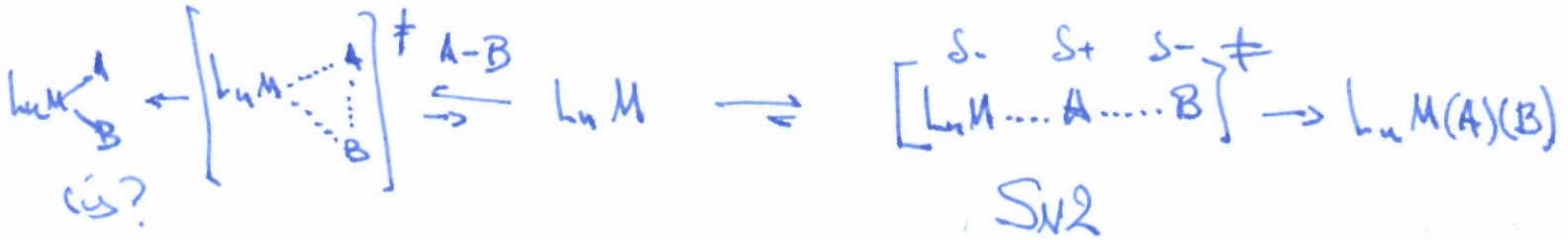
Mechanisms

- Concerted 2e⁻ transformations
- radical processes

even among 'concerted' rxns



3-center addn.

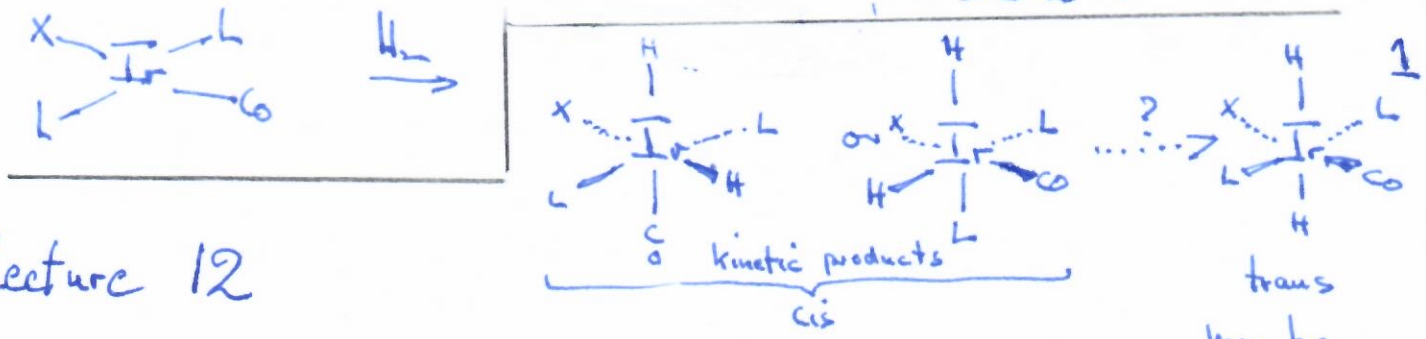
nonpolar molecules

H_2, O_2, X_2

M–H exists!

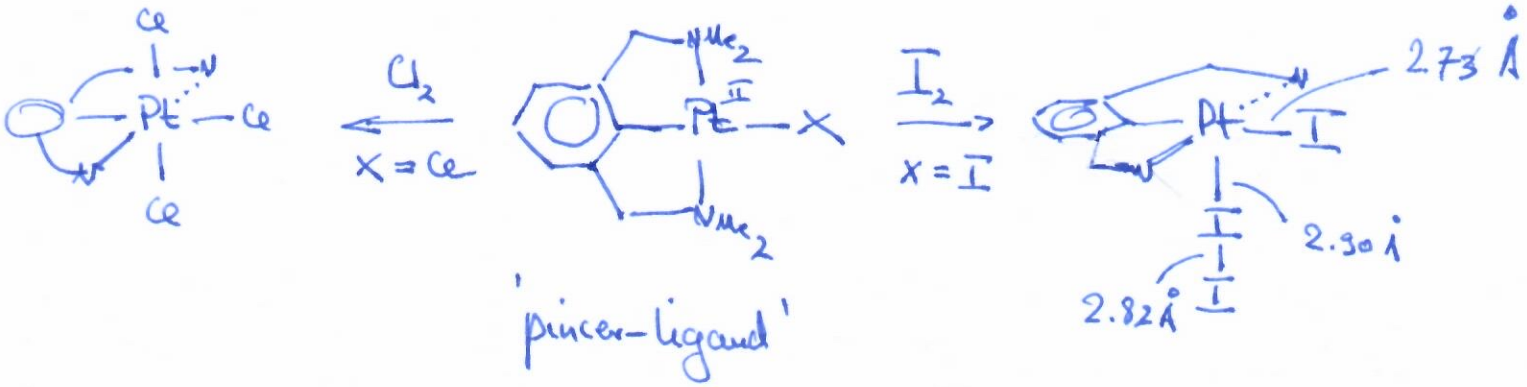
fast (1→100 $M^{-1}s^{-1}$) $\Delta H^{\ddagger}$ ~ 10-12 kcal/mol

$\Delta S^{\ddagger}$ ≈ −15 → −25 e.u.

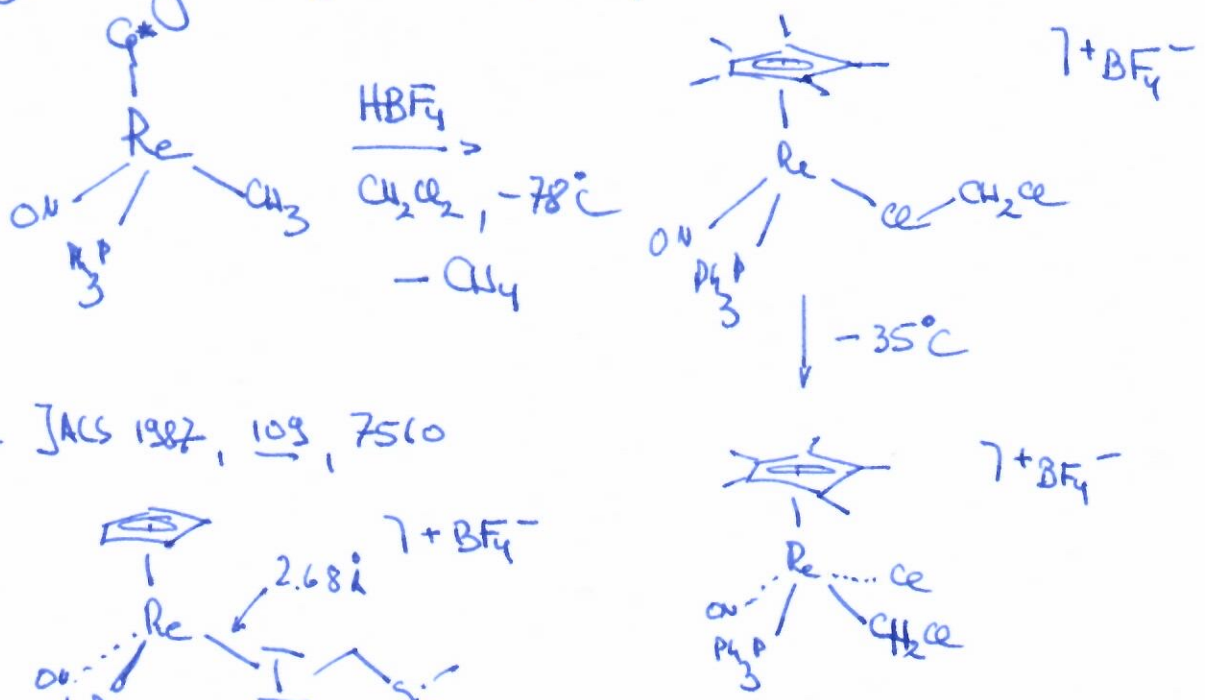


Lecture 12

van Koten (JACS 1986, 108, 5010



J. Gladysz JOMC 1988, 354, C33



See JACS 1987, 109, 7510

Review: Crabtree Coord. Chem. Rev. 1990, 99, 89

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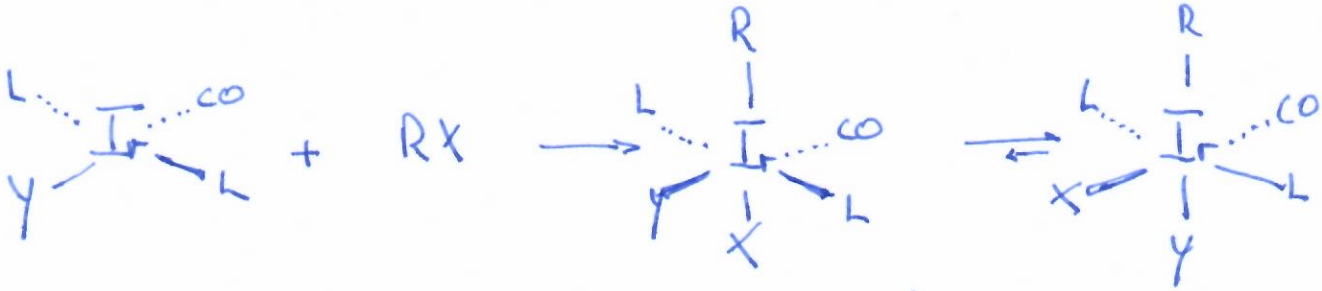
classic



other observation:

2nd order rxn: rate = k_2 [Ir'][RX]

relative rates: X = Tos > I > Br > Cl leaving grp ab...

" : Y = F > Cl > Br > I 'size'

" : L = PEt_3 > PEt_2Ph > $PEtPh_2$ > PPh_3 > $P(OPh)_3$

polar solvents increase rate: DMF, CH_3CN, THF

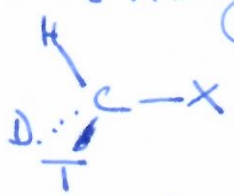
large negative $\Delta S^{\neq}$ = −43 to −51 e.u.

change R: Me > Et ≫ 2°, 3° (not at all)

→ S_N2 !?

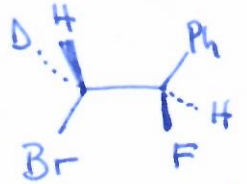
stereochemistry? inversion at C

'chiral methyl'



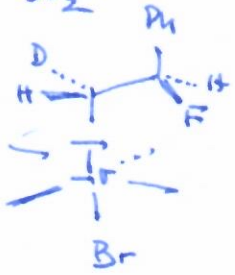
H. Floss Acc. Chem. Res. 1993, 26, 116

G. Whitesides



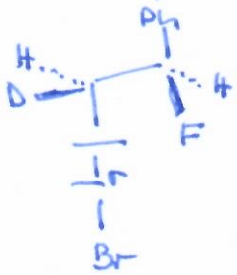
$IrCe(CO)(PMe_3)_2$

no need for enantiomerically pure mat, just one diastereomer



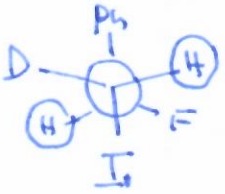
'retention'

+



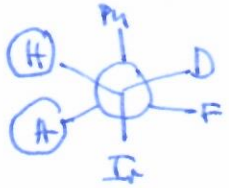
'inversion'

Kaplus relationship



'erythro'

$J_{HH} > 9Hz$

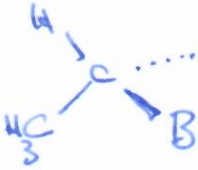


'threo'

$J_{HH} < 6Hz$

result: mixture of both!?

also:

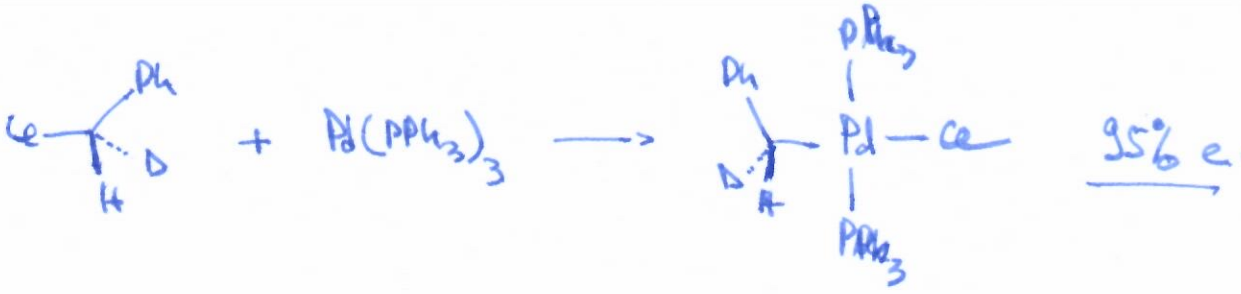


$\xrightarrow{IrCe(CO)(PMe_3)_2}$ racemate!!

opt. activ

may indicate different mech for more subst. RX.

or: subsequent racemization.!



Radical mechanisms: chain rxs vs 'non-chain' rxs

a) atom abstraction (non-chain process)

$Pt(PPh_3)_3 + BnBr \longrightarrow$ trans. $Pt(PPh_3)_2(Bu)Br$

mech: $L_3Pt \underset{+L}{\overset{-L}{\rightleftharpoons}} L_2Pt^0 \xrightarrow{BnBr} \{L_2Pt^{I}Br + Bn^{\cdot}\}$ 'inner sphere electron transfer'

$\downarrow k_{comp}$

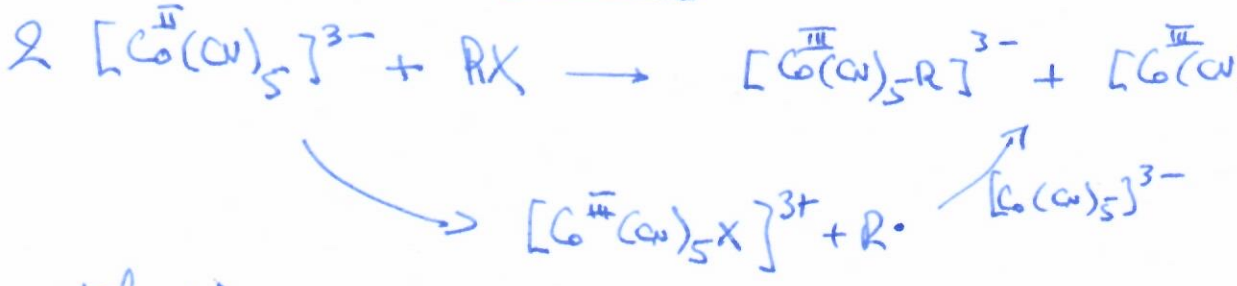
$L_2Pt^{II}(Bn)Br$

rate: $RI > RBr > RCl \approx ROTs$

$R = 3^\circ > 2^\circ > 1^\circ > Me$ stability of radical!

radical clocks:

note:  $k = 10^5\ s^{-1}$?



rel. rates $RCl < RBr < RI$

$MeI < EtI < {}^iPrI < BnI$

$2\,[Co(CN)_5]^{3-} + H_2 \longrightarrow 2\,[HCo(CN)_5]^{3-}$

~~H~~ intermediate !??

rate = ~~k~~ · $[H_2]['Co']^2$ a termolecular rxn!
