Methane Review

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March 14th, 2012

Methane Background

Industrial Use

Stoichiometric Catalysis

Catalytic Catalysis

Why Interest in Methane?

- Depletion of Oil Reserves
- Global Warming due to fossil fuels
- Public Resistance to Nuclear Energy
- Methane combustion > oil

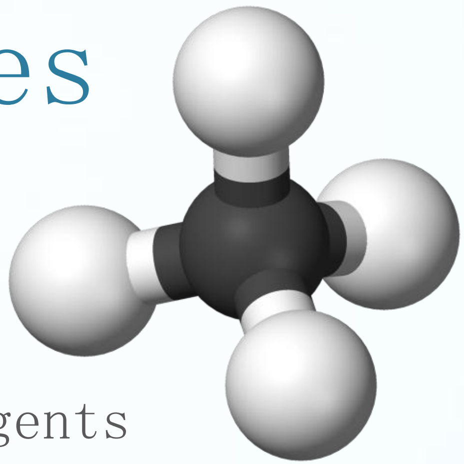
Chem. Rev. 1995, **95**, 987.

Fuel Challenges

- Permanent Gas – Pressures cannot liquefy, only low temp can
- Pipelines used – but requires high pressure and not cost effective
- Purification
  - C2 – C4 molecules
  - Sulfur
  - Water

Chem. Rev. 1995, **95**, 987.

Synthetic Issues



- Tetrahedral Geometry
- Unusually high C-H bond strength
  - Least reactive alkane by radical reagents
- Methyl cation is highly unstable
  - Least reactive alkane with hydride abstraction
- High Ionization potential
  - Unreactive toward electron transfer reactions
- Methane is sterically unhindered, so in theory a very large reactive catalyst should be selective

Chem. Rev. 1995, **95**, 987.

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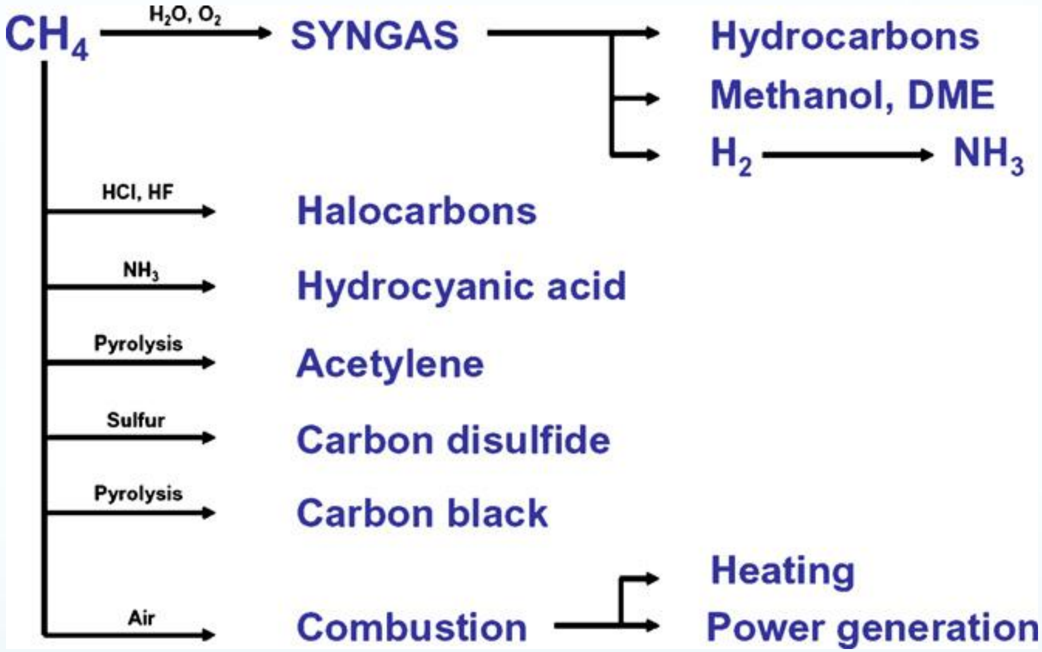
Industrial Uses of Methane



Holmen. *Cat. Today.* 2009, **142**, 2.

Methanol Conversion

- Steam Reforming
- Fischer-Tropsch
- No direct process
  - Current work: none with high conversion, yield, or catalyst stability

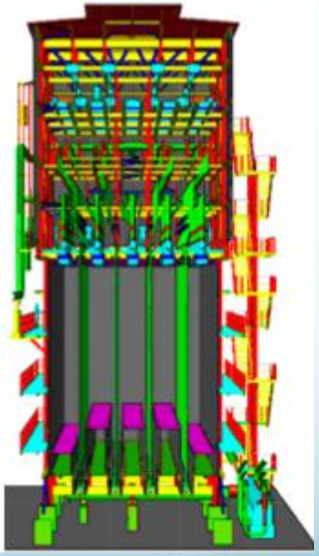
Steam Reforming

- Hydrogen gas from primary energy feedstock

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

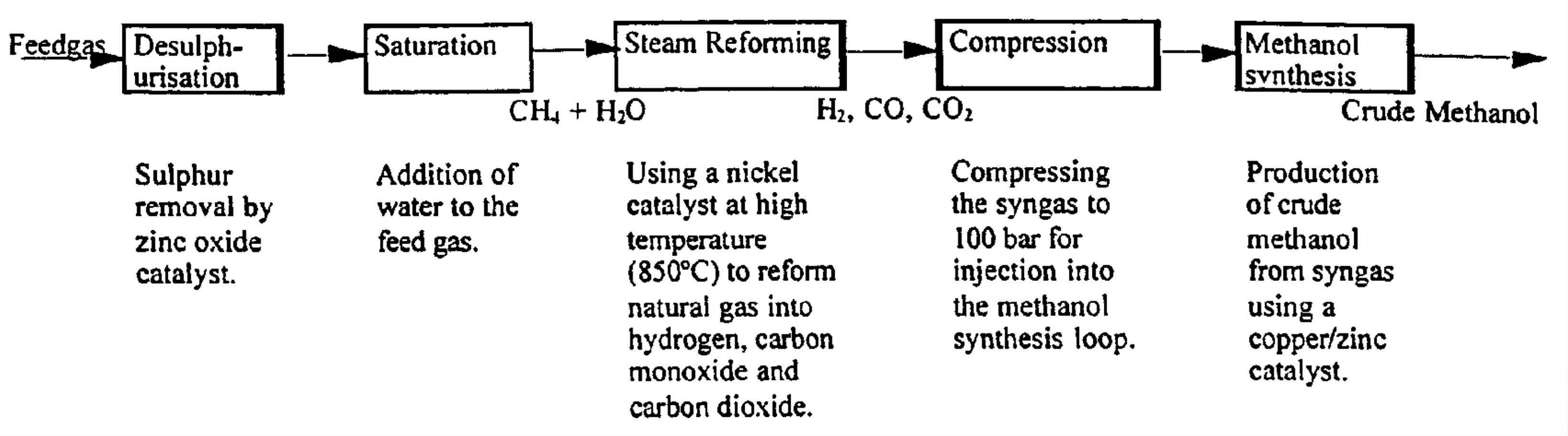
- Water Gas-Shift

$$CO + H_2O \rightleftarrows CO_2 + H_2$$



Methanol to Gasoline Process

- Take syn gas produced from steam reforming:



$$2H_2 + CO \leftrightarrows CH_3OH$$

New Zealand Institute of Chemistry

MTG Process (cont)

- Use of ZSM-5 cat

←   #   #

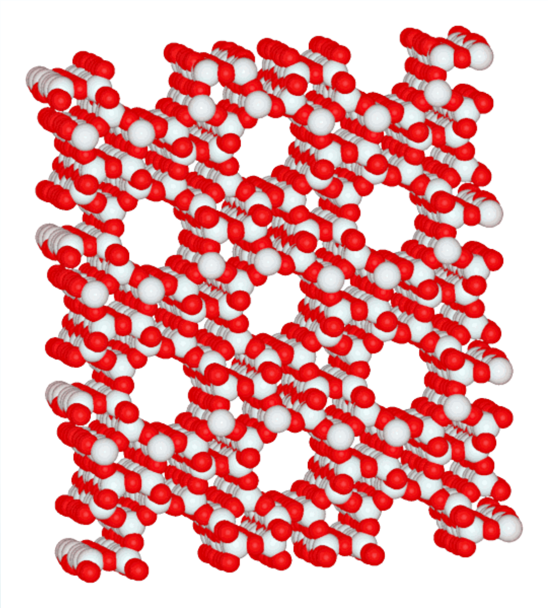
- Product Composition

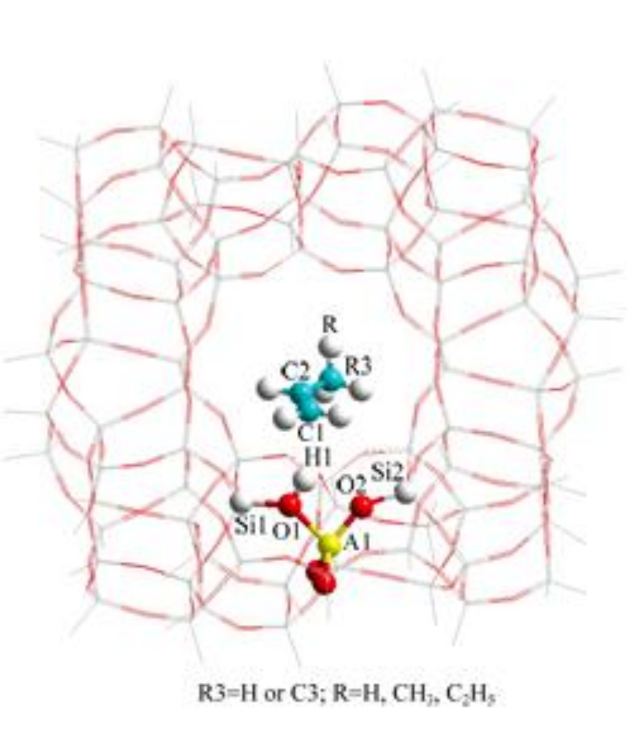
Hydrocarbon product	*w/w %*
Light Gas	1.4
Propane	5.5
Propene	0.2
Isobutane	8.6
n-Butane	3.3
Butenes	1.1
C_5^+ Gasoline	79.9

Gasoline composition	*w/w %*
Highly branched alkanes	53
Highly branched alkenes	12
Napthenes (cycloalkanes)	7
Aromatics	28

HZSM-5: Zeolite Socony Mobil

- Chemical formula: $Na_nAl_nSi_{96-n}O_{192} \cdot 16H_2O$
- Heterogeneous Catalysis





Fischer-Tropsch Process

$$CH_4 + H_2O \xrightarrow{900^oC} CO + 3\ H_2$$

$$(2n+1)\ H_2 + n\ CO \longrightarrow C_nH_{(2n+2)} + n\ H_2O$$

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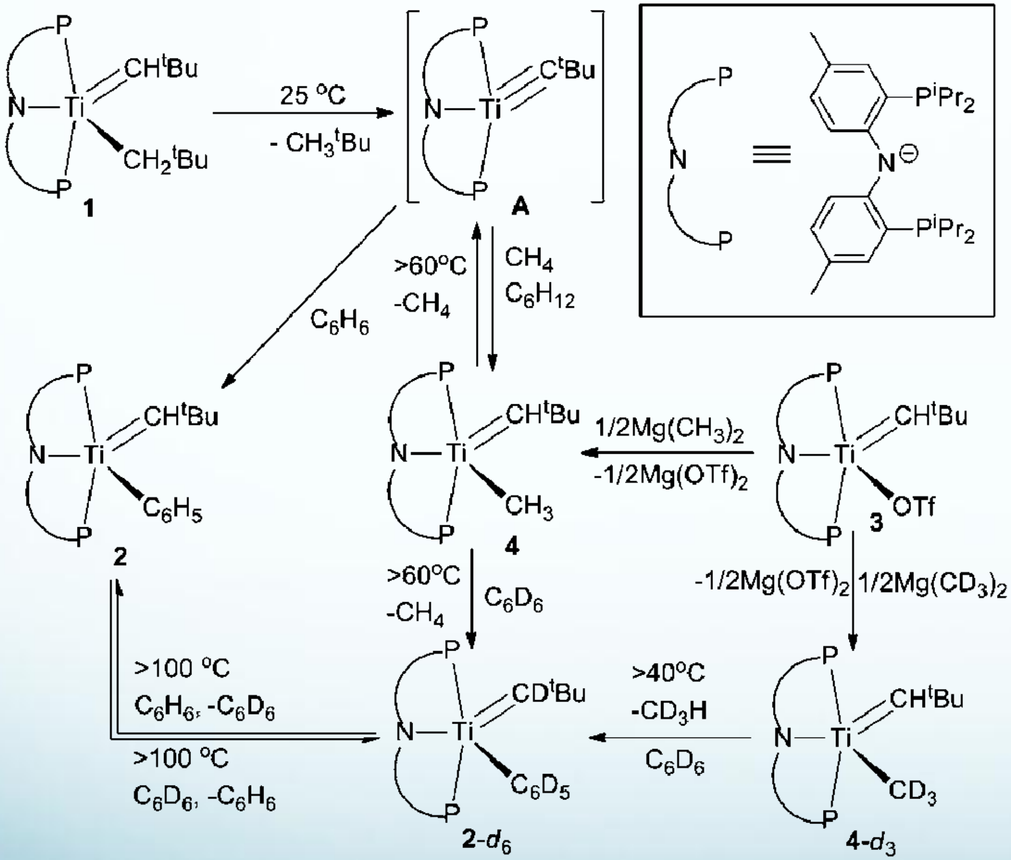
Catalytic Catalysis

Alkyidyne Complexes



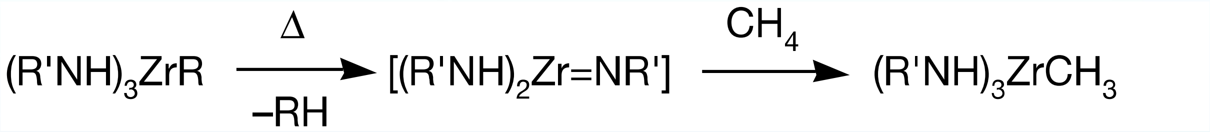
- room temp
- 1,2 C-H bond addition
- Methylidene product for polymers

Mindiola. *Chem. Sci.* 2011, **2**, 1457.

1,2-Addition

- Metal-nonmetal double bond

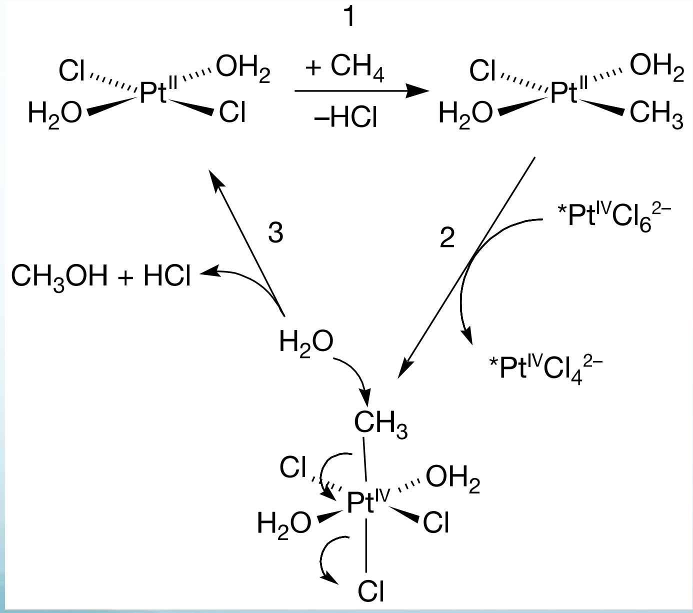
- Unexplored area

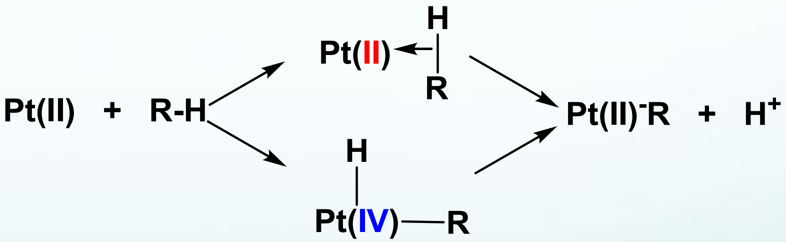


JACS. 1988, **110**, 8731.

Oxidation through Pt

- Shilov Process
  - Catalytic in Pt(II) but requires stoichiometric amounts of Pt(IV)
  - Non radical selectivity patterns (Electrophilic)

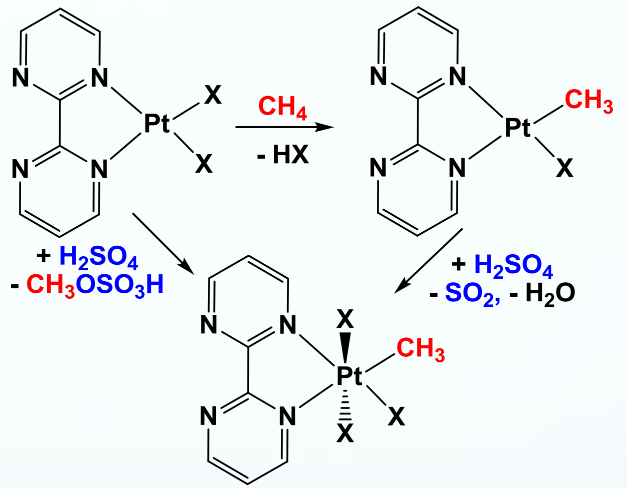




Periana. *Nature.* 2002, **417**, 507.

Low Temperature Oxidation

- Oxidation of Methane to Methyl bisulphate
- 90% selectivity
- Product is of little use
- Must go through another conversion
- 72% yield, 89% convers. 81% selectivity



$$CH_4 + 2\,H_2SO_4 \longrightarrow CH_3OSO_3H + SO_2 + 2\,H_2O$$

$$CH_3OSO_3H + H_2O \longrightarrow CH_3OH + H_2SO_4$$

$$SO_2 + 1/_2\,O_2 + H_2O \longrightarrow H_2SO_4$$

$$\text{Overall: } CH_4 + 1/_2\,O_2 \longrightarrow CH_3OH$$

Periana. *Nature*. 2002, **417**, 507.

Modified Periana's Catalyst

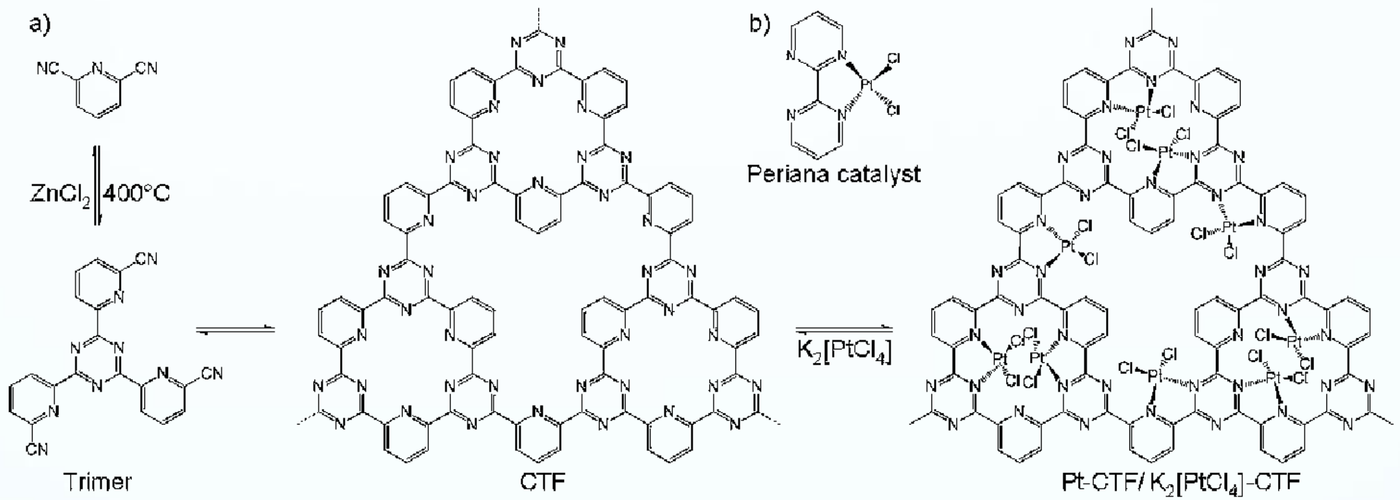


Table 1: Catalytic activity of the molecular Periana catalyst and the heterogeneous Pt-CFT and $K_2[PtCl_4]$-CFT catalysts in methane oxidation.

Catalyst[a]	Final methanol conc. [mol L^{-1}]	TON[b]
Periana catalyst[c]	1.65	158
Periana catalyst[d]	1.49	355
$K_2[PtCl_4]$-CTF[e]	1.54	201
Pt-CTF[f]	1.80	246

[a] Reaction conditions: 15 mL H_2SO_4 (30% SO_3), 40 bar CH_4 pressure (258C), 2.5 h at 2158C. [b] TON based on the platinum content determined from SEM/EDX. [c] 65 mg Periana catalyst. [d] 26 mg Periana catalyst. [e] 48 mg CTF with 92 mg $K_2[PtCl_4]$. [f] Data from the second run with 62 mg Pt-CTF.

ACIEE. 2009, **48**, 6909.

Super Acid Catalysis

- Oxygen-free electrophilic oligomerization

$$nCH_4 \xrightarrow[P=1\ \text{atm},\ T=200-400\,°C]{HBr+AlBr_3} -(CH_x)_n- + H_2$$

- Lewis Acid + Bronstead Acid

Table 1 Results of CH_4 oligomerization using different acid catalysts and the effect of temperature; P = 1 atm, $T(AlBr_3)$ = 373 K, $n(CH_4):n(AlBr_3):n(HBr)$ = 1 : 0.005 : 1.32, residence time = 60 s; selectivities are at reaction time = 4 h except [a]

Catalyst	T (K)	%CH_4 conv.	Hydrocarbons yield (%C)					
			C_2	$C_2^{=}$	C_3	$C_3^{=}$	$C_3^{=}$	C_5–C_8
Blank	673	0.0	—	—	—	—	—	—
HBr	673	20.0	—	—	—	—	—	—
$AlBr_3$	673	0.0	—	—	—	—	—	—
HBr + $AlBr_3$	473[a]	98.2 ± 1.8	—	—	0.15	—	0.001	0.01
HBr + $AlBr_3$	573	99.1 ± 1.4	—	—	0.14	—	0.001	0.03
HBr + $AlBr_3$	623	99.9	—	—	—	0.35	0.001	0.02
HBr + $AlBr_3$	673	>99.9	0.11	0.04	—	—	—	0.04

[a] Selectivities at reaction time 3rd h.

Chem. Commun. 2011, **47**, 785.

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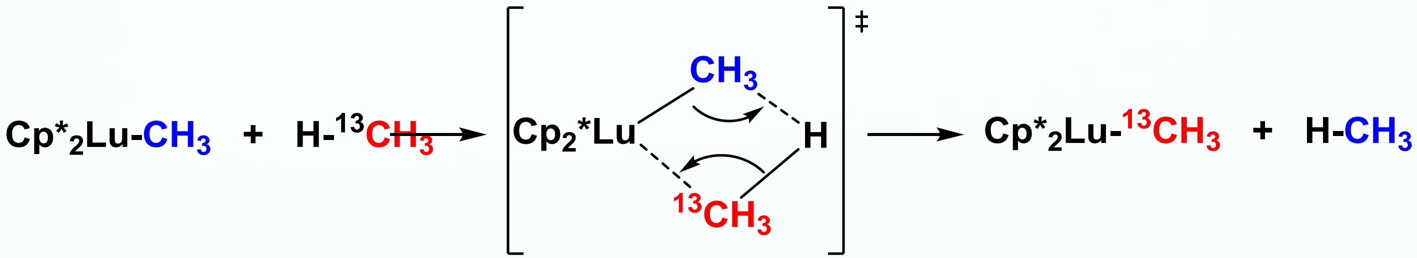
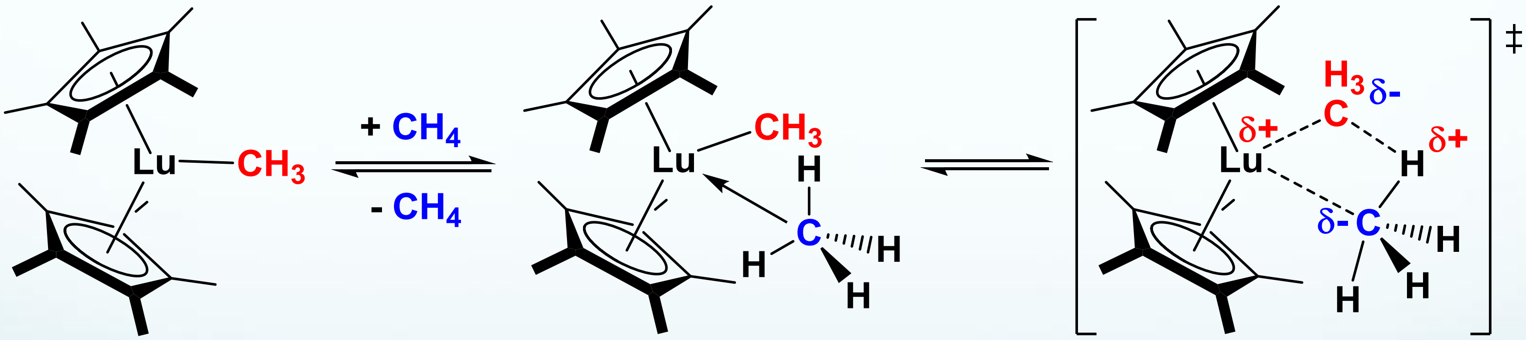
Catalytic Catalysis

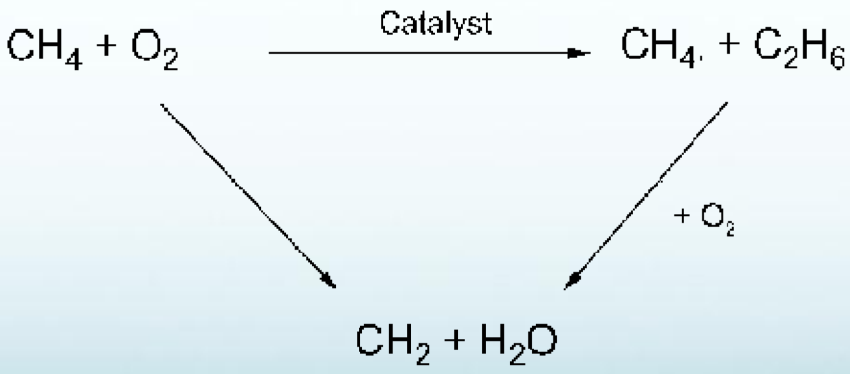
Sigma Bond Metathesis



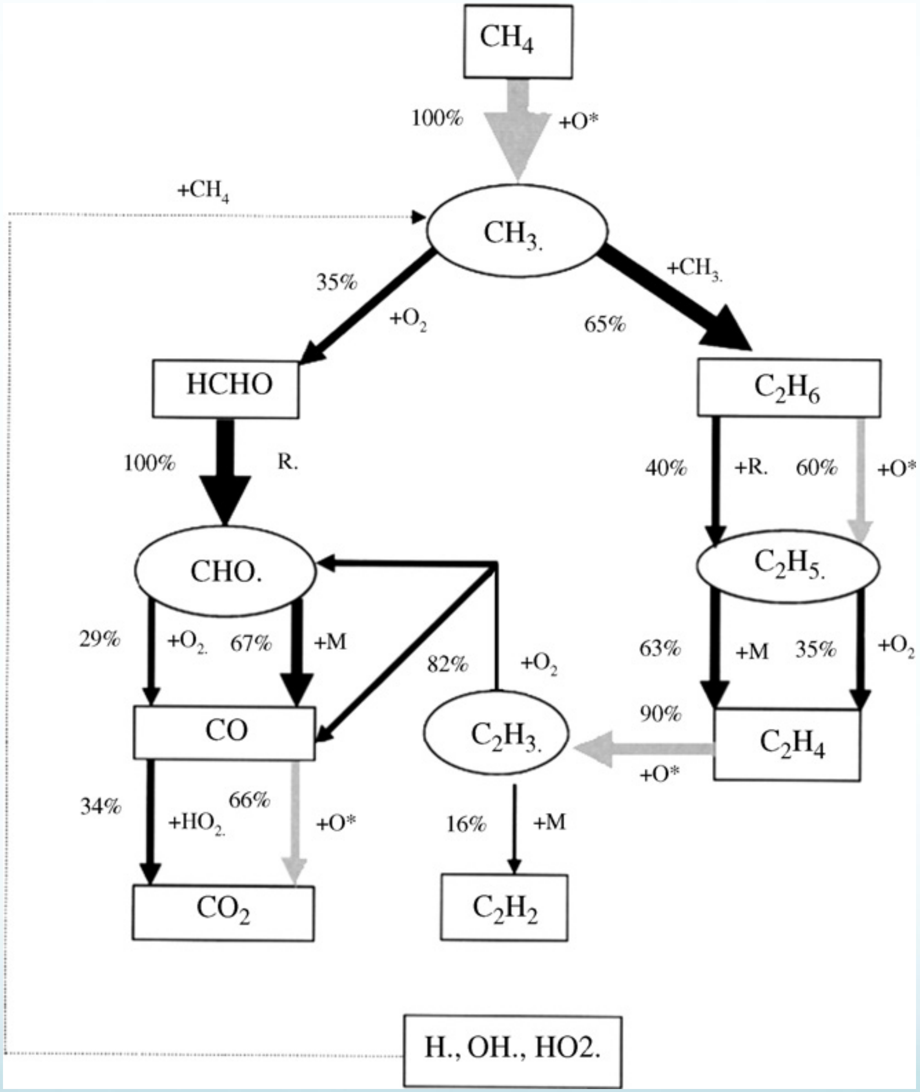


Oxidative Coupling

- Active site in catalyst activates C–H bond, combusting the reagent
- Goal: find catalytic material where secondary C–H activation is inhibited
  - Membrane separation of methane and O_2



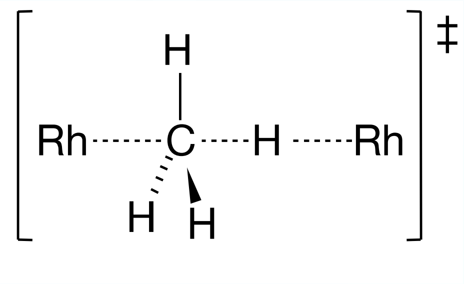
Holmen. *Cat. Today.* 2009, **142**, 2.

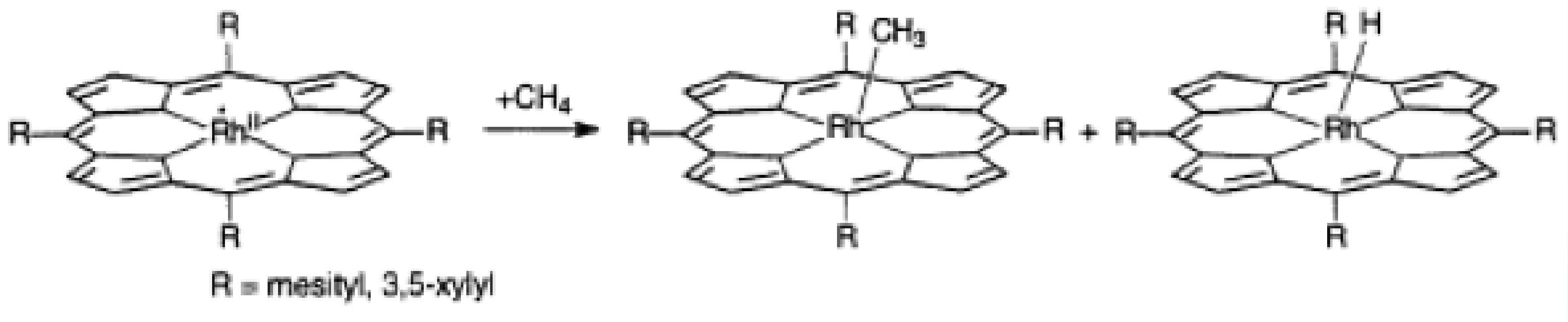


Holmen. *Cat. Today.* 2009, **142**, 2.

Rh(II) Porphyrin

- (TMS)Rh dimer





Wayland

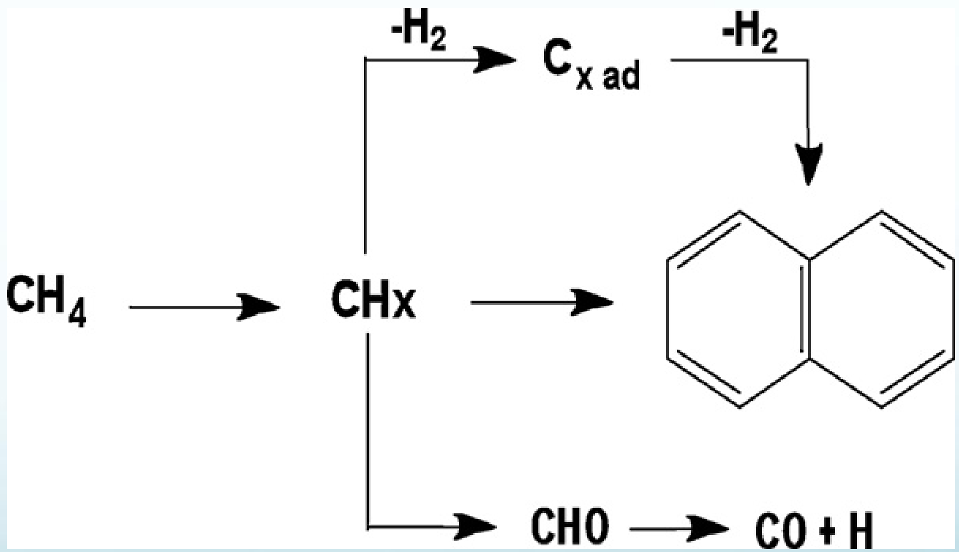
Methane Aromatization

- Dehydrogenated methane (absense of oxygen)
  - Benzene, naphthalene, and hydrogen
- Metal Oxide Cat (Mo, W, V, Cr) / Common: MnO_3

$$CH_4 \xrightarrow{Mo^{n+}} CH_3^{\bullet} + H^{\bullet}$$

$$2CH_3^{\bullet} \xrightarrow{Mo^{n+}} C_2H_4 + H_2$$

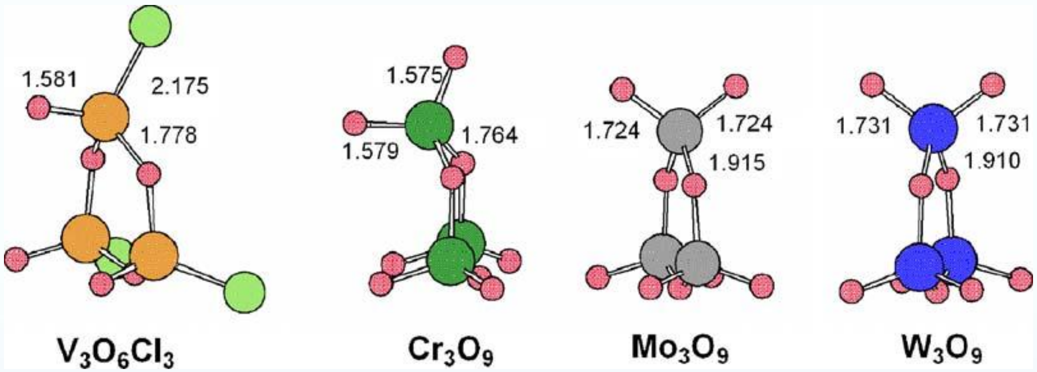
$$3C_2H_4 \xrightarrow{HZSM\text{-}5} C_6H_6 + 3H_2$$



Ind. Eng. Chem. Res. 1999, **38**, 3860.

Methane Oxidation Study

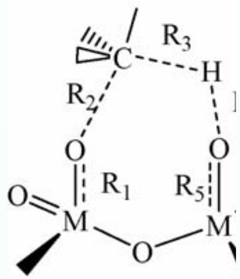
- Active oxidant in solution and gas phase

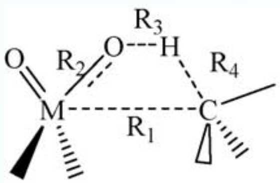


Fu. *Cat. Today.* 2006, **117**, 133.

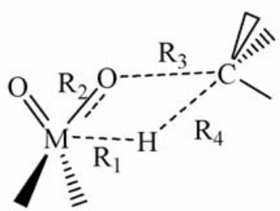
Oxidative Pathways

T3 (3+2)

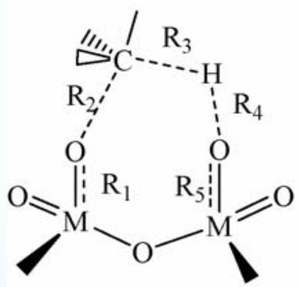




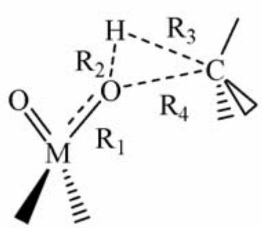
T1 (2+2)



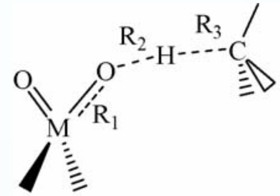
T2 (2+2)



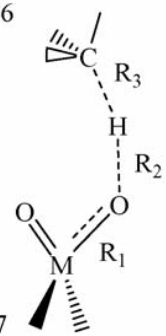
T4 (5+2)



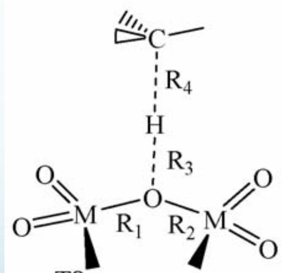
T5 oxenoid insertion



T6



T7

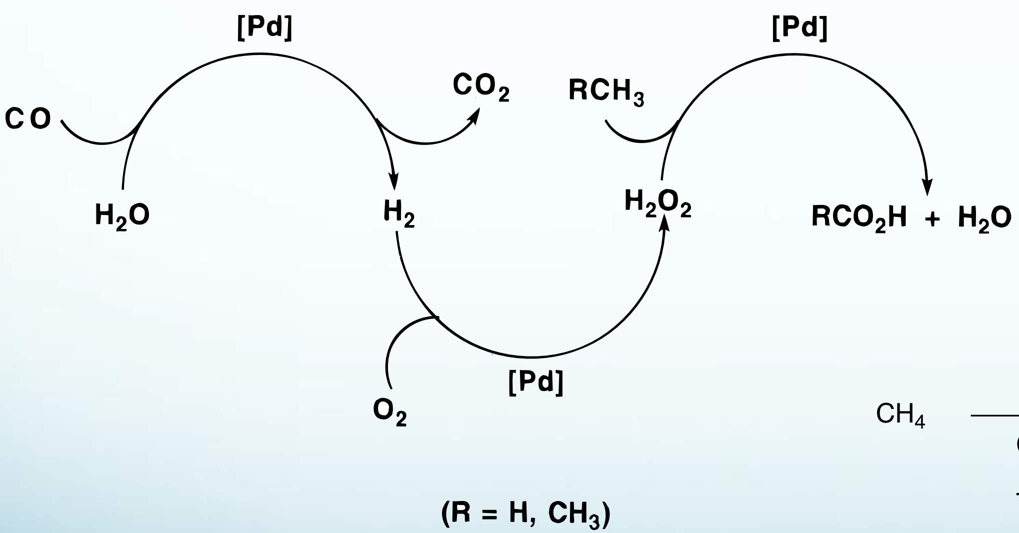


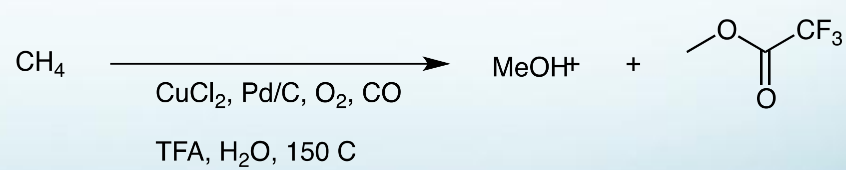
T8

Fu. *Cat. Today.* 2006, **117**, 133.

Catalytic Bimetallic Oxidation

- Use of $CuCl_2$ with Pd catalyst yielded methanol and its ester as only products, without acetic or formic acid byproducts





Sen. *JACS.* 1997, **119**, 6048.

Acetic Acid Synthesis

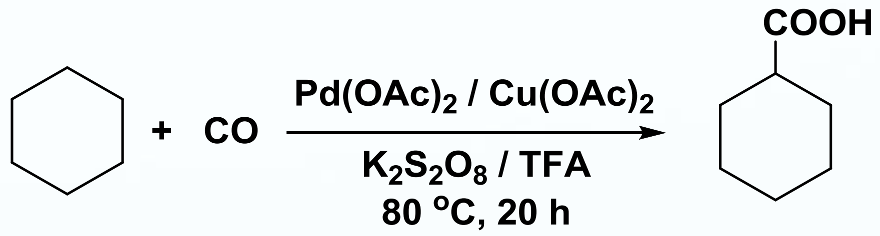
- Rh cat one step process
- Only byproducts were methanol and formic acid
- Additives: Pd/C or I^-
- High [CO] preserve catalyst

observations are consistent with a solut
ıer than metallic rhodium being the act
ıcid formation. In the absence of adde

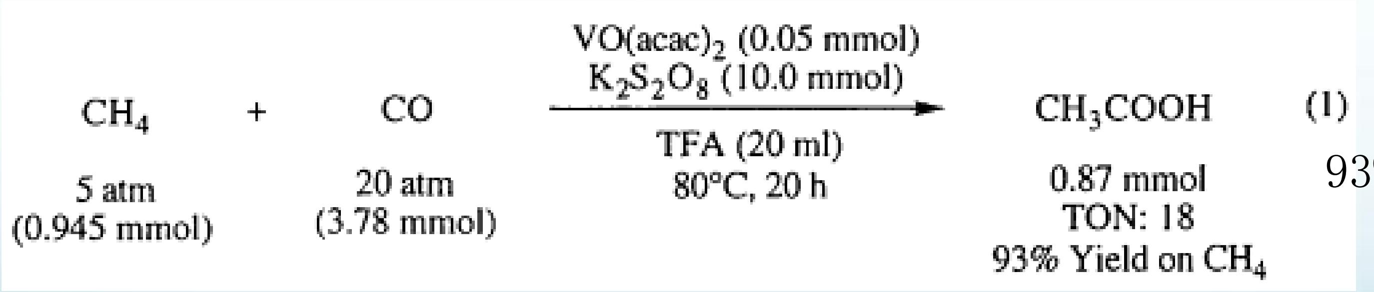
Sen. *Nature.* 1994, **368**, 613.

Improvement

- Fujiwara



- This process used for methane, 1% yield
- Shifted to new catalytic system

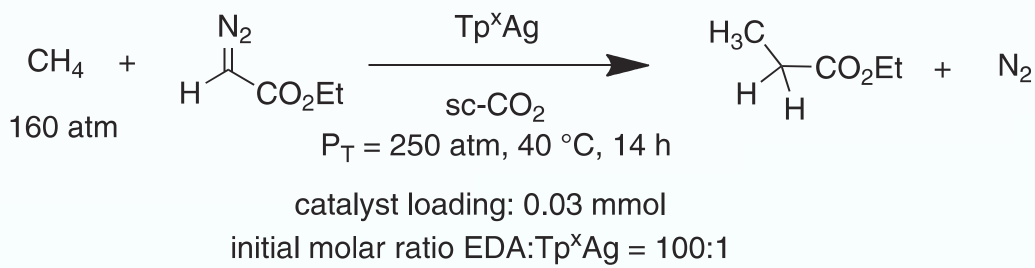


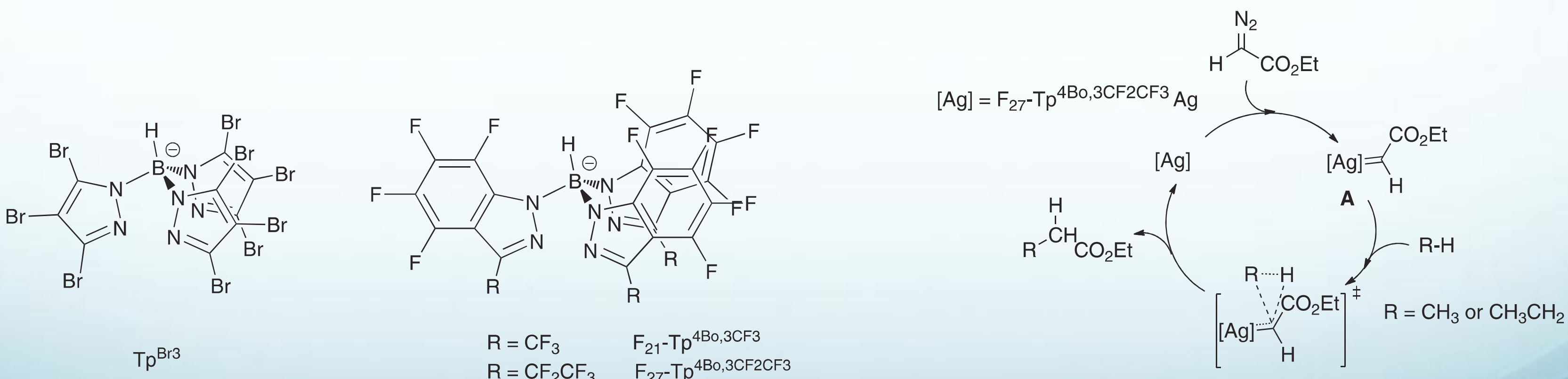
93% Yield

Fujiwara. *Studies in Surface Science and Catalysis.* 1997

Carbene Insertion

- Supercritical CO_2 - methane soluble
- 19% Yield



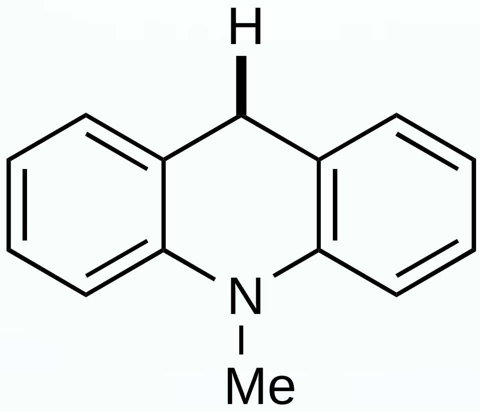


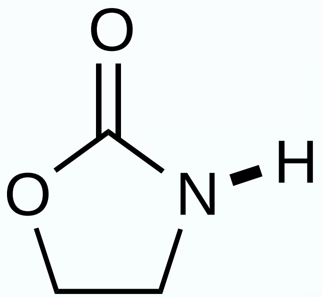
Science. 2012, **332**, 835.

Conclusions

- Most current methods require harsh conditions and yield bad selectivity
- Over oxidation common
- Heterogeneous pathways are hard to control
- Stoichiometric pathways are too costly and impractical
- Methane activation will become a necessary pathway to fuel in the near future.

Bond Strength | pKa

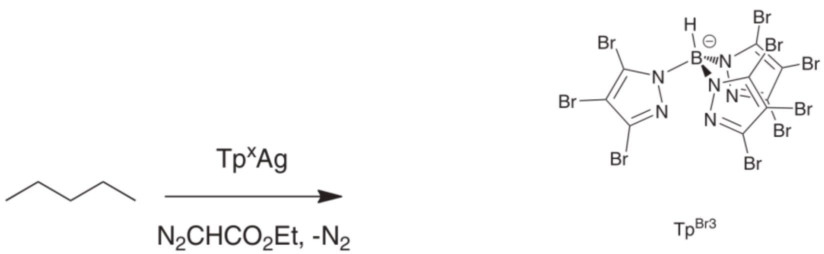




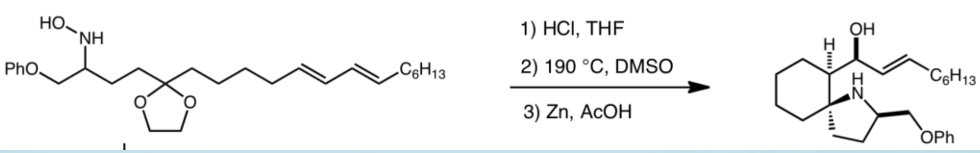
1. Provide the mechanism for the super acid oligomerization of methane.

$$n\mathrm{CH_4} \xrightarrow[P=1\,\mathrm{atm},\ T=200-400^\circ\mathrm{C}]{\mathrm{HBr+AlBr_3}} -(\mathrm{CH}_x)_n- + \mathrm{H_2}$$

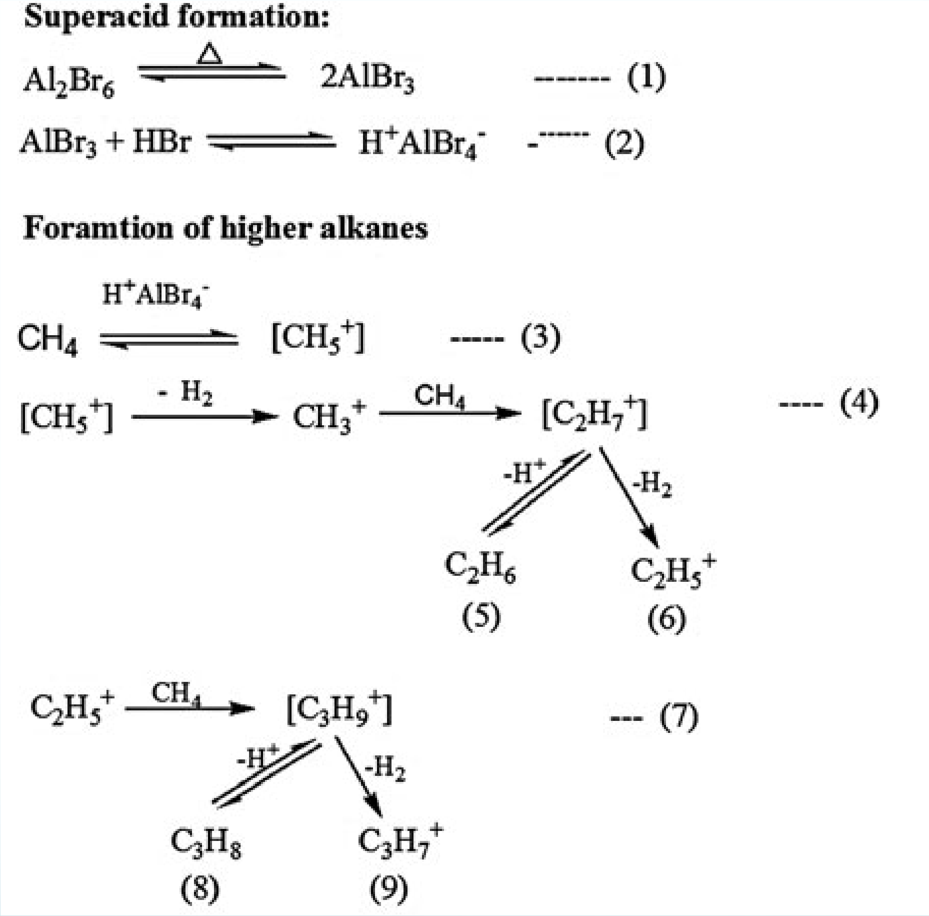
2. What are the 3 products of the carbene insertion below? (Select major product).



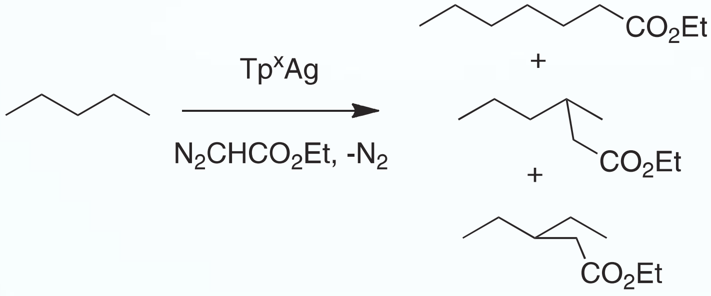
3. Provide an arrow pushing mechanism for the transformation below. (Hint: Zn/AcOH cleaves N-O bonds)



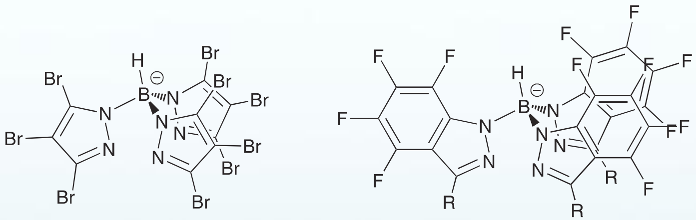
Question


Superacid formation:
Al2Br6 ⇌ 2AlBr3 ------- (1)
AlBr3 + HBr ⇌ H+AlBr4- ------- (2)
Foramtion of higher alkanes
H+AlBr4-
CH4 ⇌ [CH5+] ----- (3)
[CH5+] - H2 → CH3+ CH4 → [C2H7+] ---- (4)
-H+
-H2
C2H6
(5)
C2H5+
(6)
C2H5+ CH4 → [C3H9+] --- (7)
-H+
-H2
C3H8
(8)
C3H7+
(9)

Carbene Insertion (Alkanes)



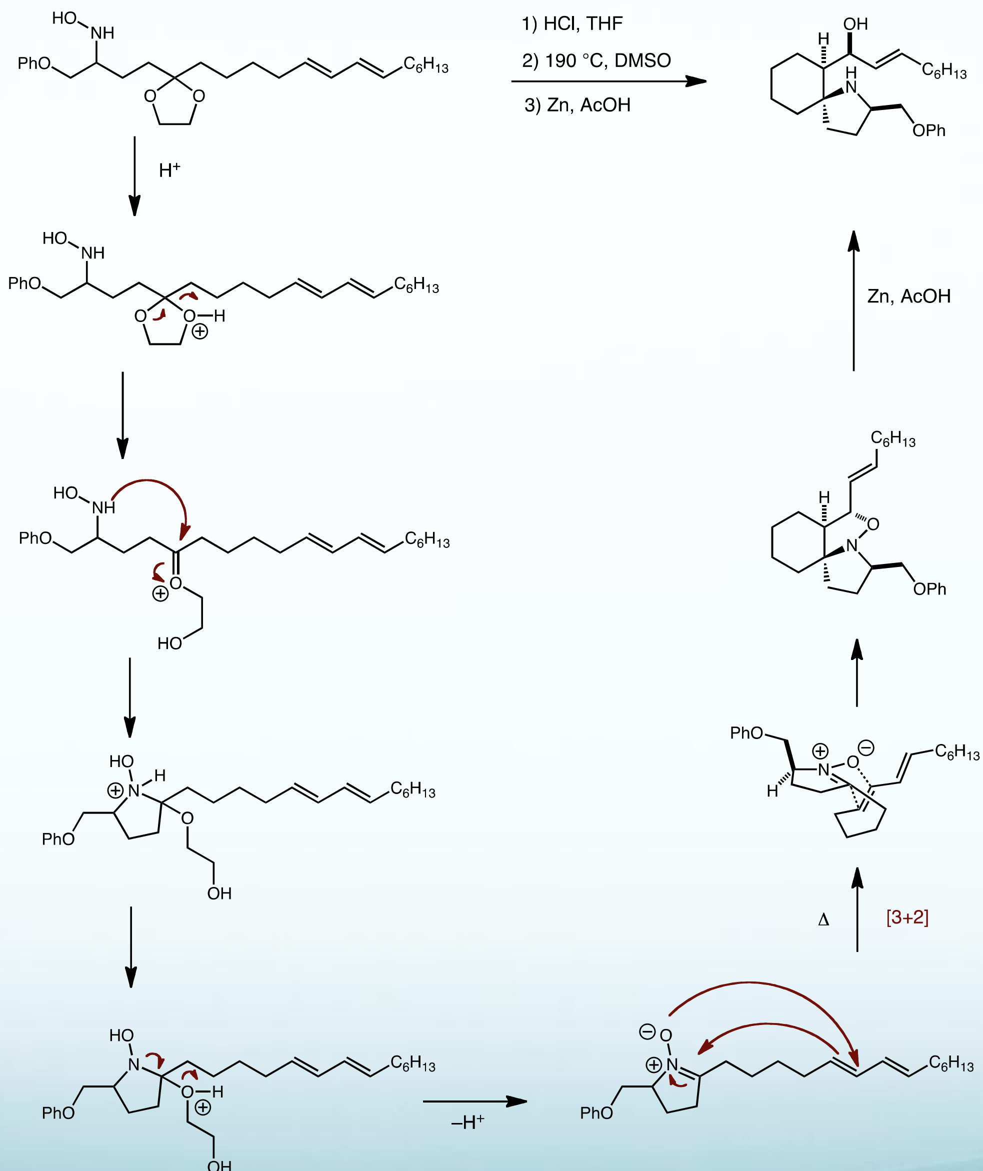
$Tp^{Br3}Ag$ (**1**)	F_{21}-$Tp^{4Bo,3CF3}Ag$ (**2**)	F_{27}-$Tp^{4Bo,3CF2CF3}Ag$ (**3**)
27%	37%	47%
53%	49%	44%
13%	14%	9%



Tp^{Br3}

R = CF_3 F_{21}-$Tp^{4Bo,3CF3}$

R = CF_2CF_3 F_{27}-$Tp^{4Bo,3CF2CF3}$


1) HCl, THF
2) 190 °C, DMSO
3) Zn, AcOH
H+
Zn, AcOH
Δ
[3+2]
−H+
PhO
HO
NH
OH
OPh
C6H13