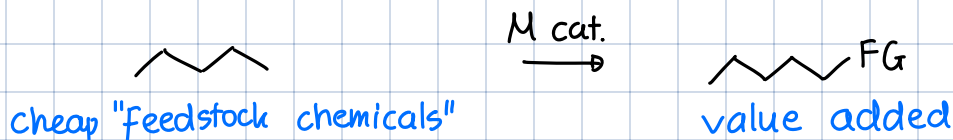


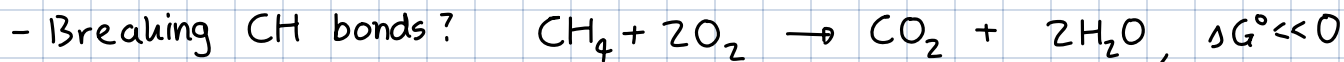
29.11.

Catalytic C-H Functionalization

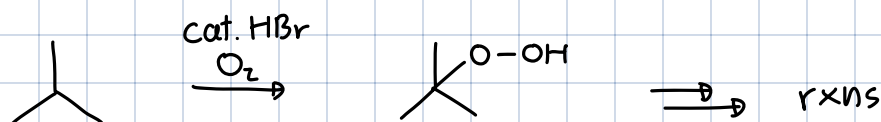
Motivation:



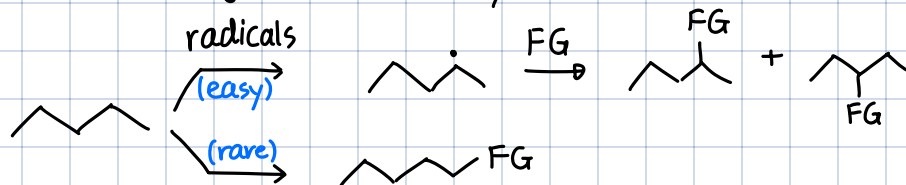
↳ Why is this so difficult?



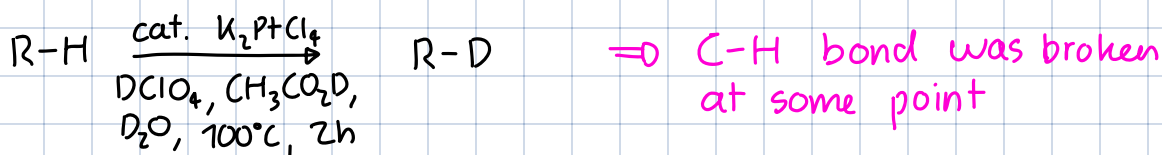
Or Auto oxidation:




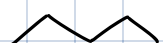
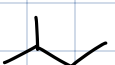
↳ The real challenge: Selectivity (the above rxn are out of control)



Pd-cat. Alkane Ox.



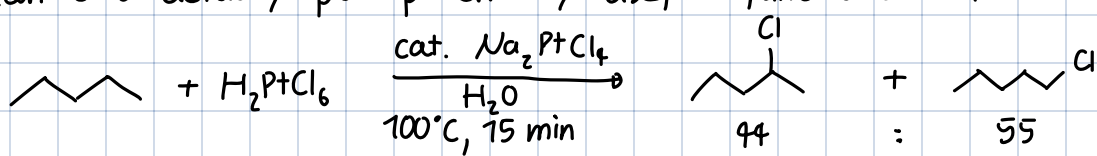
↓
Where exactly does the D go? (what fraction)

Alkane	D-Incorporation		
	CH ₃ —	—CH ₂ —	—CH—
	91%	—	—
	92%	57%	—
	83%	37%	9%

* C-H BDFE would suggest other way around

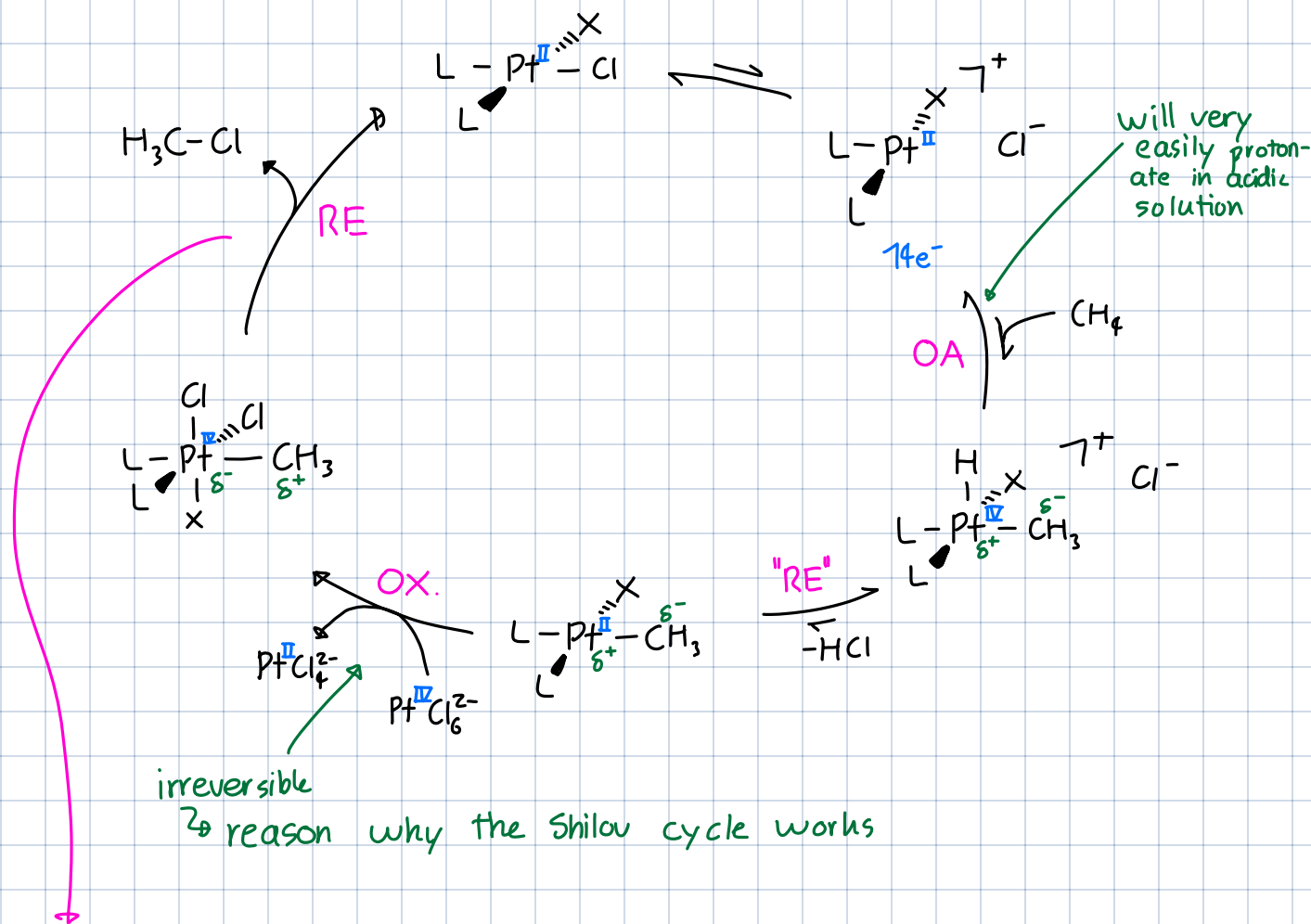
↳ We selectively functionalize the stronger bond!

↓
We can also actually put potentially useful functionalities:

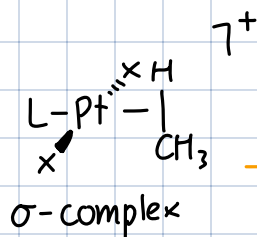


↳ Mechanism: "Shilov cycle"

$\text{L} = \text{H}_2\text{O}$, $\text{X} = \text{Cl}$ or OH



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



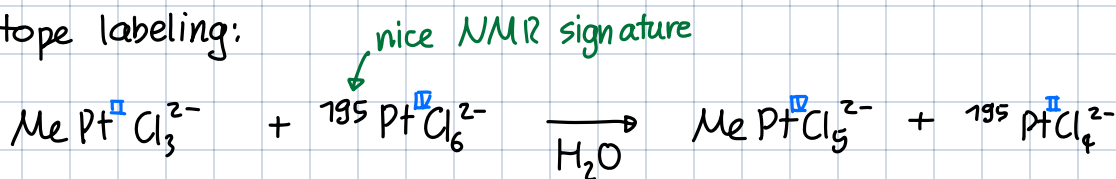
↳ prefers 1° C-H due to steric accessibility

How does ox. work?

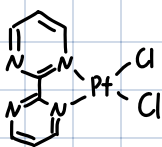
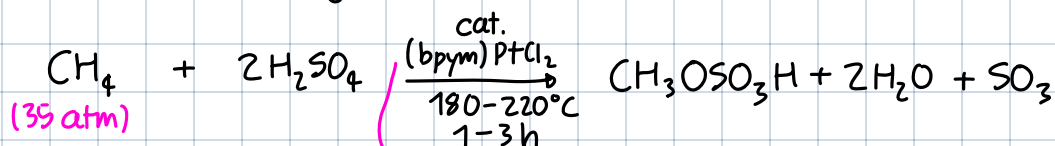
2 possibilities:

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

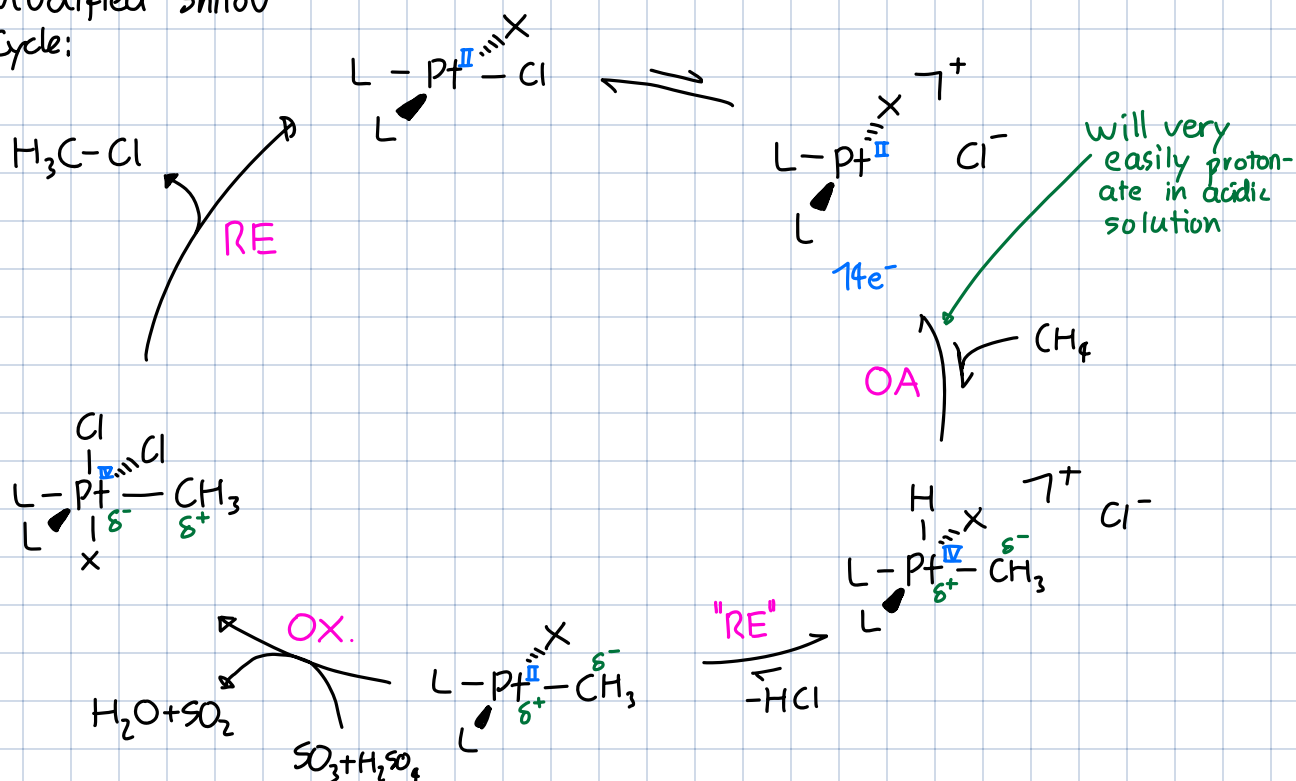
→ Isotope labeling:



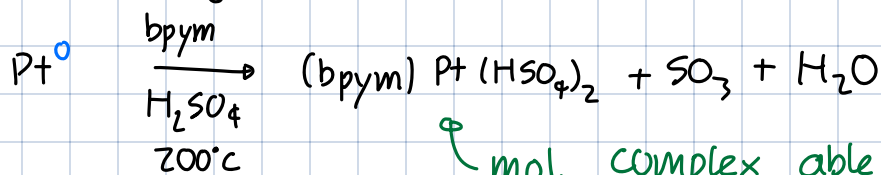
More practical: Exchange stoich. PtCl_6^{2-} oxidant with SO_3



Modified Shilov Cycle:

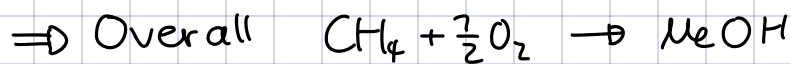
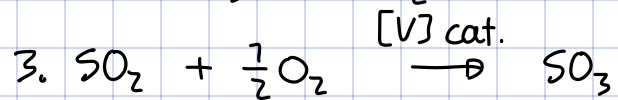
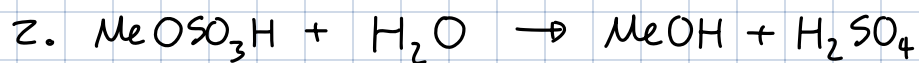
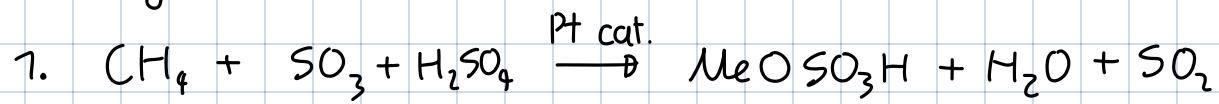


↳ What's amazing:



mol. complex able to survive under these harsh conditions

How to get MeOH?



↳ But not industrially applied because it's impossible to sep. MeOH & H₂SO₄ energy efficiently!