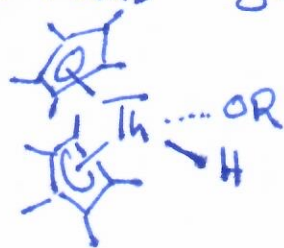


Insertion/Elimination cont'd

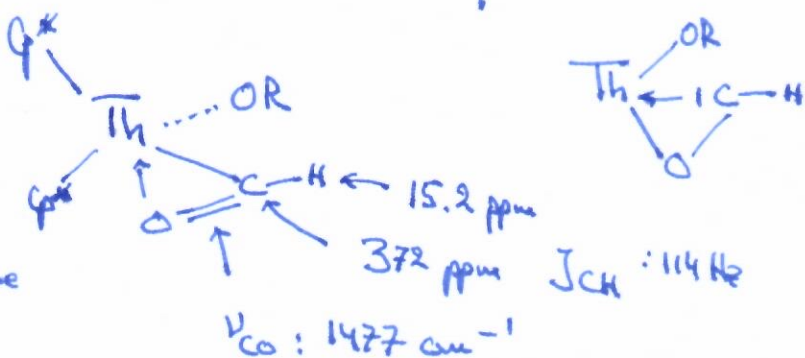
Lecture 15

T. Marks JACS 1981, 103, 6959

'oxycarbene' resonance form



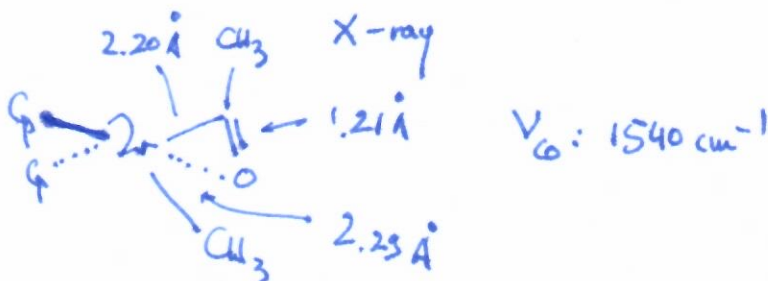
eq. in fast
on 'H-NMR time
scale



eq. thermodynamics:

$\Delta H = -4.5 \text{ kcal/mol}$ due to added oxophilic interaction
of actinide
 $\Delta S = -11.7 \text{ e.u.}$

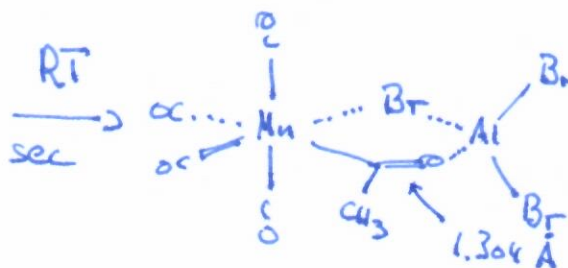
other ' η^2 -acyls' C. Floriani



external Lewis Acid?



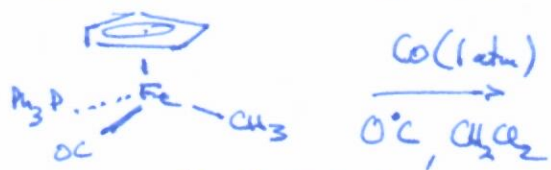
very fast!



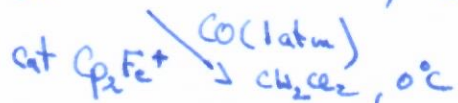
$\nu_{CO} = 1483 \text{ cm}^{-1}$

'Oxidatively induced CO-insertion'

R. Magnusson OM 1983, 2, 460

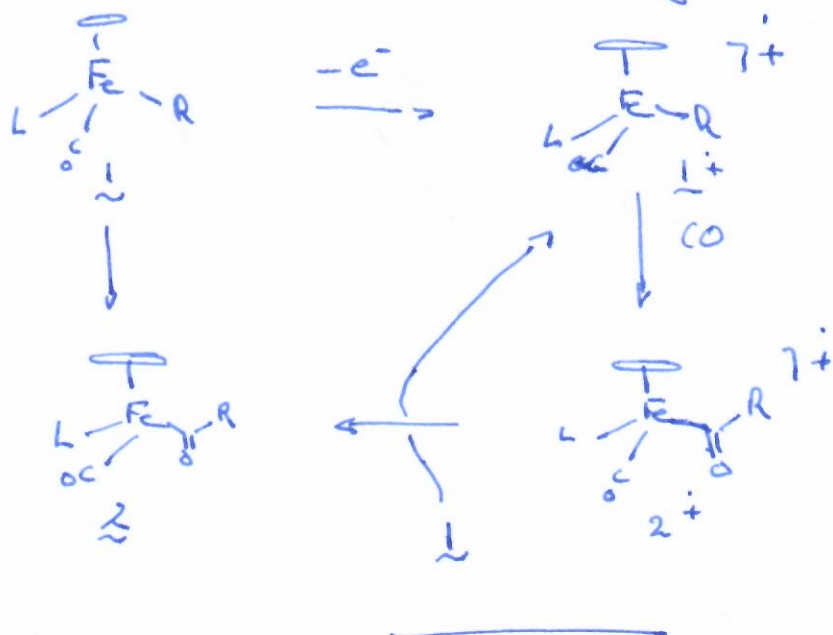


no rxn after 5d



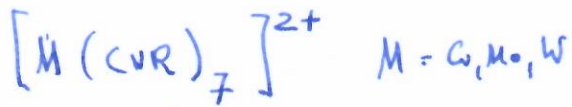
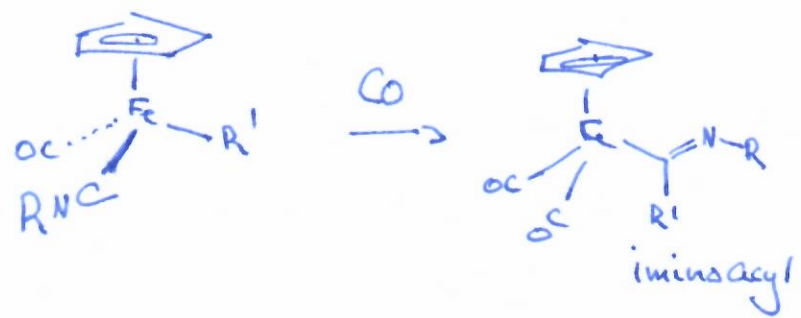
complete after 2 mins!

Mechanism? ; electron transfer catalysis (ETC)



other 1,1 insertions

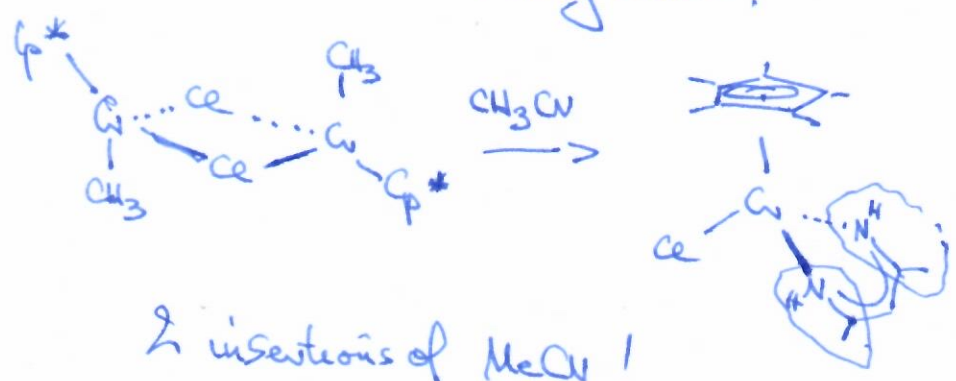
isonitriles (isocyanides) : $R-N\equiv C$ ($O\equiv C$) better σ -donors weaker π -acceptors } than CO



isonitriles insert into $M-H$ and $M-C$

→ polymerization! of RNC w/ Ni-alkyls

? nitriles ?? $R-C\equiv N$ rarely insert!

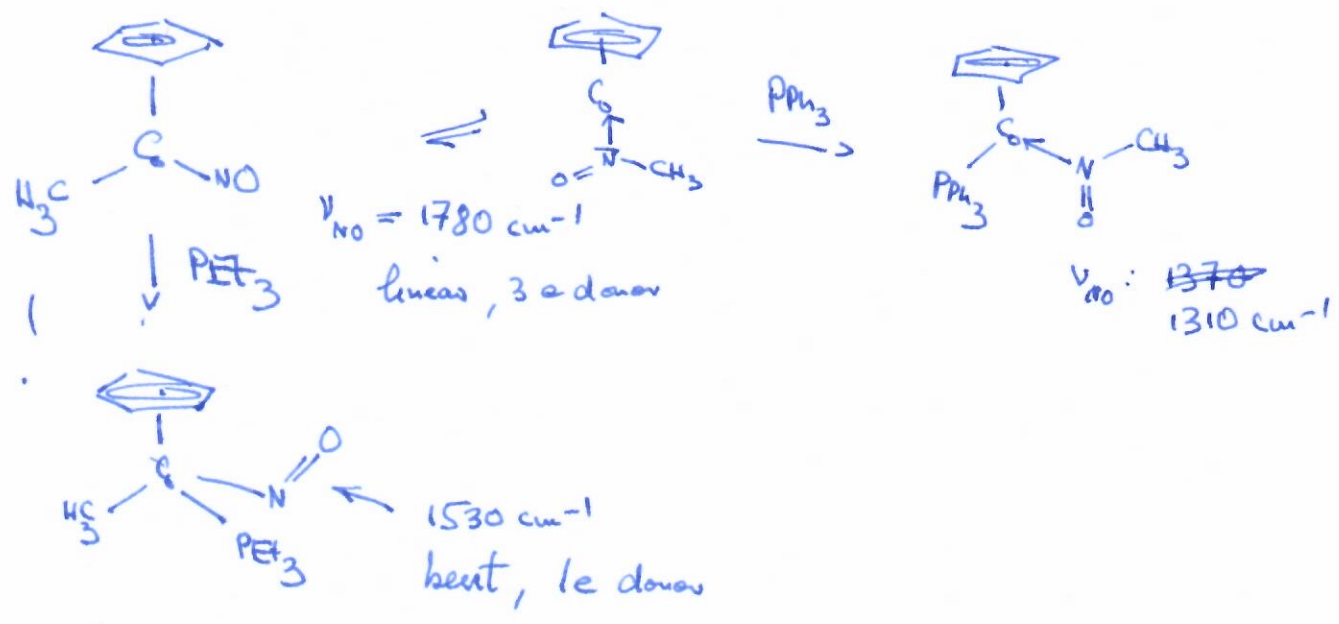


2 insertions of MeCN!

'nacnac' isoelectronic to acac

a 1,2 insertion!

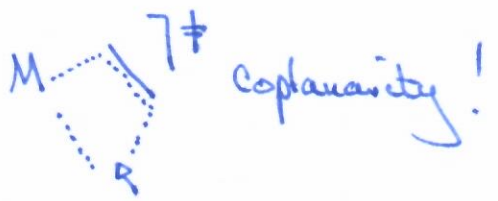
nitrosyl: NO



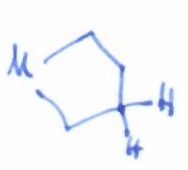
1,2 insertions: alkene insertion



R = H microscopic reverse of β -hydrogen elimination very fast, reversible



R = alkyl, aryl \rightarrow olefin polymerization
 microscopic reverse: β -alkyl elimination, rare but exists!



Selective trimerization of \equiv

