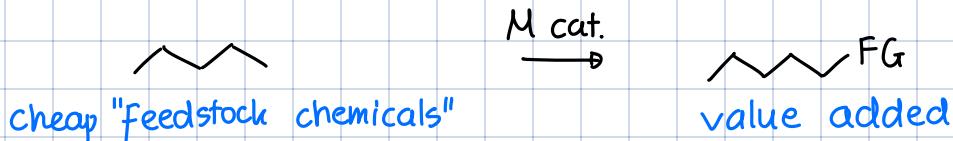


29.11.

Catalytic C-H Functionalization

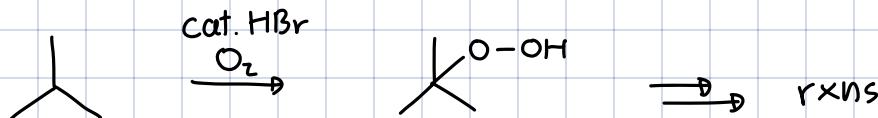
Motivation:



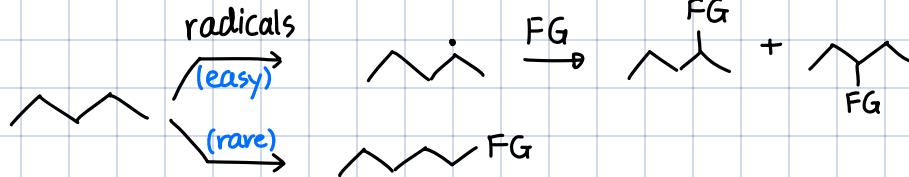
↳ Why is this so difficult?

- Breaking CH bonds? $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$, $\Delta G^\circ \ll 0$

Or Auto oxidation:



~ The real challenge: Selectivity (the above rxn are out of control)



Pd-cat. Alkane Ox.



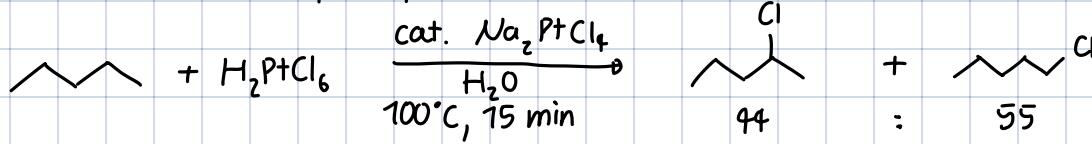
↓
Where exactly does the D go? (what fraction)

Alkane	D-Incorporation		
	CH_3-	$-\text{CH}_2-$	$-\overset{\text{H}}{\underset{\text{D}}{\text{CH}}}-$
	91%	-	-
	92%	57%	-
	83%	37%	9%

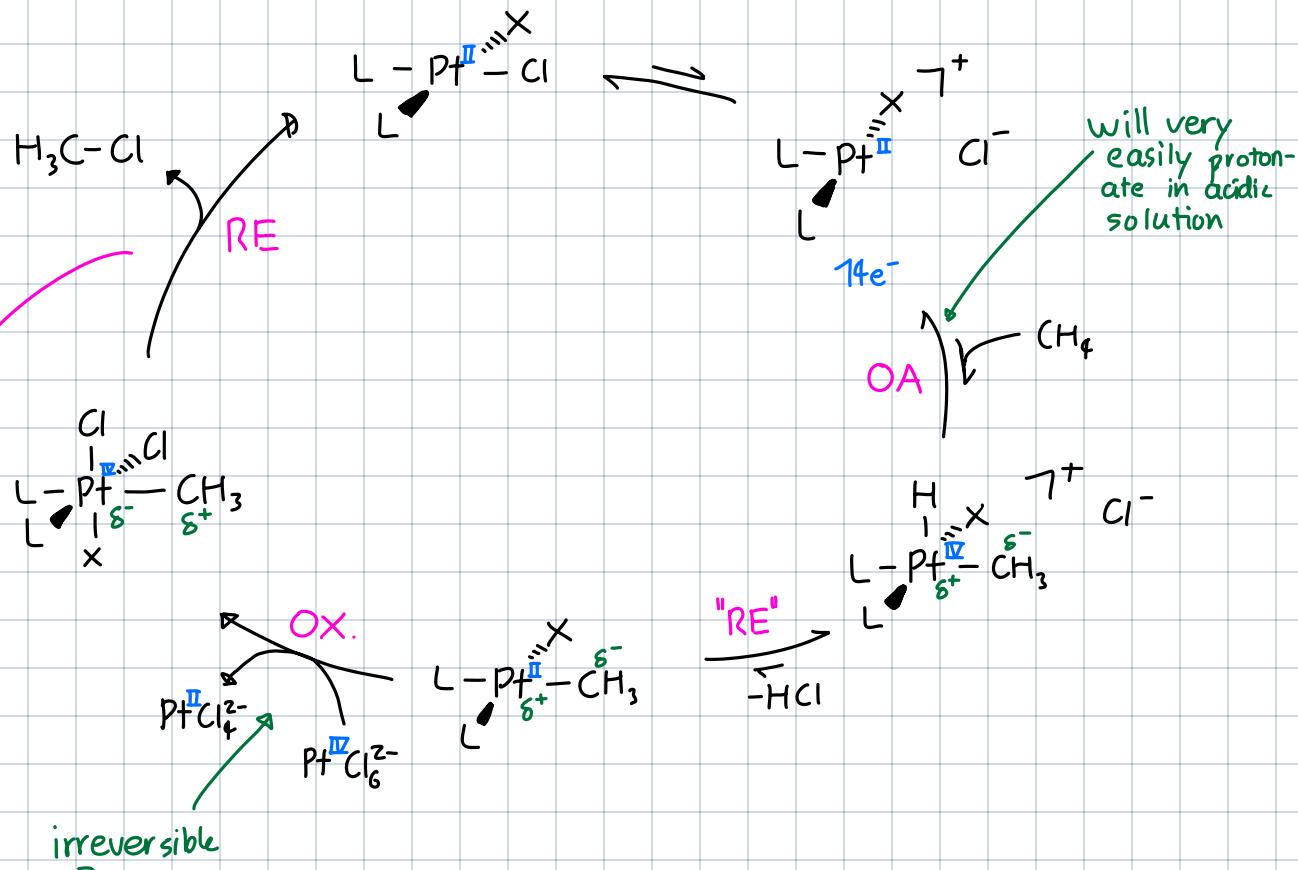
↳ C-H BDFE would suggest other way around

↳ We selectively functionalize the stronger bond!

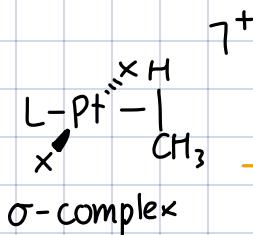
We can also actually put potentially useful functionalities:



↳ Mechanism: "Shilov cycle" $L = \text{H}_2\text{O}, X = \text{Cl} \text{ or } \text{OH}$



Key feature that leads to selectivity for funct. of terminal C-H



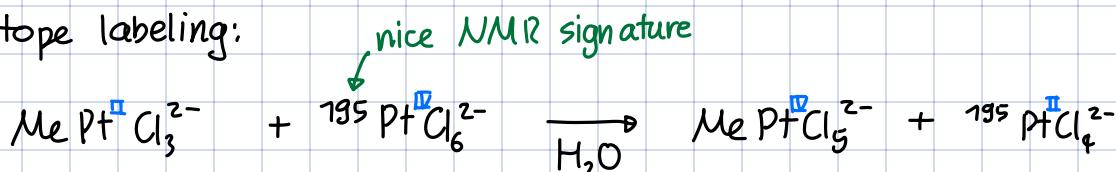
↳ prefers 1° C-H due to steric accessibility

How does OX. work?

2 possibilities:

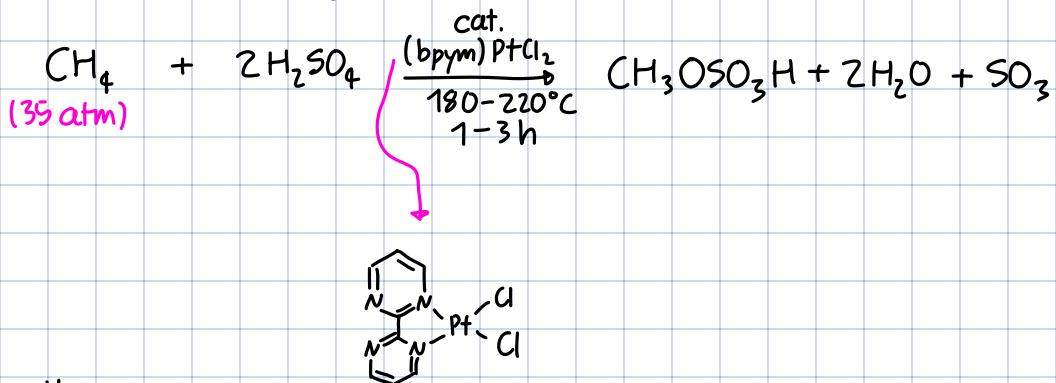
- ① Transfer of $-\text{CH}_3$ from $\text{Pt}^{\text{II}} \rightarrow \text{Pt}^{\text{IV}}$
- ② Transfer of $-\text{Cl}$ from $\text{Pt}^{\text{IV}} \rightarrow \text{Pt}^{\text{II}}$

→ Isotope labeling:

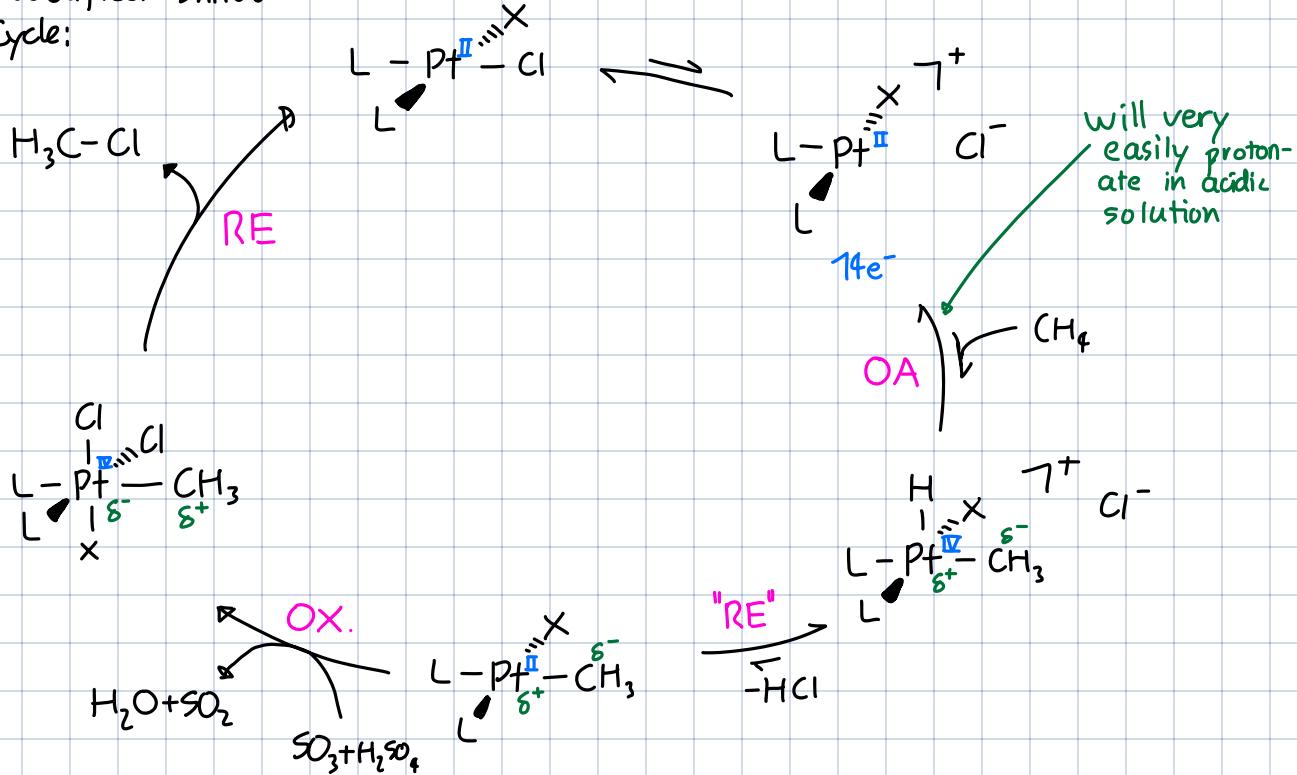


⇒ Option ②

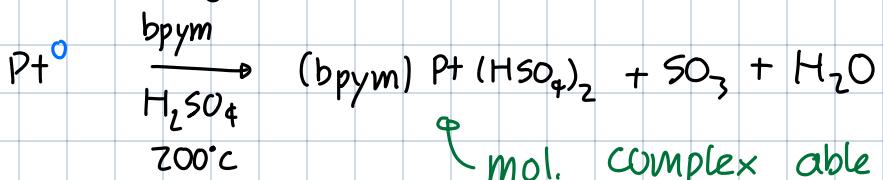
More practical: Exchange stoich. $\text{PtCl}_6^{\text{2-}}$ oxidant with SO_3



Modified Shilov Cycle:

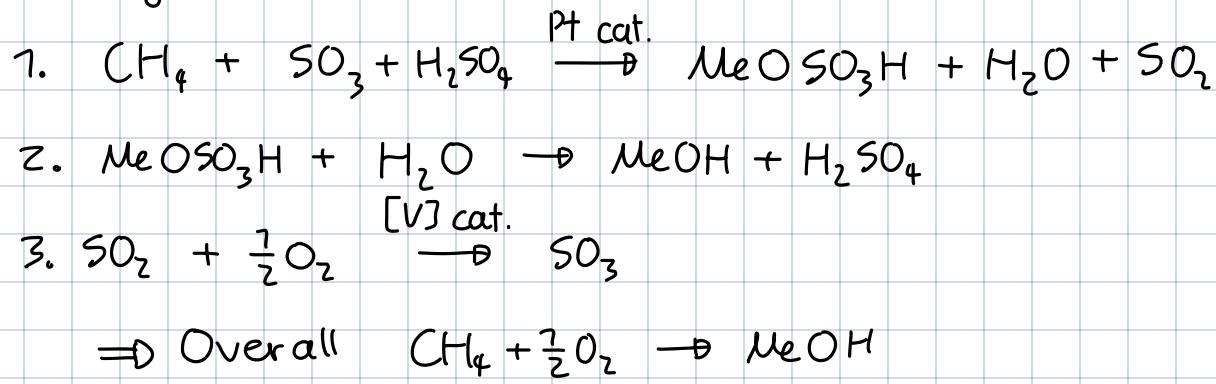


⇒ What's amazing:



mol. complex able to survive under these harsh conditions

How to get MeOH?



↳ But not industrially applied because it's impossible to sep. MeOH & H_2SO_4 energy efficiently!