

# Literature Report

**Ying Chen**  
**2013-8-18**

CO<sub>2</sub> Utilization

# Ruthenium-Catalyzed Direct Methylation of Primary and Secondary Aromatic Amines Using Carbon Dioxide and Molecular Hydrogen\*\*

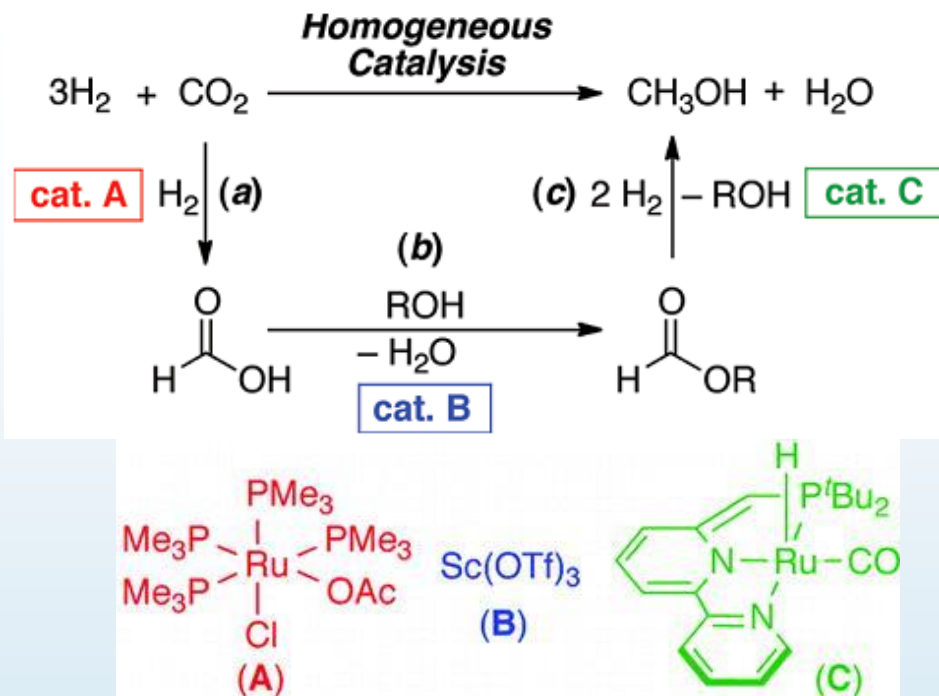
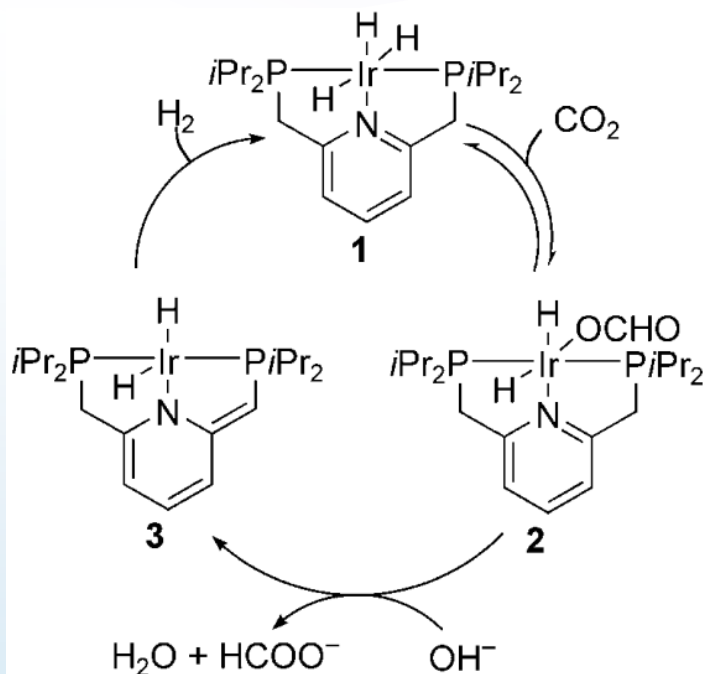
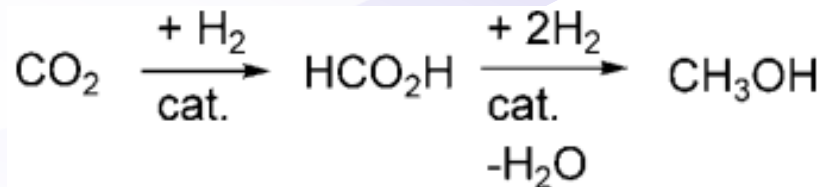
Kassem Beydoun, Thorsten vom Stein, Jürgen Klankermayer,\* and Walter Leitner



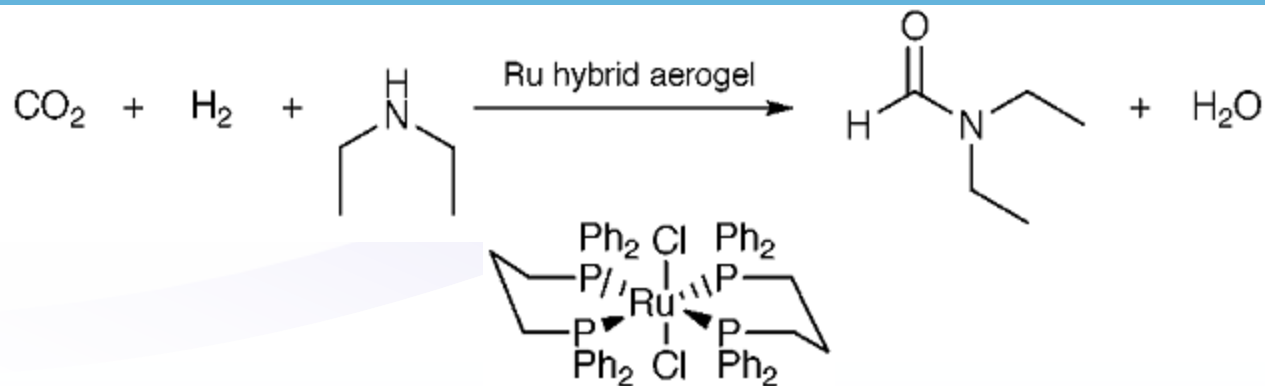
Article first published online: 14 AUG 2013

# Carbon Dioxide as Chemical Feedstock

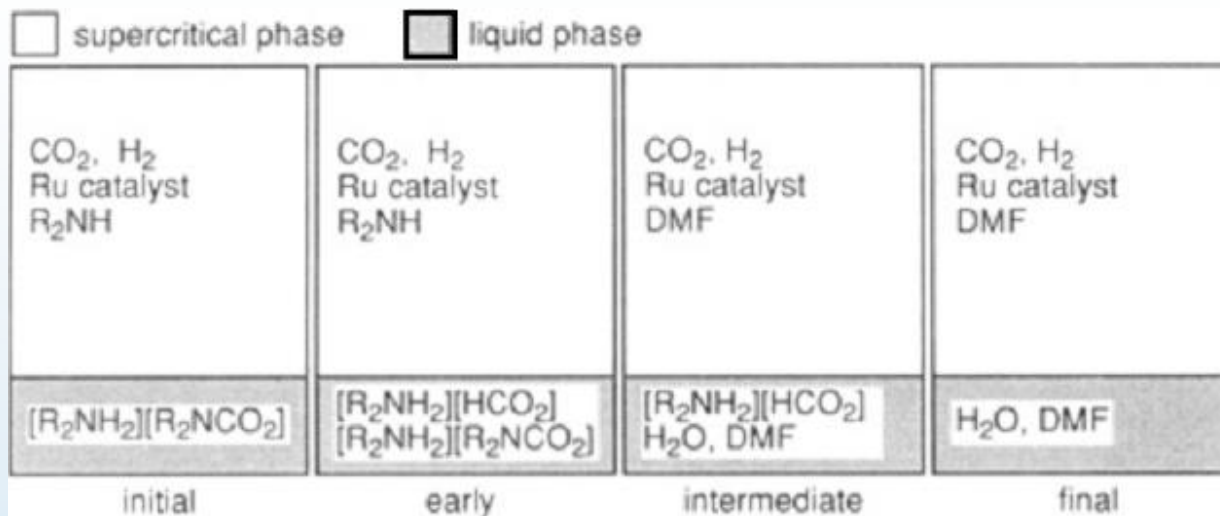
Organometallic catalytic methods for the hydrogenation of CO<sub>2</sub> to the valuable C1 chemicals formic acid and methanol



# Hydrogenation of $\text{CO}_2$ with primary or secondary amine substrates

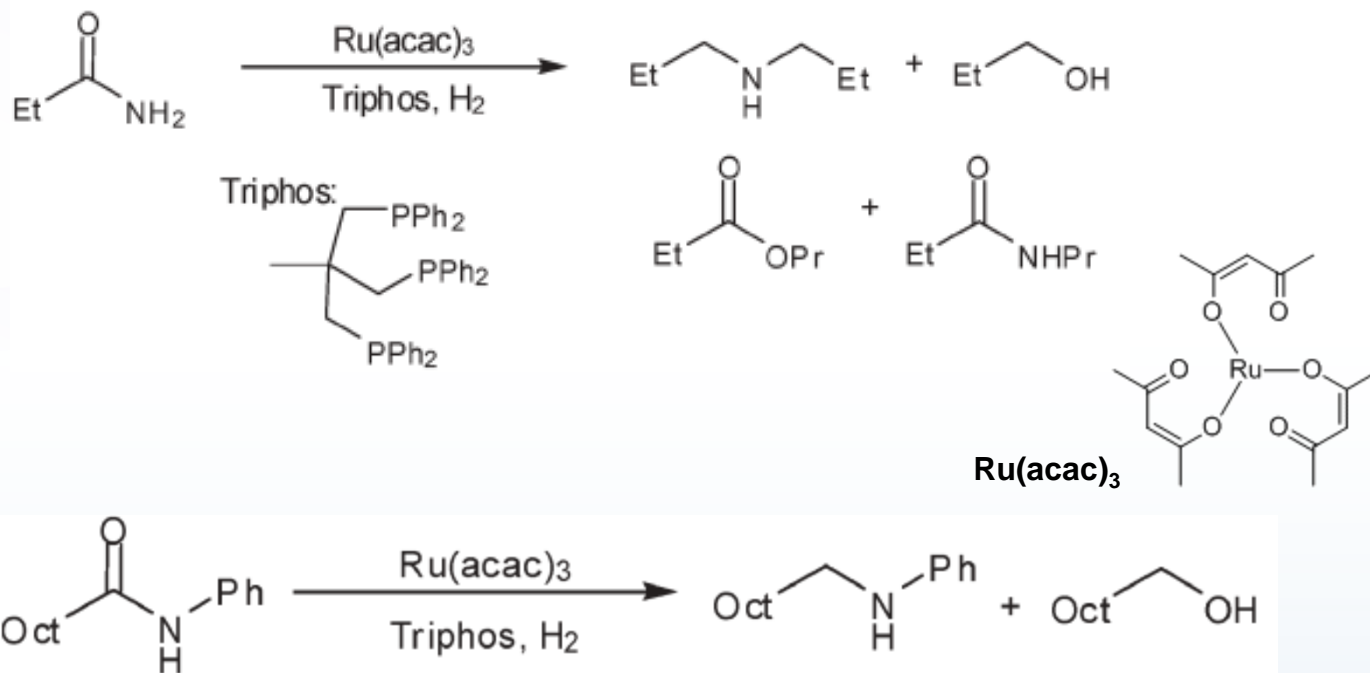


*L. Schmid, M. Rohr, A. Baiker, Chem. Commun. 1999, 2303;*



*P. G. Jessop, Y. Hsiao, T. Ikariya, R. Noyori, J. Am. Chem. Soc. 1994, 116, 8851;*

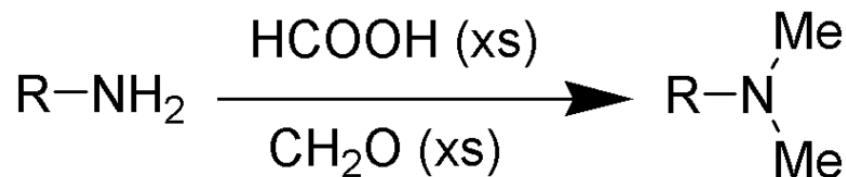
# Organometallic catalyzed reduction of amides with molecular hydrogen



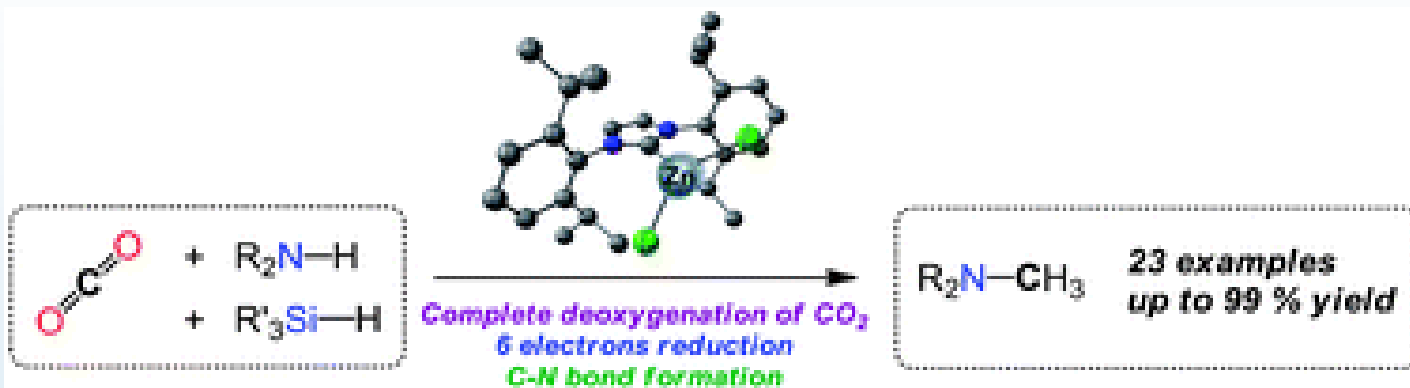
A. A. Nfifchez Magro, G. R. Eastham, D. J. Cole-Hamilton, *Chem. Commun.* 2007, 3154

# Traditional pathways for N-methylation

Alkylation with methyl iodide, orthoesters, or dimethyl carbonate or reductive alkylations such as the Eschweiler–Clark method using formaldehyde and formic acid as C<sub>1</sub> source.



*Eschweiler–Clark reaction*

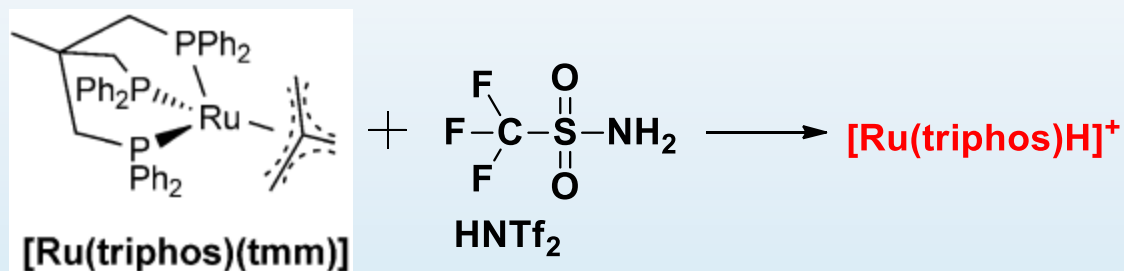
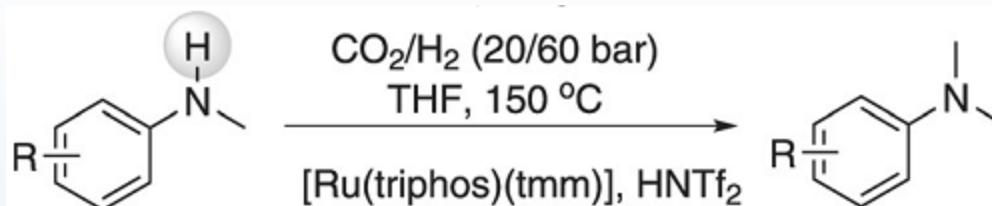
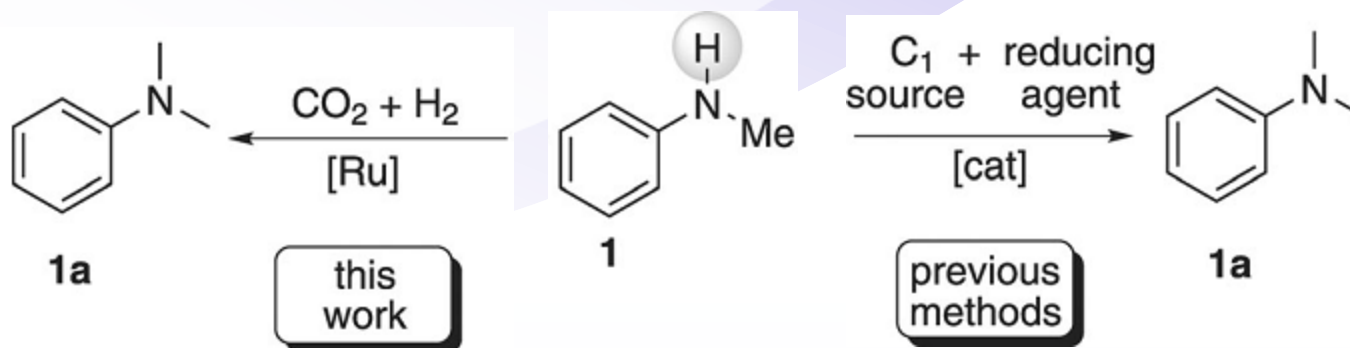


C<sub>1</sub> source: CO<sub>2</sub>

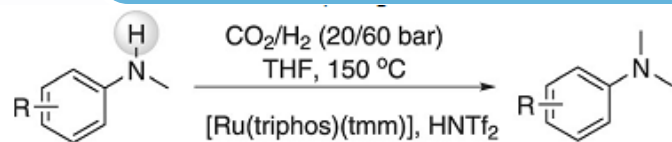
Reducing agent: R'<sub>3</sub>Si-H

O. Jacquet, X. Frogneux, C. Das Neves Gomes, T. Cantat, *Chem. Sci.* 2013, 4, 2127;

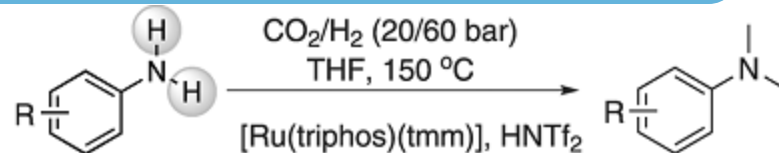
# The bright spot



# Methylation of primary or secondary amine substrates



Entry	Aniline	Product	t [h]	Yield [%] <sup>[b]</sup>
1			22	90
2			10	90
3			10	35
4 <sup>[c]</sup>			20	73
5 <sup>[c]</sup>			20	70
6			15	64
7			48	27

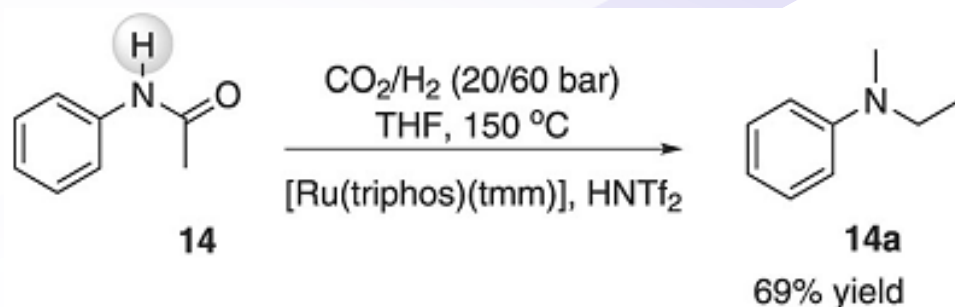


Entry	Aniline	Product	t [h]	Yield [%] <sup>[b]</sup>
1			15	94
2			10	93
3			24	93
4			20	94
5			15	84

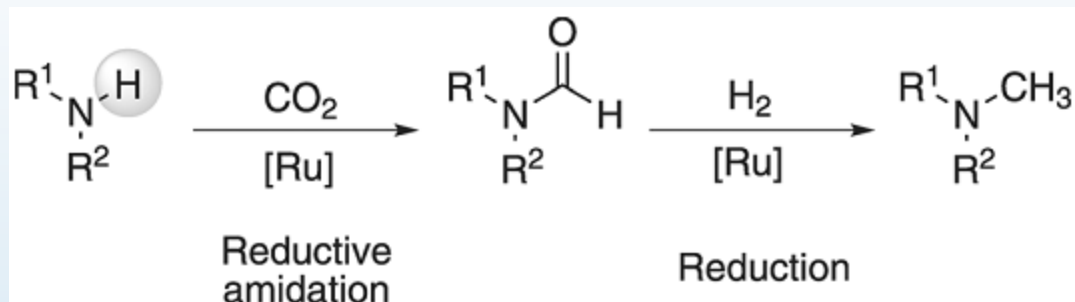


# Mechanism research

## Sequential hydrogenation/N-methylation of acetanilide



## Proposed reaction pathway for the catalytic formation of methylamine from $\text{CO}_2$ and molecular hydrogen.



# 6-1

