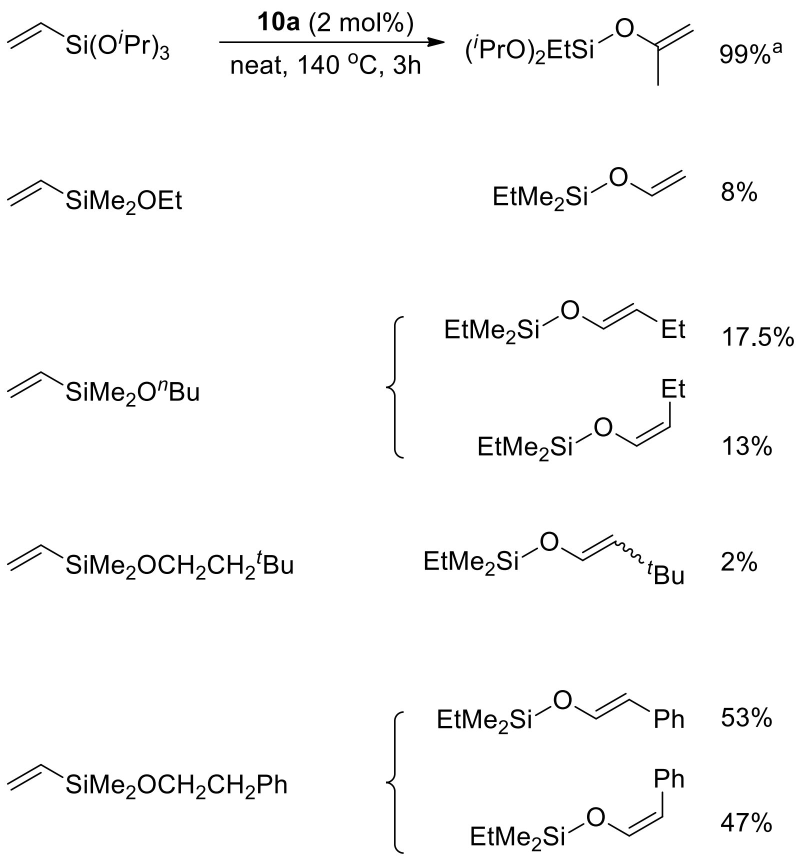
10a

Lenges, C. P., *et. al. J. Am. Chem. Soc*. **1999**, *121*, 4385-4396.

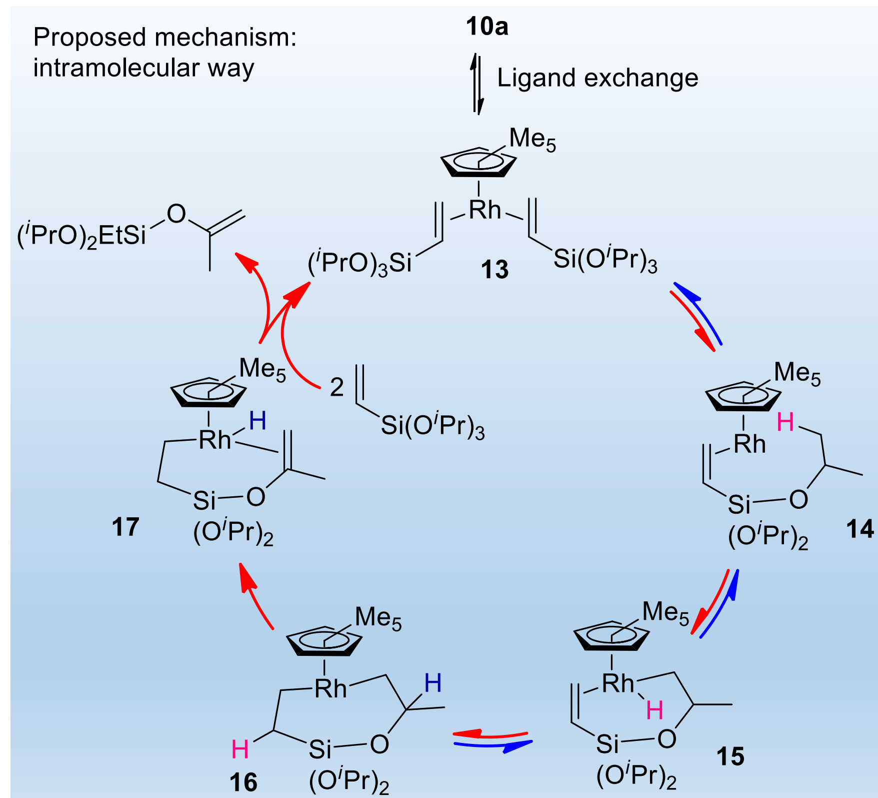
1. Inert Bond Activation *C—H bond*

3) $[C_5Me_5Rh(olefin)_2]$ catalyzed Hydrogen/Deuterium Exchange Reactions

Table 2. Isomerization of Alkoxysilanes to Silyl Enolates



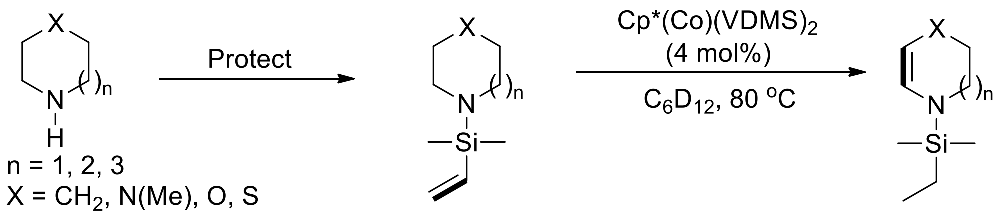
[a]NMR yield.

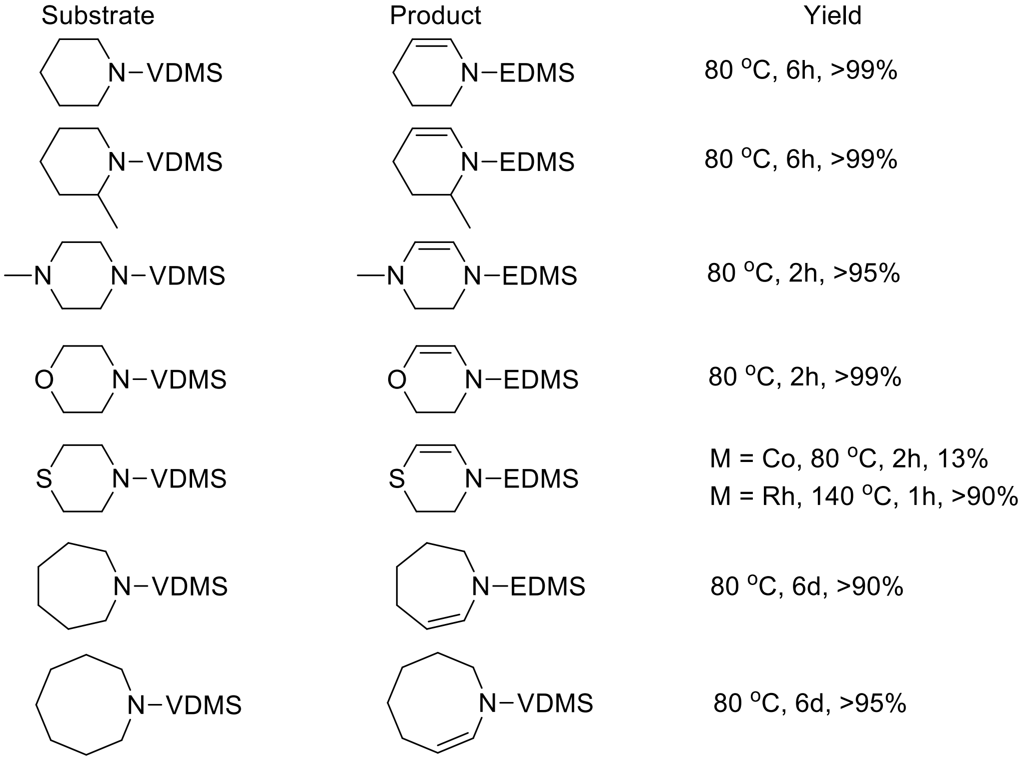


Lenges, C. P., *et. al. J. Am. Chem. Soc*. **1999**, *121*, 4385-4396.
Diaz-Requejo, M. N., *et. al. J. Am. Chem. Soc*. **2003**, *125*, 2038-2039.

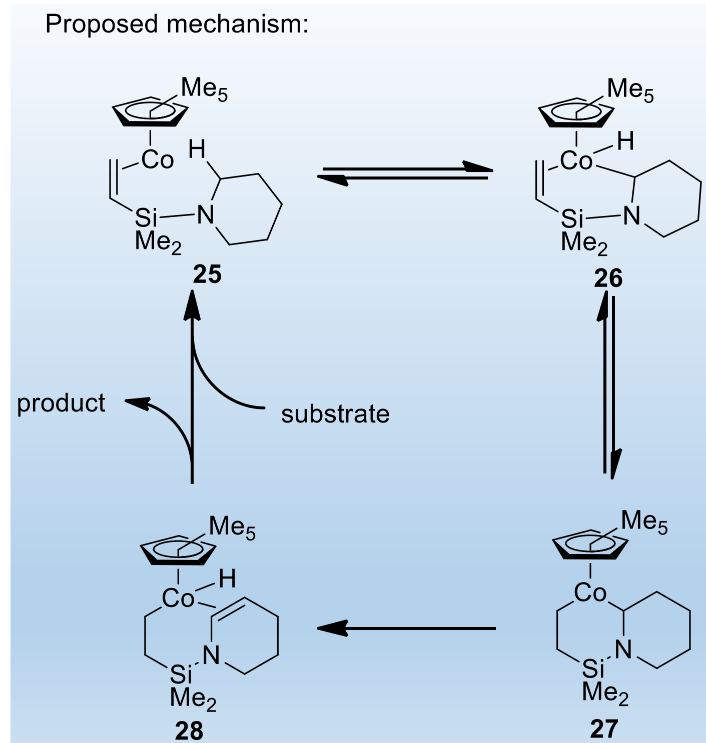
1. Inert Bond Activation *C—H bond*

4) Co(I) Catalyzed sp3 C—H Bond: Catalytic Synthesis of Enamines





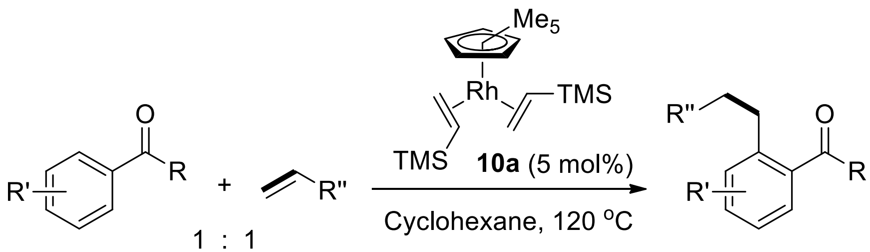
VDMS: vinyl(dimethyl)silyl; EDMS: ethyl(dimethyl)silyl.



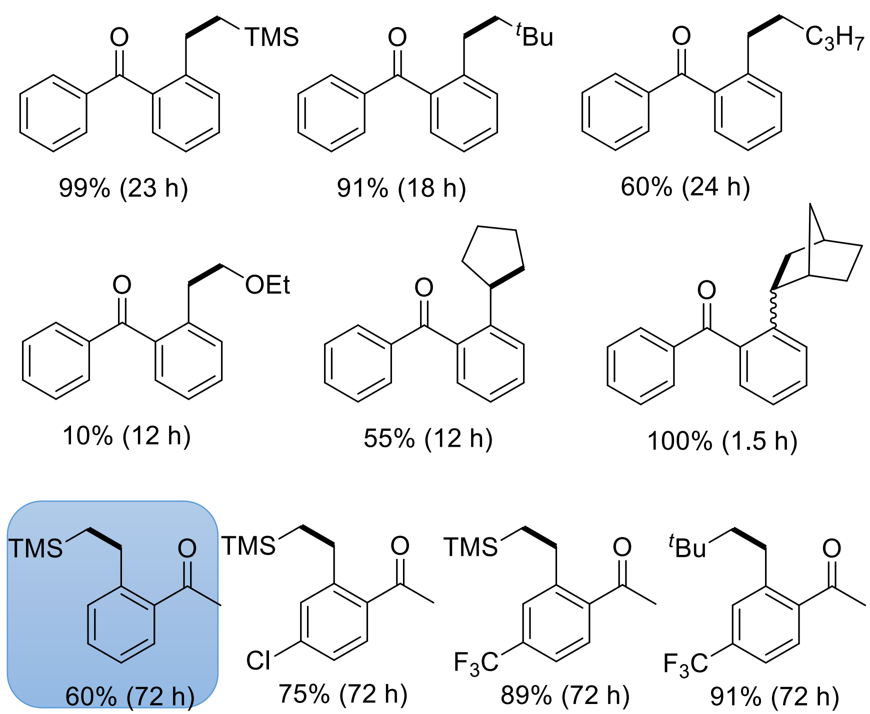
Bolig, A. D., *et. al. J. Am. Chem. Soc.* **2007**, *129*, 14544-14545.

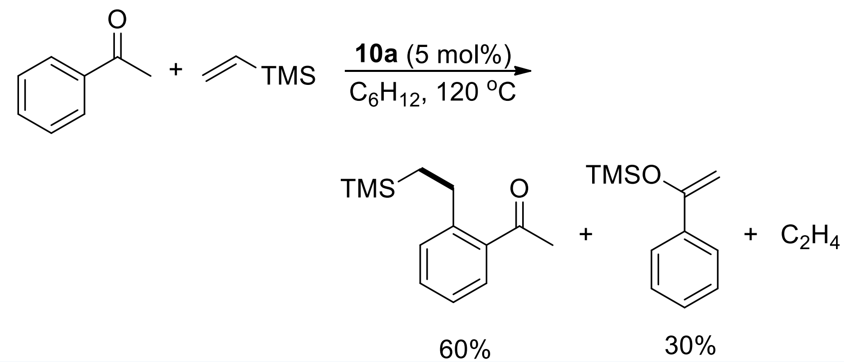
1. Inert Bond Activation *C—H bond*

5) $[C_5Me_5Rh(olefin)_2]$ catalyzed Addition of Olefins to Aromatic Ketones

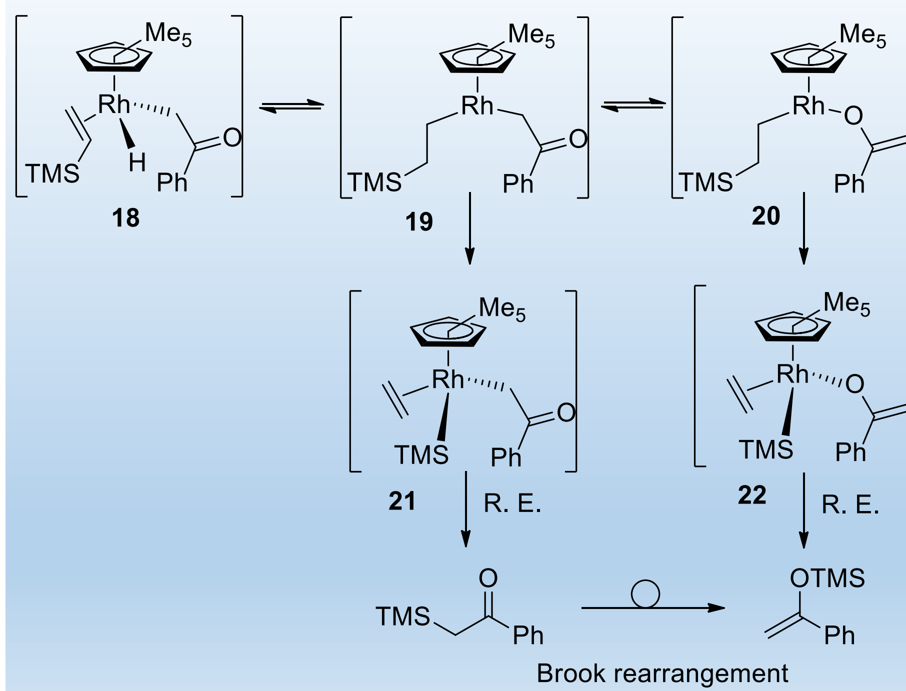


Selected examples:





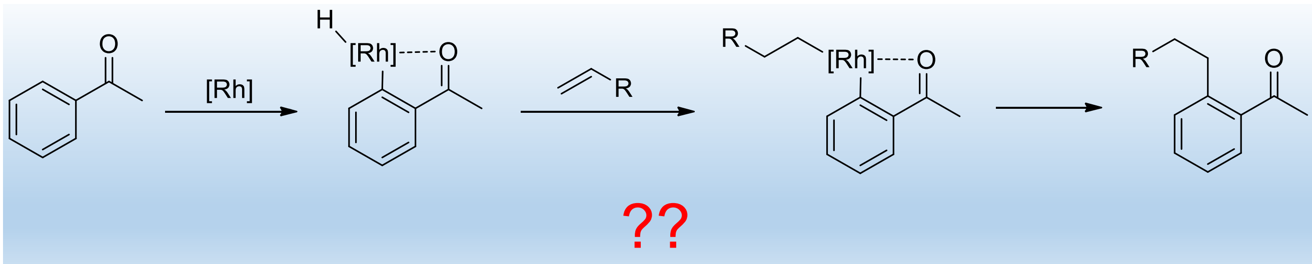
Possible pathway:

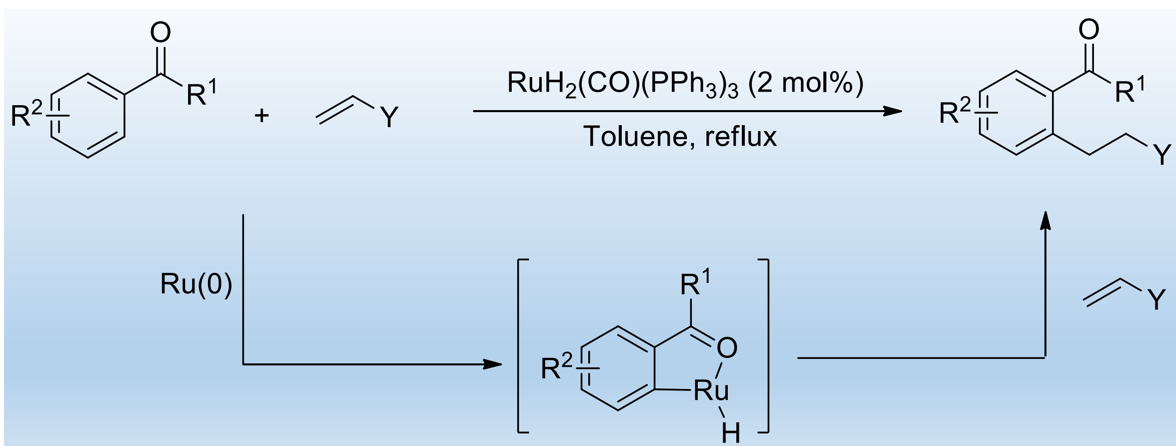


Lenges, C. P., *et. al. J. Am. Chem. Soc*. **1999**, *121*, 6616-6623.

1. Inert Bond Activation *C—H bond*

5) [$C_5Me_5Rh(olefin)_2$] catalyzed Addition of Olefins to Aromatic Ketones

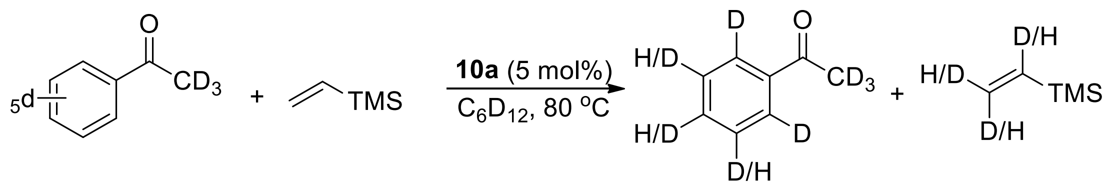


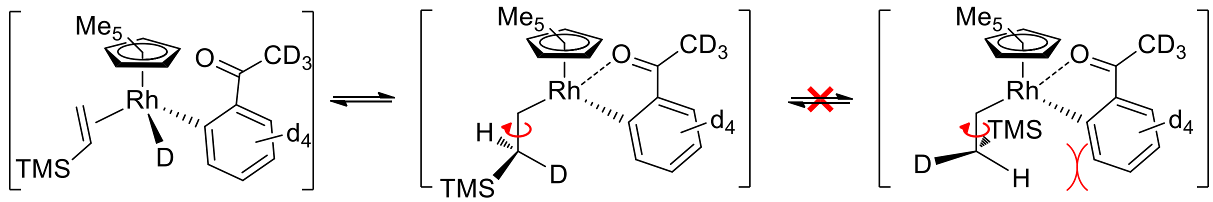


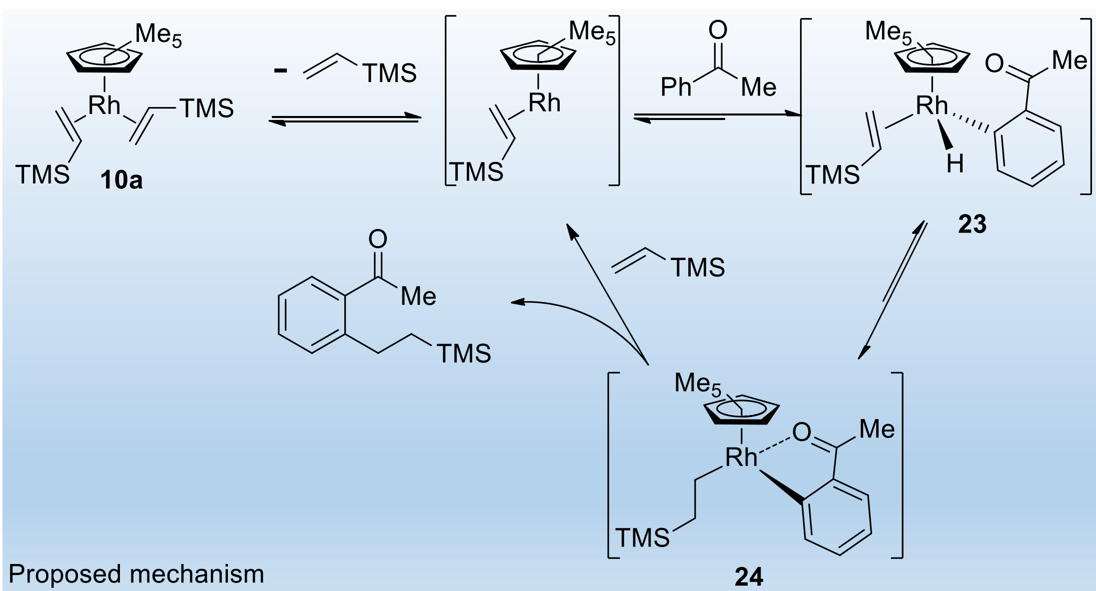
Murai, S., *et. al*. *Nature* **1993**, *366*, 529-531.

1. Inert Bond Activation *C—H bond*

5) [$C_5Me_5Rh(olefin)_2$] catalyzed Addition of Olefins to Aromatic Ketones



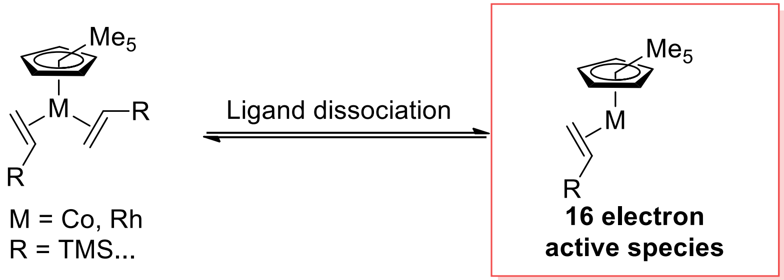


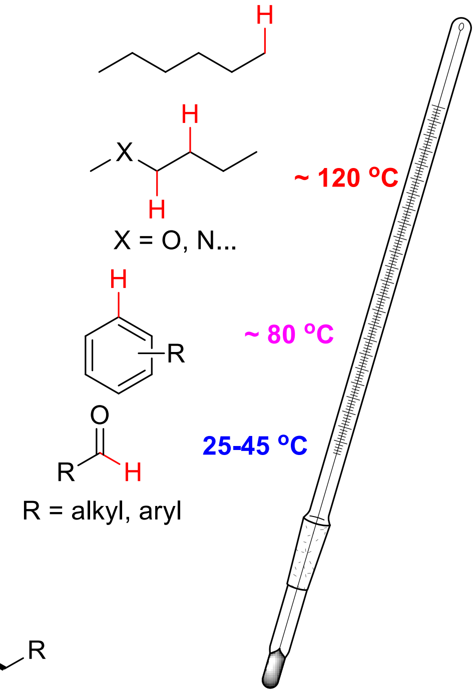


Lenges, C. P., *et. al. J. Am. Chem. Soc*. **1999**, *121*, 6616-6623.

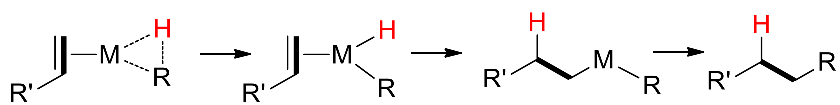
1. Inert Bond Activation *C—H bond*

6) Summary for Cp*M(olefin)2 catalyzed C—H bond activation.



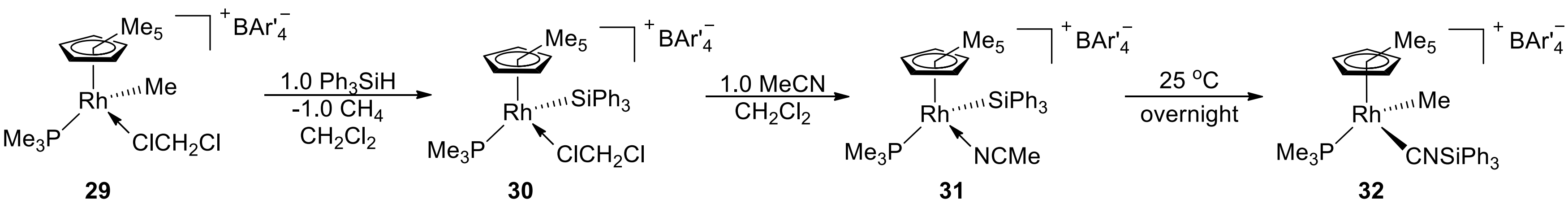


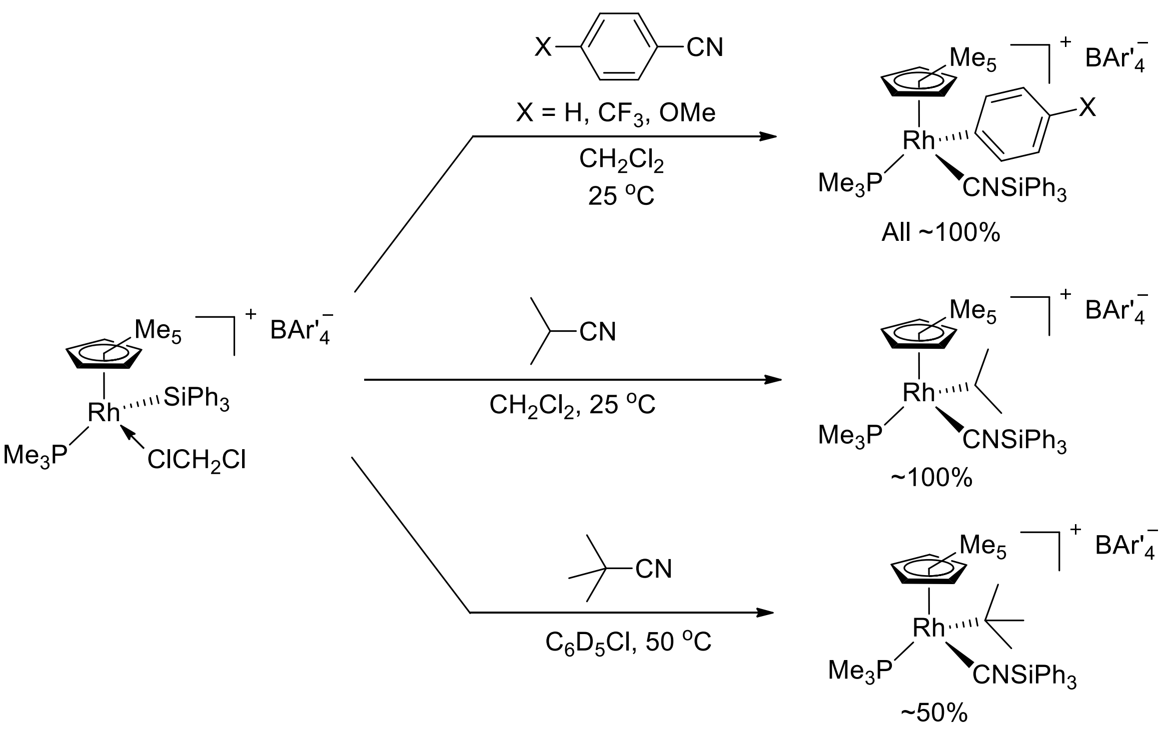
frequently used solvent: <u>cyclohexane</u>...

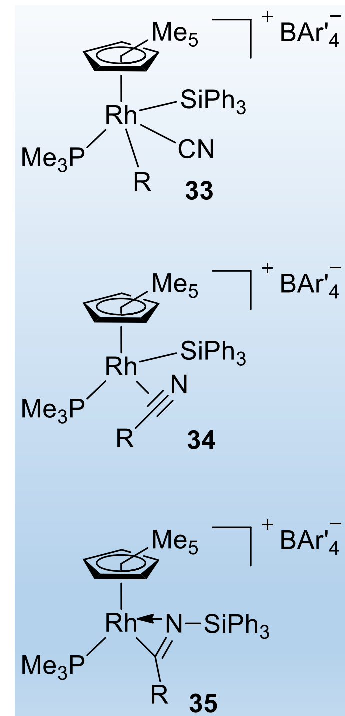


1. Inert Bond Activation *C—C bond*

8) C—C bond activation of R—CN Using a Cationic Rh(III) complex.





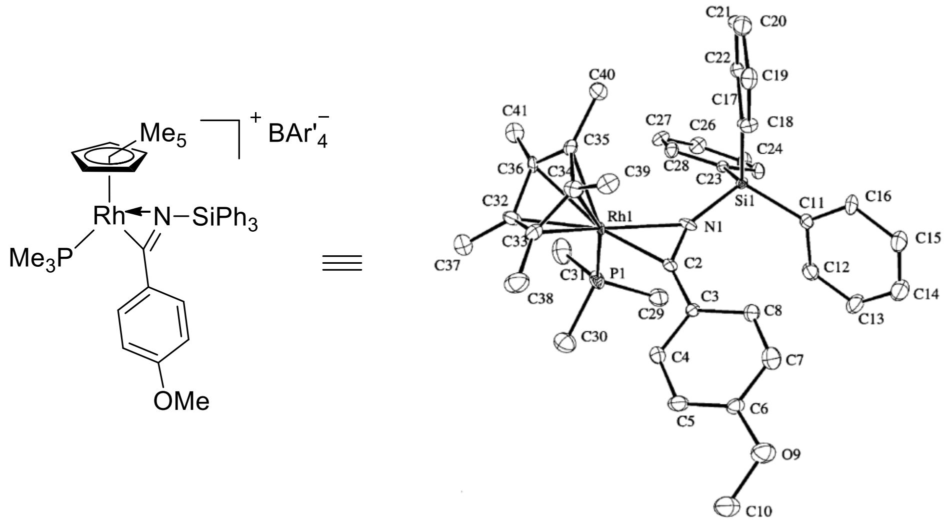


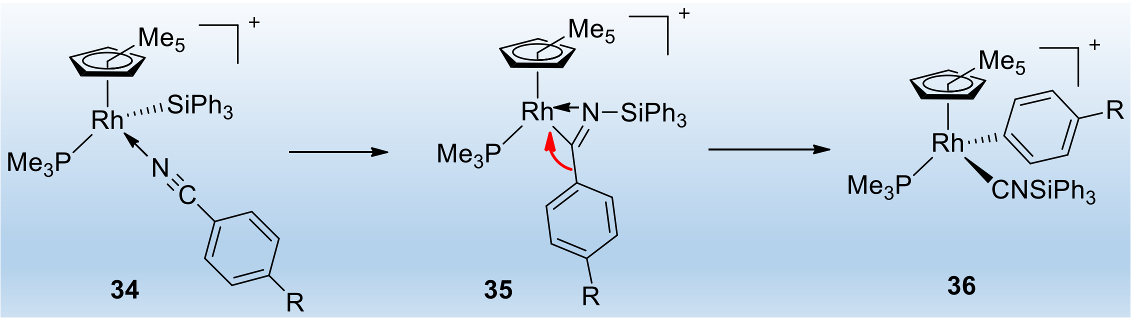
Possible intermediates

Taw, F. L., *et. al. J. Am. Chem. Soc*. **2002**, *124*, 4192-4193.

1. Inert Bond Activation *C—C bond*

8) C—C bond activation of R—CN Using a Cationic Rh(III) complex.

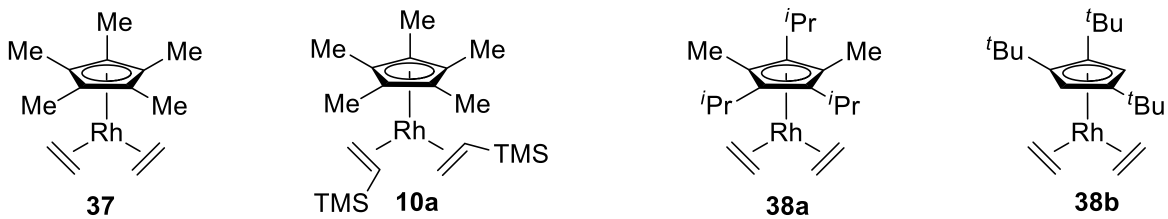


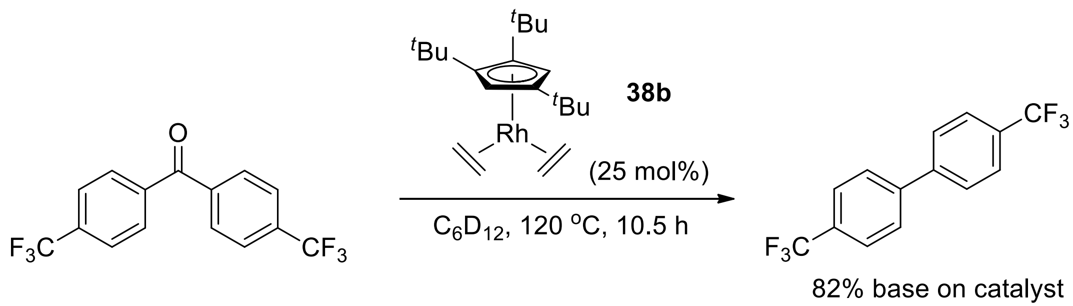


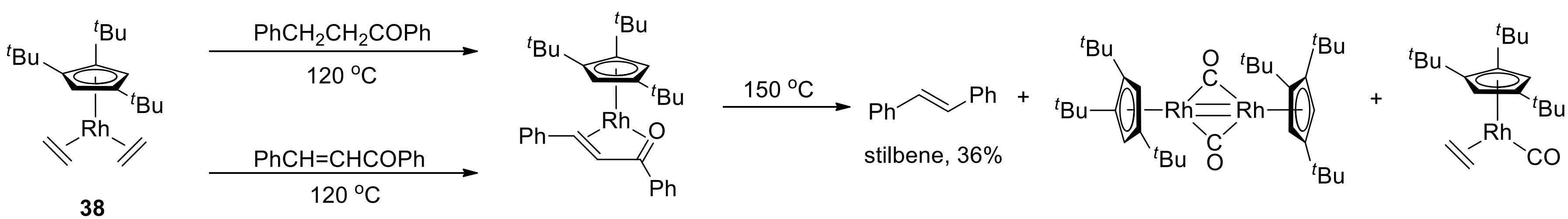
Taw, F. L., *et. al*. *J. Am. Chem. Soc*. **2003**, *125*, 9808-9813.

1. Inert Bond Activation *C—C bond*

9) Decarbonylation of Aryl Ketones Mediated by Bulky Cp*Rh(ethylene)$_2$.



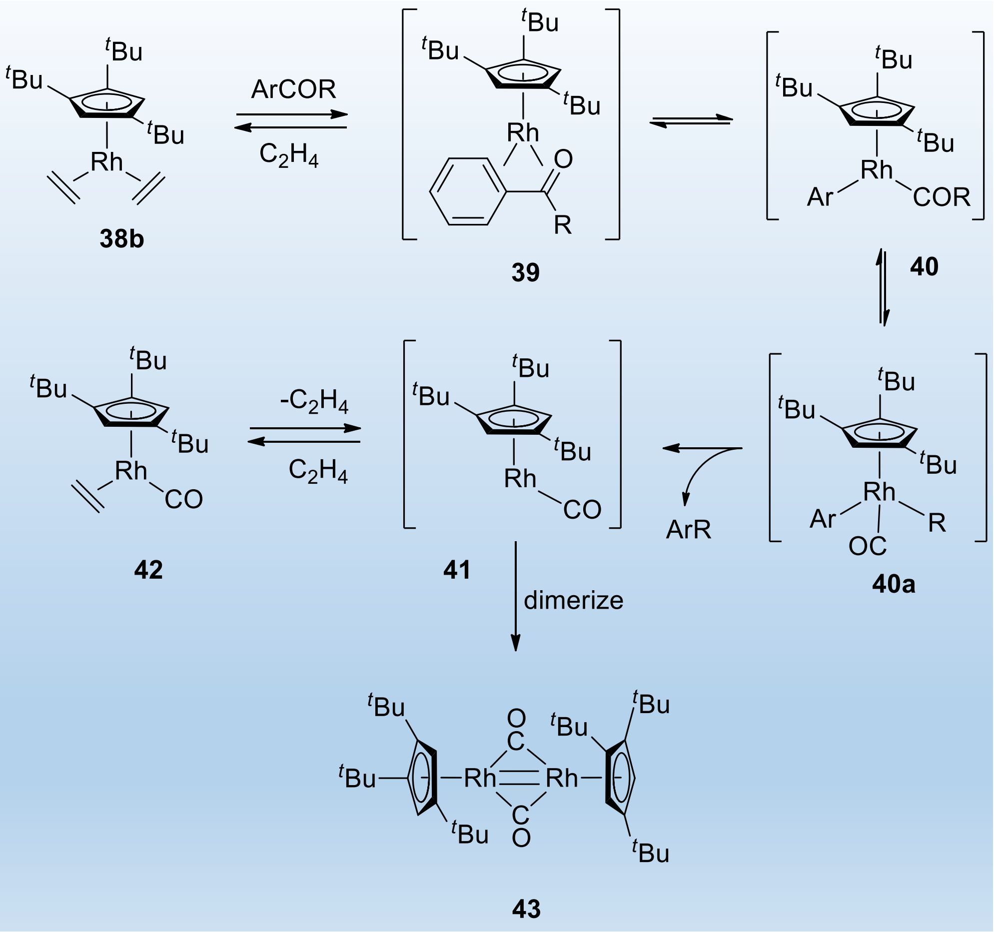




Daugulis, O., *et. al*. *Organometallics* **2004**, *23*, 527-534.

1. Inert Bond Activation *C—C bond*

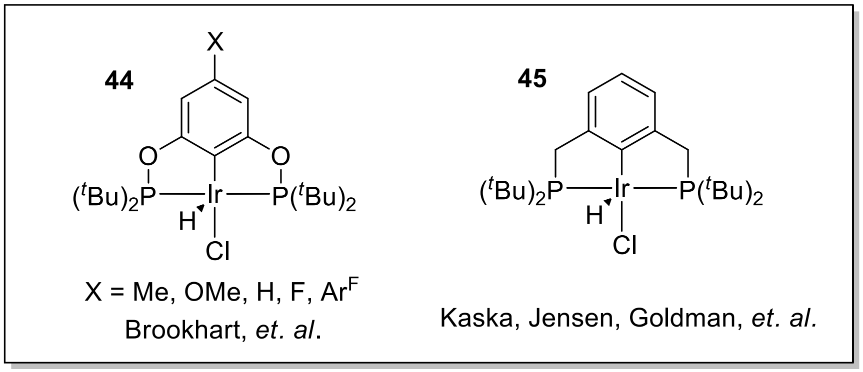
9) Decarbonylation of Aryl Ketones Mediated by Bulky Cp*Rh(ethylene)$_2$.



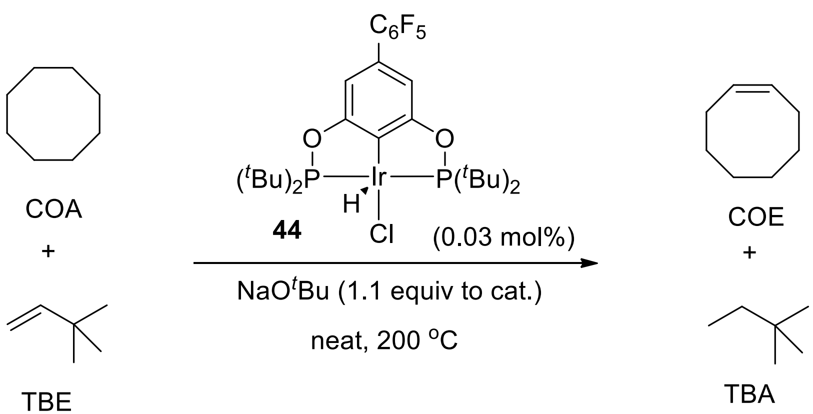
Daugulis, O., *et. al*. *Organometallics* **2004**, *23*, 527-534.

2. Dehydrogenation

1) Ir Pincer complex catalyzed alkane dehydrogenation reaction.



Catalyst for alkane dehydrogenation



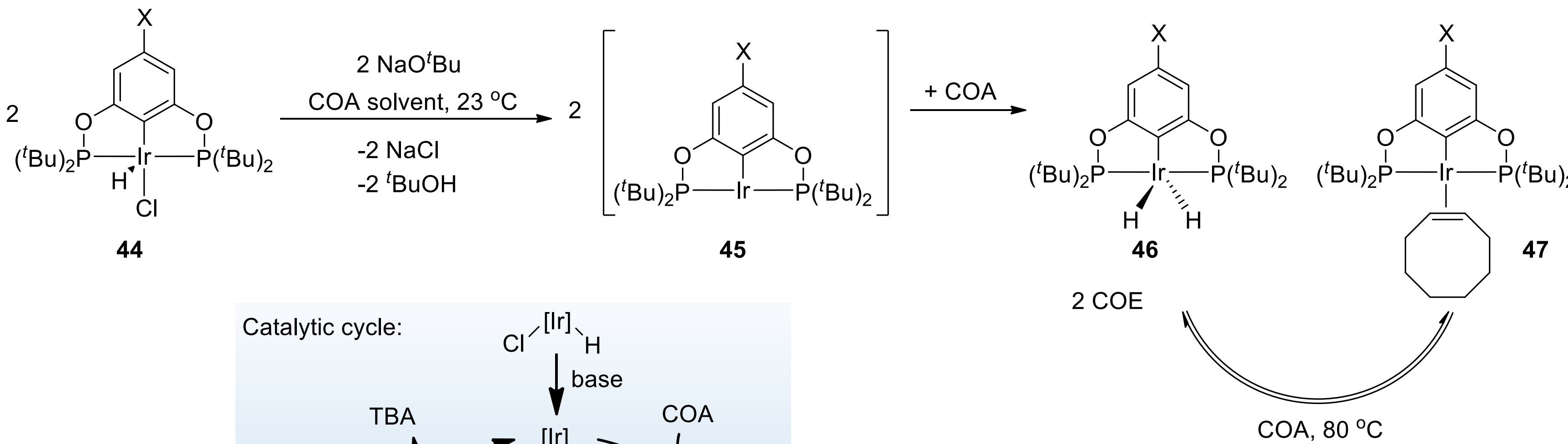
TON = 1150 in 8 min

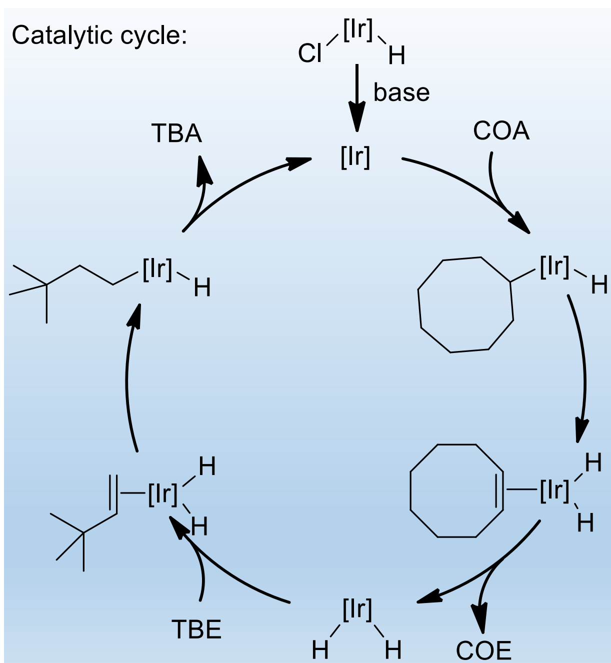
Göttker-Schnetmann, I., *et. al*. *J. Am. Chem. Soc*. **2004**, *126*, 1804-1811.
Göttker-Schnetmann, I., *et. al*. *Organometallics* **2004**, *23*, 1766-1776.
For review, see: Goldman, A. S., *et. al*. *Chem. Rev.* **2011**, *111*, 1761–1779.

2. Dehydrogenation

1) Ir Pincer complex catalyzed alkane dehydrogenation reaction.

Mechanism Study:





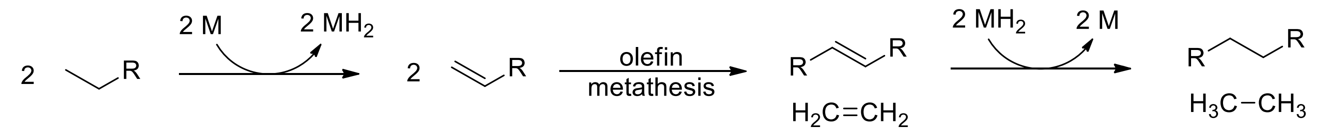
Other related papers:
J. Am. Chem. Soc. **2006**, *128*, 17114-17119.
Advanced Synthesis & Catalysis **2009**, *351*, 188-206.
Organometallics **2009**, *28*, 5432-5444.

Göttker-Schnetmann, I., *et. al. J. Am. Chem. Soc*. **2004**, *126*, 9330-9338.

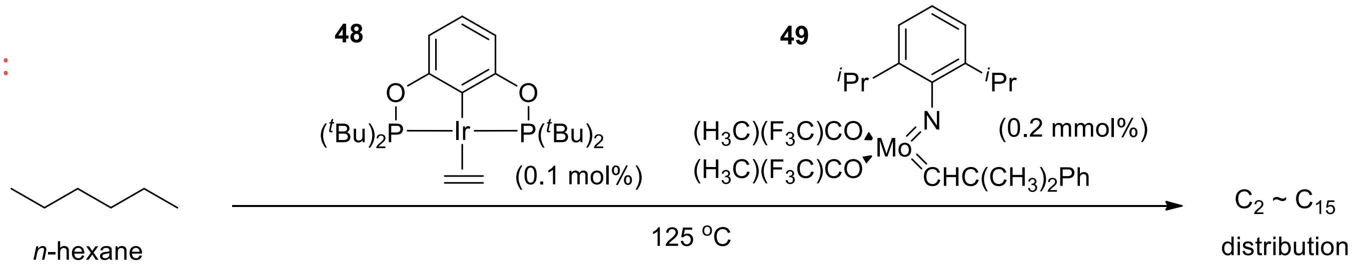
2. Dehydrogenation

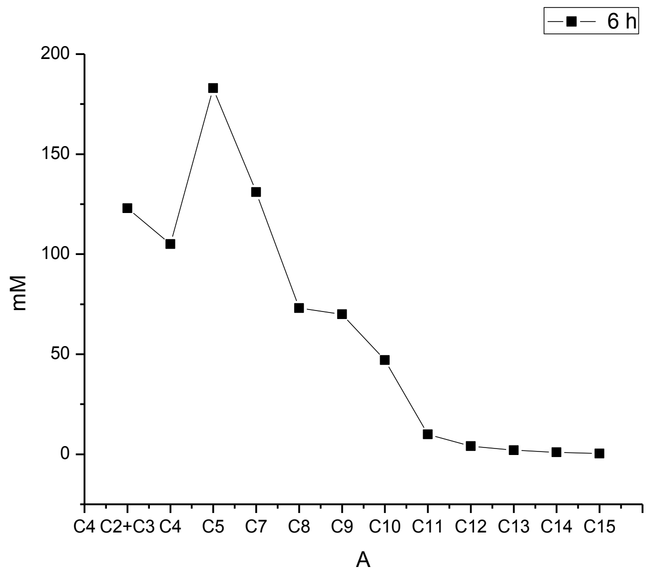
2) Catalytic Alkane Metathesis by Tandem Alkane Dehydrogenation-Olefin Metathesis .

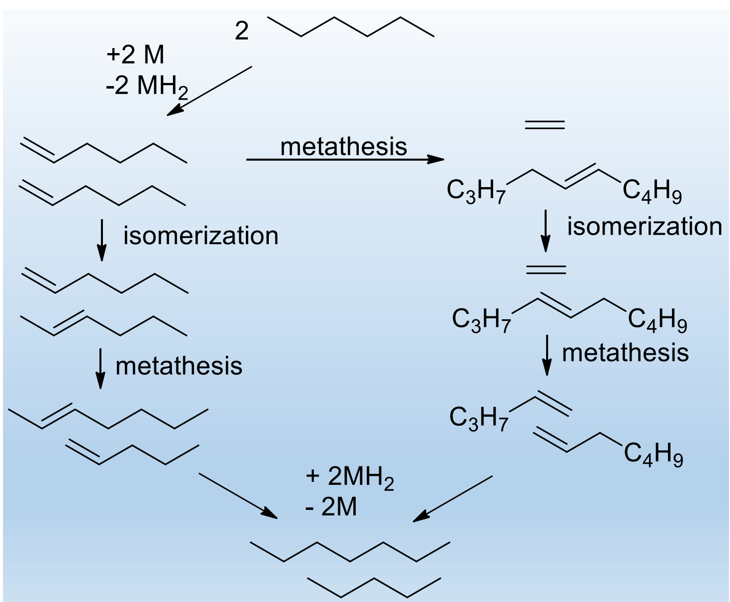
The idea:



The reaction:

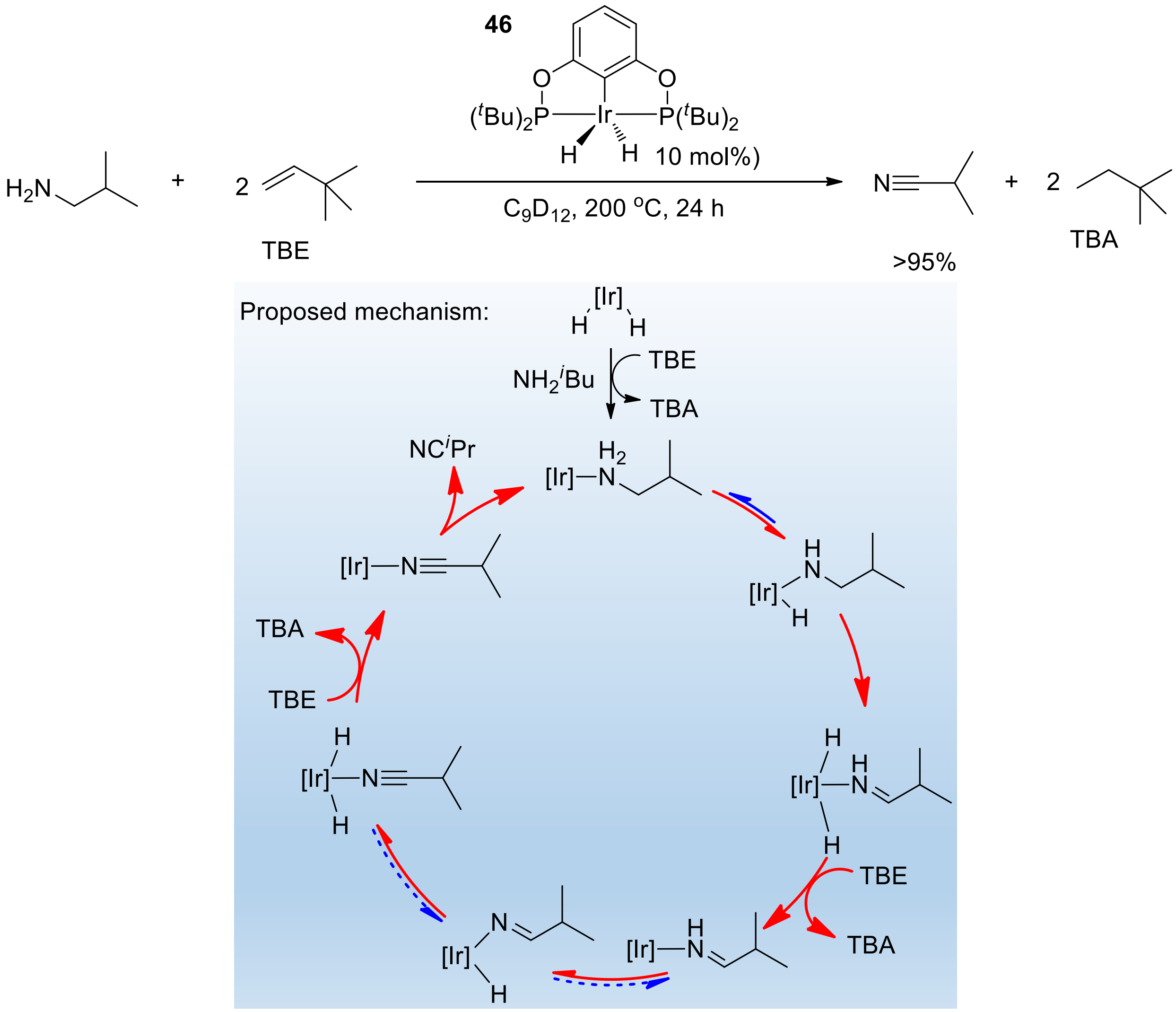






Goldman, A. S., *et. al*. *Science* **2006**, *312*, 257-261.

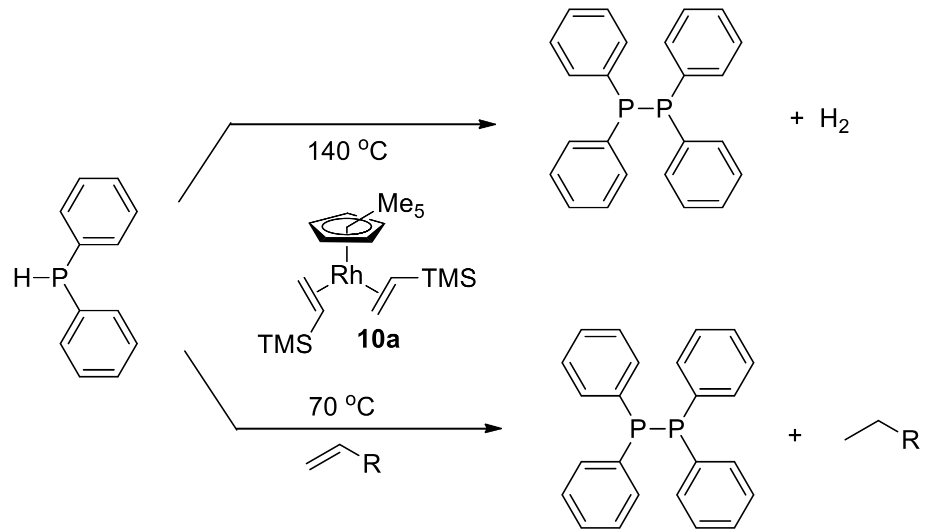
3) Ir Pincer complex-Catalyzed Dehydrogenation of Primary Amines to Nitriles.

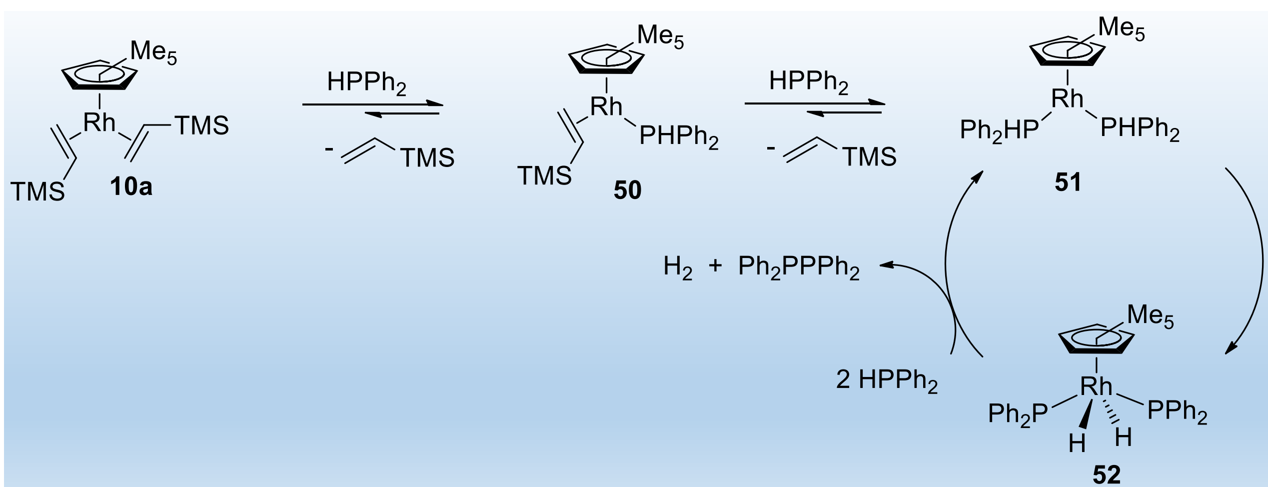


Bernskoetter, W., *et. al*. *Organometallics* **2008**, *27*, 2036-2045.

2. Dehydrogenation

4) Rh(I)-catalyzed Dihydrocoupling of Phosphanes.

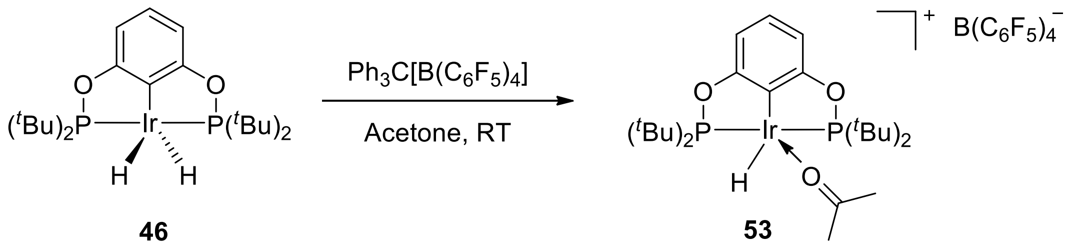




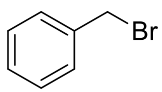
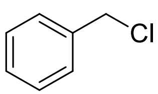
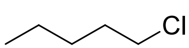
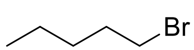
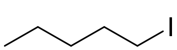
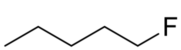
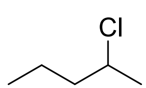
Böhm, V. P. W., *et. al*. *Angew. Chem., In. Ed*. **2001**, *40*, 4694-4696.

3. Reduction reaction

1) Ir Pincer complex-Catalyzed Reduction of Alkyl Halides by Triethylsilane.



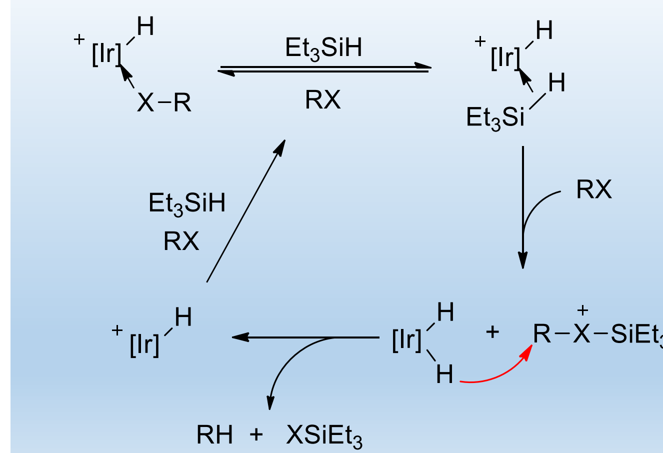
$$R{-}X + Et_3SiH \xrightarrow[C_6D_5Cl,\ 23 - 60\ ^oC]{0.5\ mol\%\ \mathbf{53}} R{-}H + Et_3SiX$$

Halide	Yield
	23 °C, 0.3 h, 99%
	23 °C, 0.3 h, 99%
	60 °C, 7 h, 99%
	60 °C, 1.5 h, 99%
	60 °C, 48 h, 99%
	60 °C, 50 h, 92% (2 mol% **A**)
	60 °C, 2.3 h, 99%

Reaction rate:

Separate flasks	R−Br > R−Cl > R−I
Same flask	R−I > R−Br > R−Cl

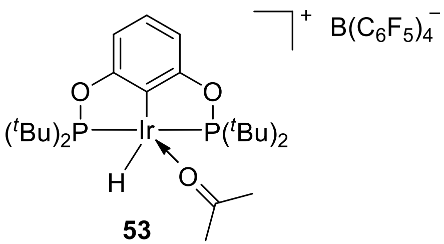
Proposed mechanism:



Yang, J., *et. al. J. Am. Chem. Soc*. **2007**, *129*, 12656-12657.

3. Reduction reaction

2) Ir Pincer complex-Catalyzed Cleavage of Alkyl Ethers with Triethylsilane.



53

R^1OR^2 + Et_3SiH —(1 mol%)→ R^1OSiEt_3 + R^2H — 1st cleavage
1.0 equiv. / 2.2 equiv.

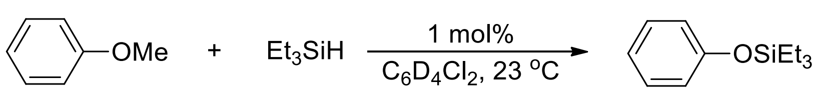
R^1OSiEt_3 + Et_3SiH —(1 mol%)→ $Et_3SiOSiEt_3$ + R^1H — 2nd cleavage

Four examples:

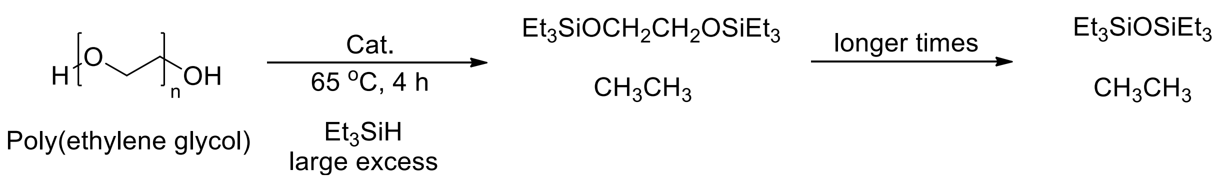
Et_2O + Et_3SiH —(1 mol%, $C_6D_4Cl_2$, 23 °C)→ $EtOSiEt_3$ + CH_3CH_3 — 3 h, 99%

$Et_3SiOSiEt_3$ + CH_3CH_3 — 23 h, 98%

$^iPr_2O$ + Et_3SiH —(1 mol%, $C_6D_4Cl_2$, 23 °C)→ $^iPrOSiEt_3$ + $CH_3CH_2CH_3$ — 43.5 h, 95%



3 h, 99%

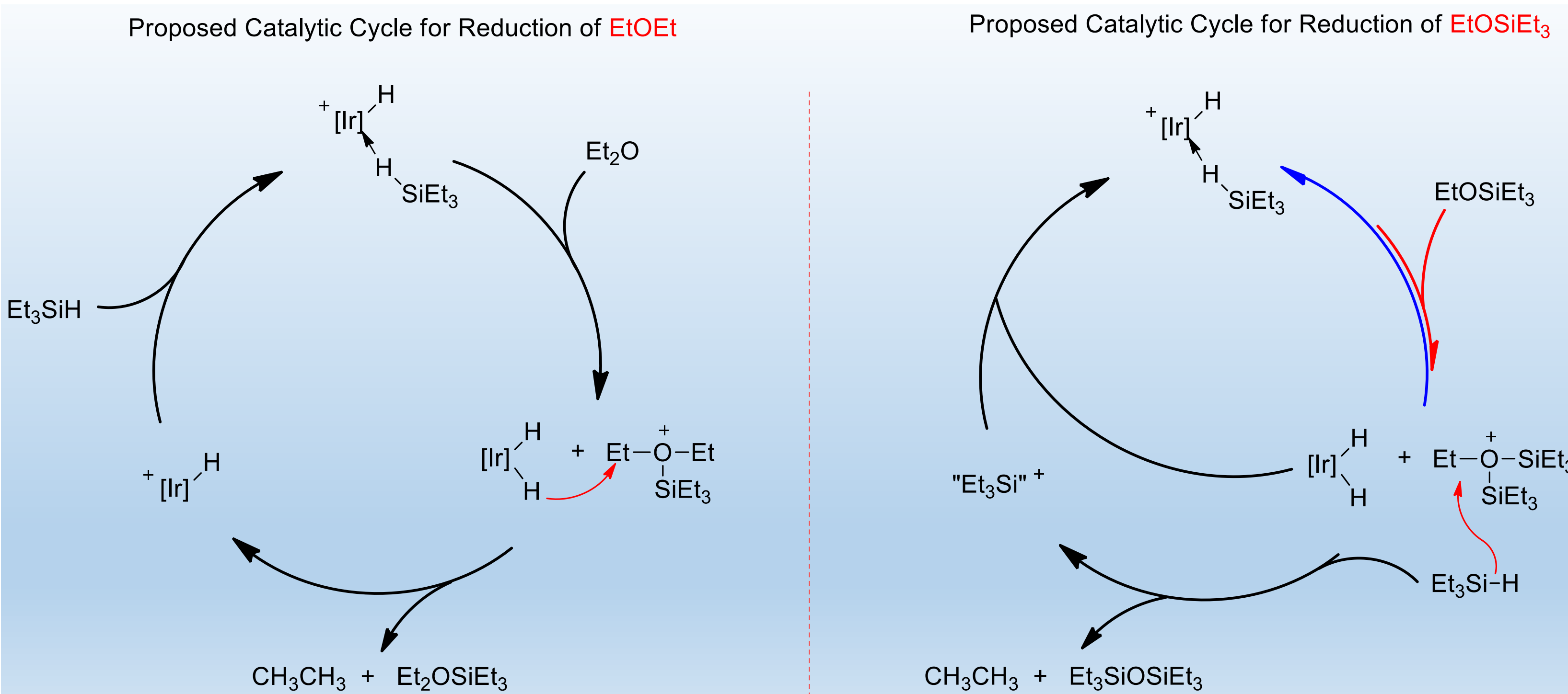


Limitation: Aromatic ether does not work

Yang, J., *et. al*. *J. Am. Chem. Soc*. **2008**, *130*, 17509-17518.

3. Reduction reaction

2) Ir Pincer complex-Catalyzed Cleavage of Alkyl Ethers with Triethylsilane.



Yang, J., *et. al*. *J. Am. Chem. Soc*. **2008**, *130*, 17509-17518.

3. Reduction reaction

3) Ir Pincer complex-Catalyzed Hydrosilation of Ketones and Aldehydes.

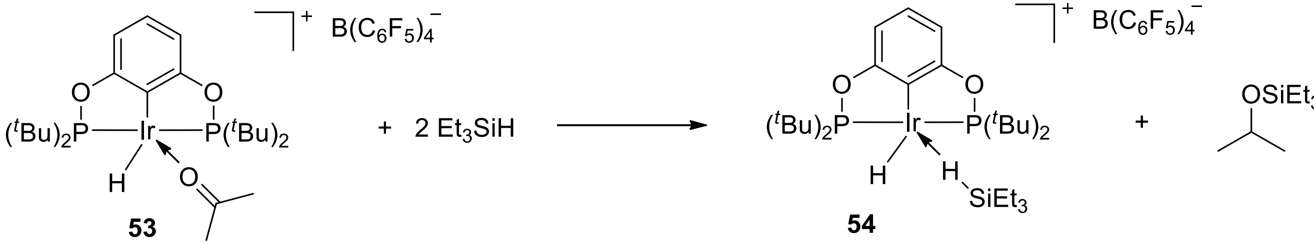
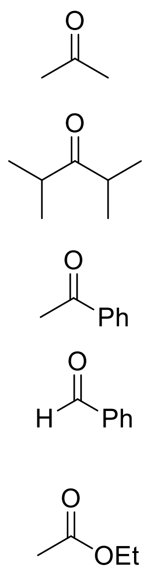
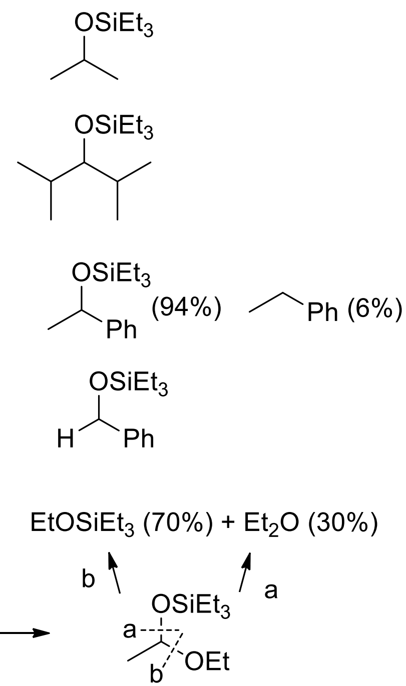


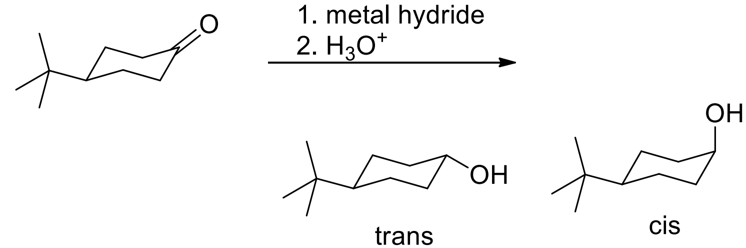
Table 3. Hydrosilylation of Carbonyl Functions

entry	substrate	t / h	conversion / %	product
1		0.3	quant.	
2		0.5	quant.	
3		0.3	quant.	(94%) Ph (6%)
4		0.3	quant.	
5		0.3	quant.	$EtOSiEt_3$ (70%) + Et_2O (30%)

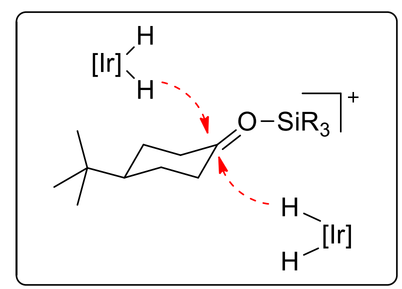




0.5 mol% cat., 3 equiv. Et_3SiH, RT, C_6D_5Cl



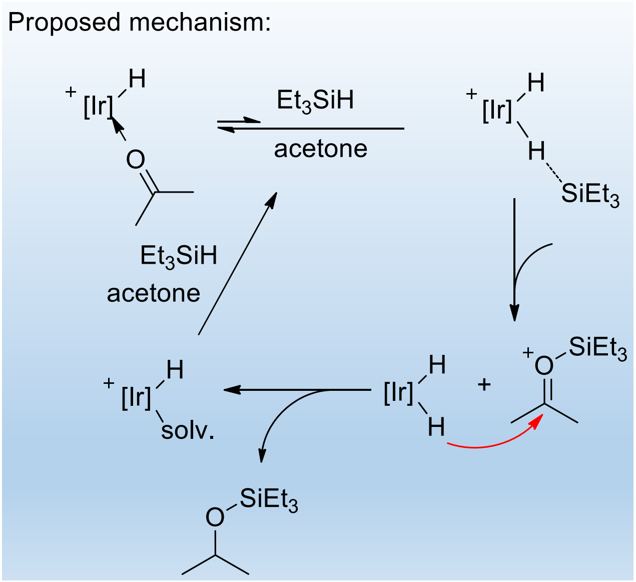
T	trans/cis
-60 °C	92:8
-30 °C	86:14
0 °C	77:23
17 °C	70:30



Park, S., *et. al. Organometallics* **2010**, *29*, 6057-6064.

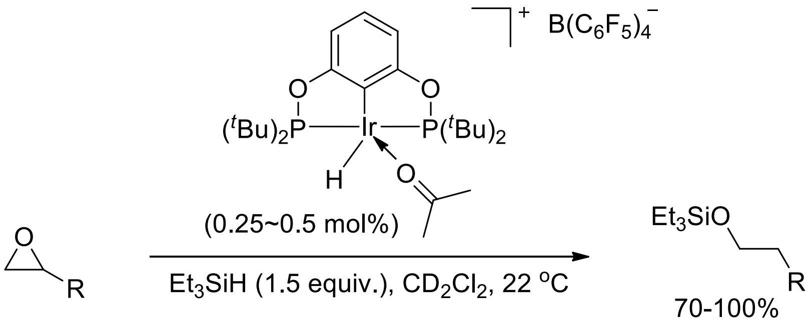
3. Reduction reaction

3) Ir Pincer complex-Catalyzed Hydrosilation of Ketones and Aldehydes.



Park, S., *et. al*. *Organometallics* **2010**, *29*, 6057-6064.

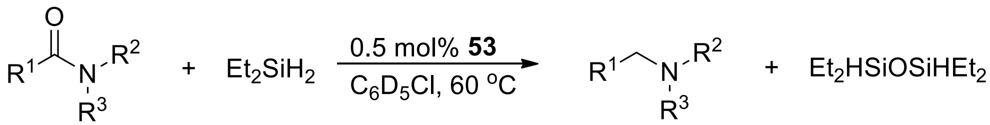
4) Ir Pincer complex-Catalyzed Hydrosilation of Epoxides.

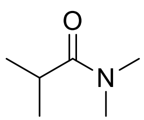
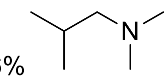
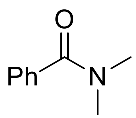
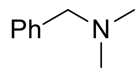
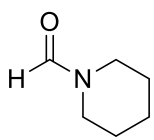
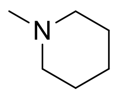
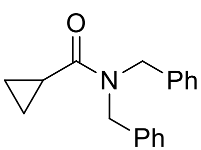
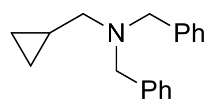
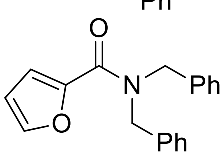
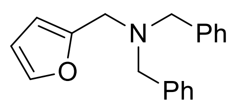
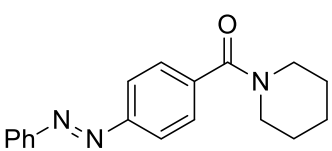
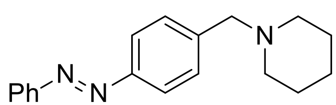


Park, S., *et. al*. *Chem. Commun.* **2011**, *47*, 3643-3645.

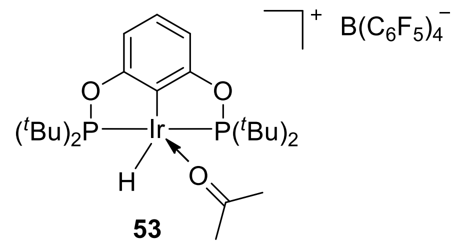
3. Reduction reaction

5) Ir Pincer complex-Catalyzed Reduction of Amides to Amines.



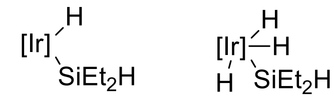
entry	substrate	t / h	product	yield
1		1.5 $EtMe_2SiH$ 22 h, 66%		94%
2		1		quant.
3		0.5		quant.
4		5		quant.
5		1		quant.
6		1.2		quant.

0.5 mol% cat, 3 equiv. of Et_2SiH_2

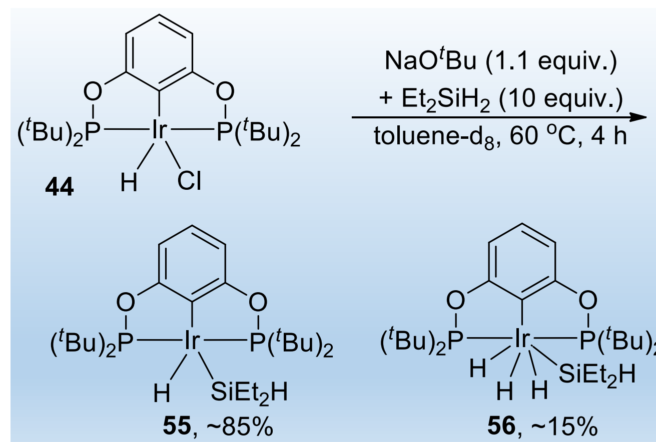


53

catalyst resting states:



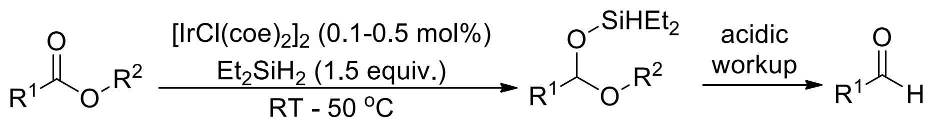
~90% ~10%

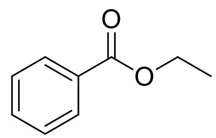
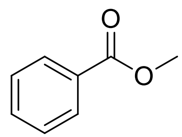
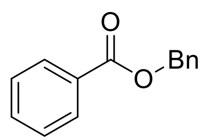
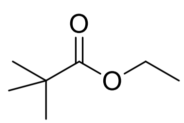
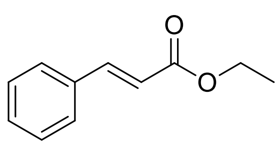
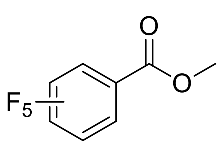


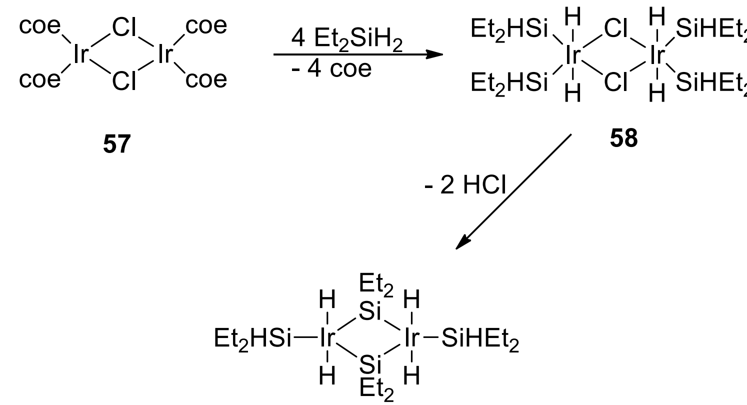
Park, S., *et. al. J. Am. Chem. Soc*. **2012**, *134*, 640-653.

3. Reduction reaction

6) Ir-Catalyzed Reduction of Esters to Aldehydes.



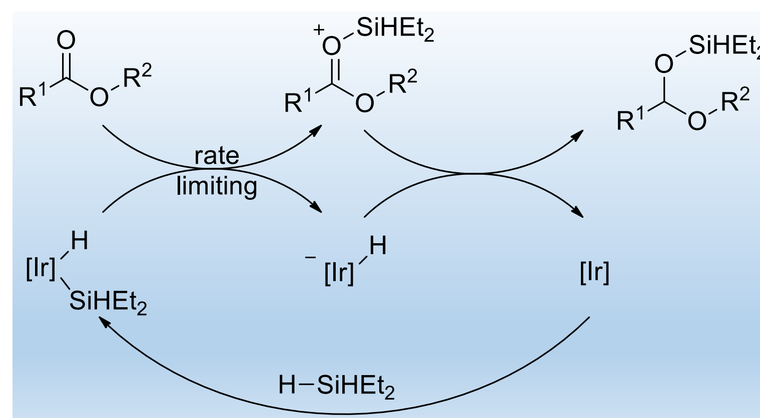
entry	substrate	T / °C	t / h	yield
1		23	1	95%
2		23	2	99%
3		23	1	99%
4		23	3	99%
5		23	1	99%
6		50	4	90%



57

58

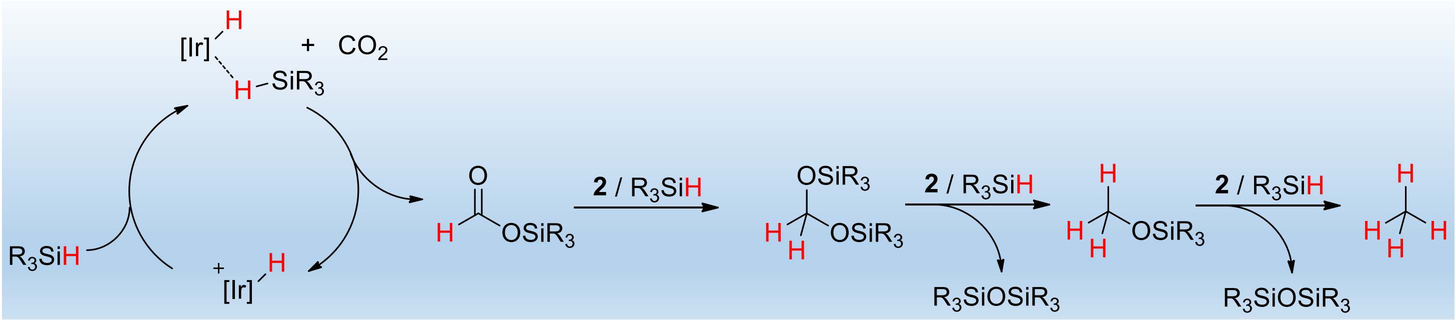
59



Cheng, C., *et. al. Angew. Chem., In. Ed*. **2012**, *51*, 9422-9424.

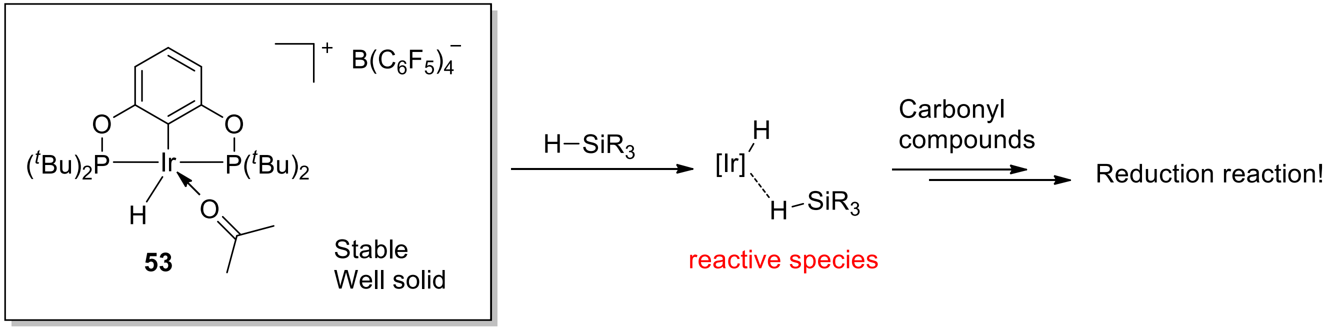
3. Reduction reaction

7) Ir-Catalyzed Reduction of Carbon Dioxide to Methane.



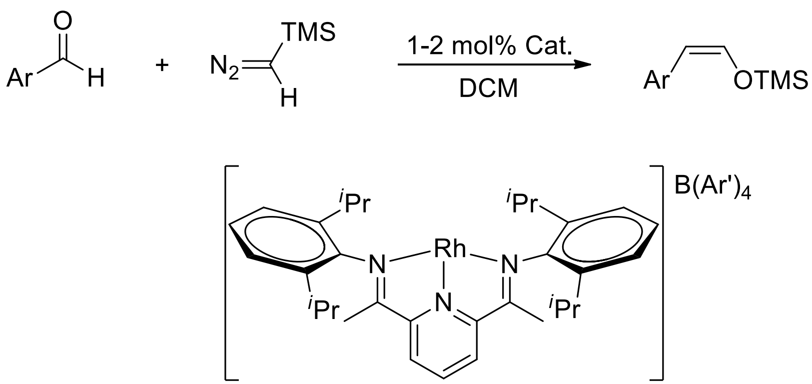
Park, S., *et. al. J. Am. Chem. Soc*. **2012**, *134*, 15708-15711.

8) Summary for Ir Pincer complex catalyzed Reduction reactions.

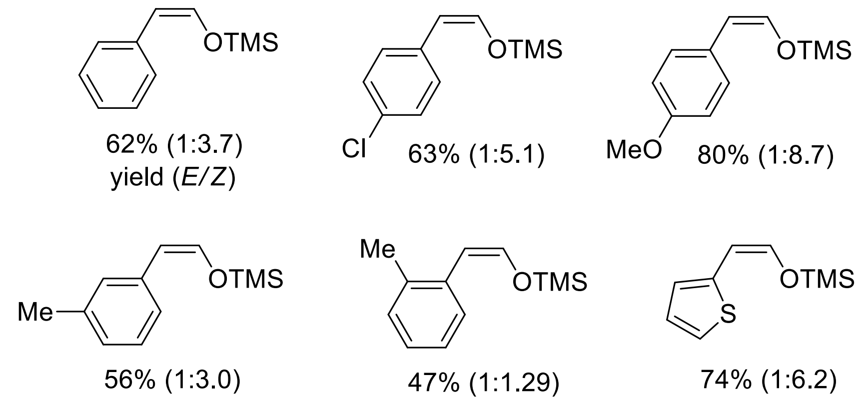


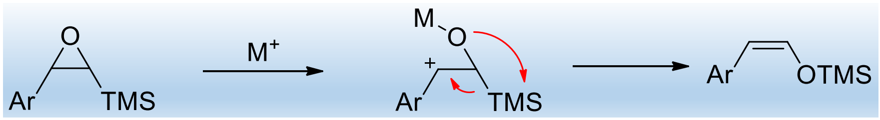
4. Miscellaneous

1) Rh (I)-Catalyzed Homologation of Aromatic Aldehydes with Trimethylsilyldiazomethane.



59

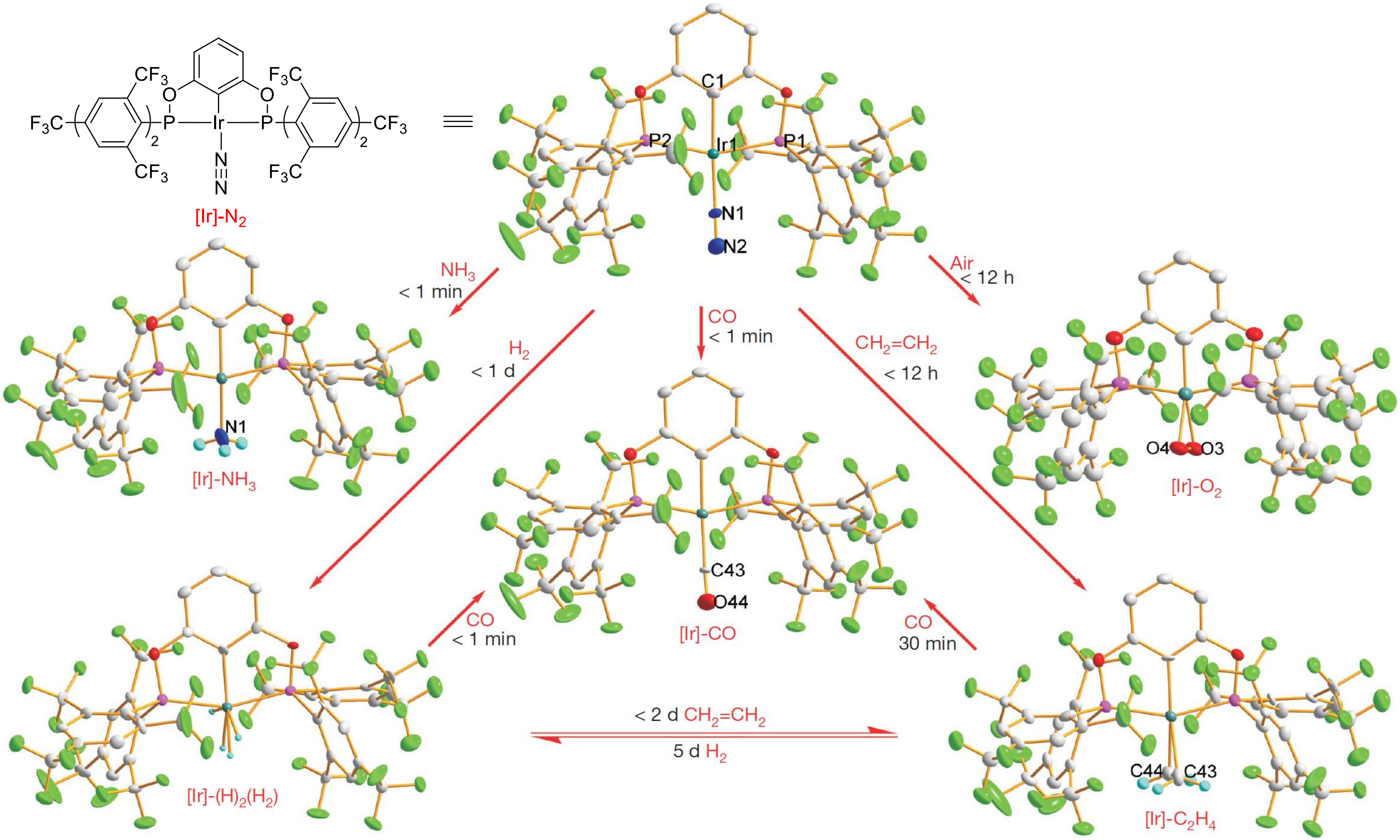




Dias, E. L., *et. al. J. Am. Chem. Soc.* **2001**, *123*, 2442-2443.

3. Miscellaneous

2) Ligand exchange and Selective Catalytic Hydrogenation in Molecular Single Crystal.



Huang, Z., *et. al*. *Nature* **2010**, *465*, 598-601.

Acknowledgement