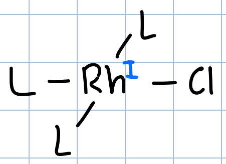
13.12.

Metal Hydrides cont'd

Wilkinson catalysts

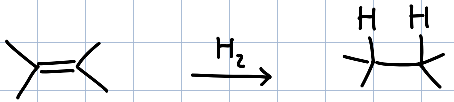


1960s, first X-ray str. in 1980s

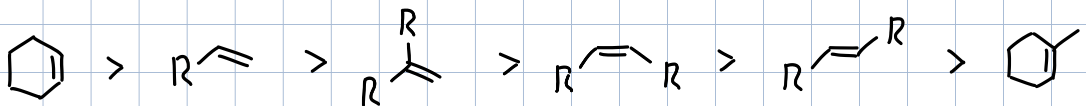
d^8, 16e^-

$L = PPh_3$

→ Well known to catalyze hydrogenation of alkenes (cis-addition):



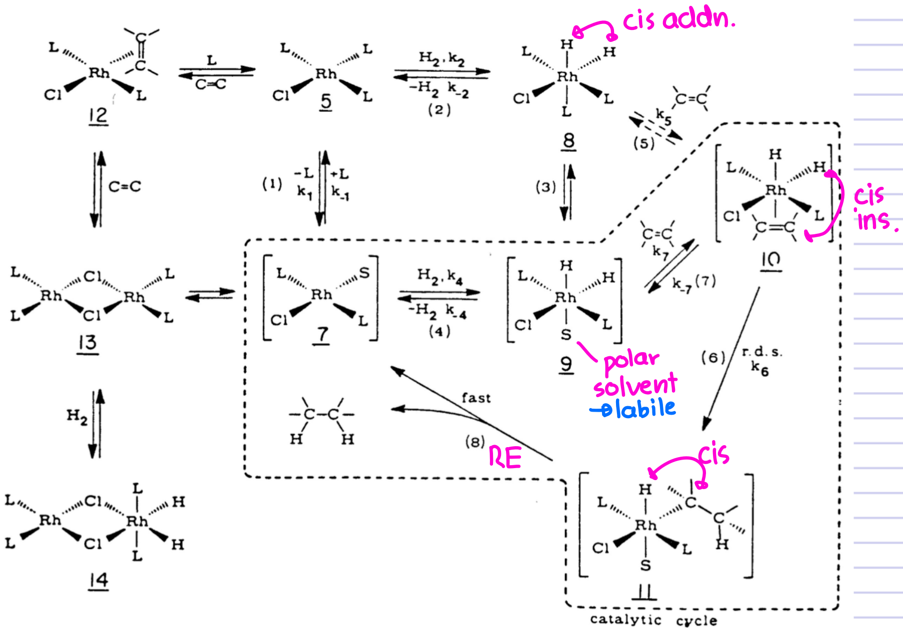
Reactivity:



→ It's sterics & strain that control the reactivity

Proposed mechanism

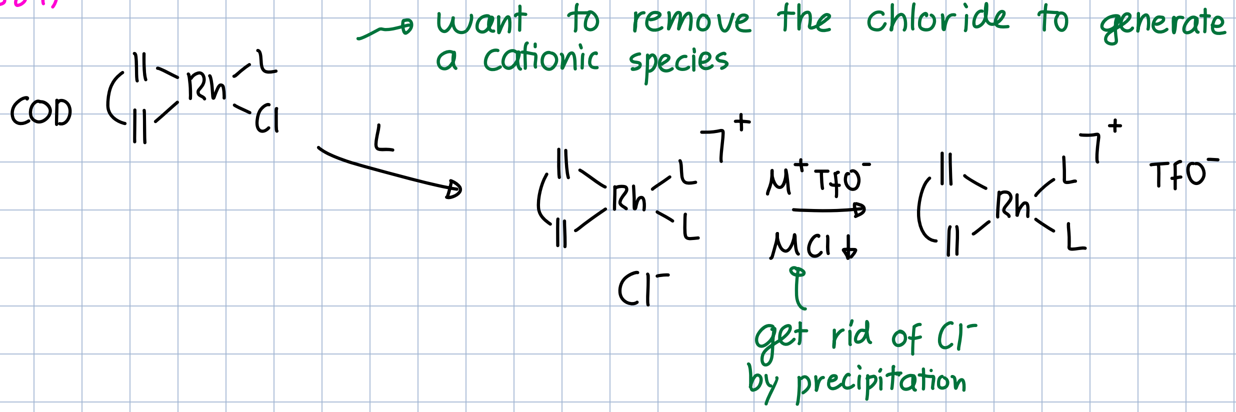
The Wilkinson Catalysts



For Asym., see J Halpern *Science* 1982, *217*, 401-407.

Schrock developed a post-Wilkinson cat. (make it more reactive)

(1981)

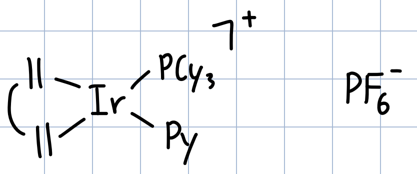


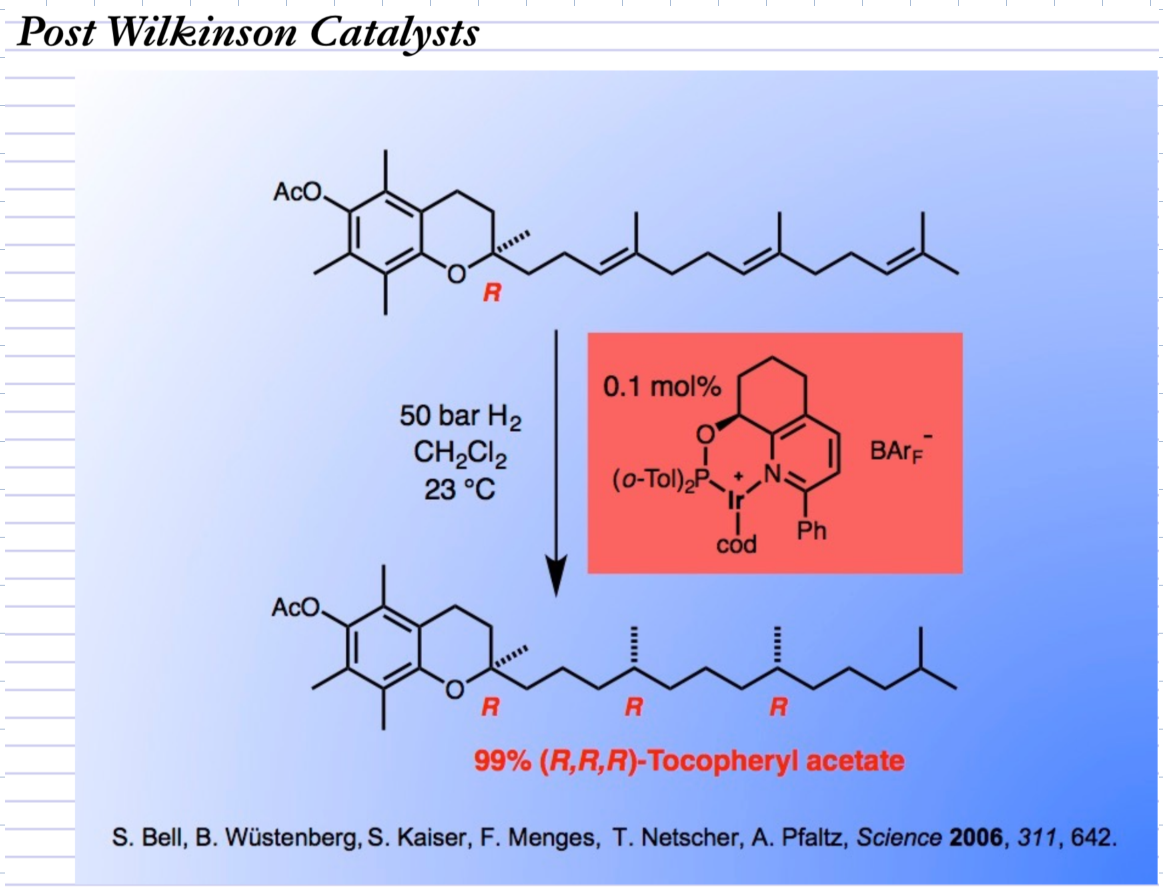
want to remove the chloride to generate a cationic species

get rid of Cl^- by precipitation

Crabtree most performant today

(1979)





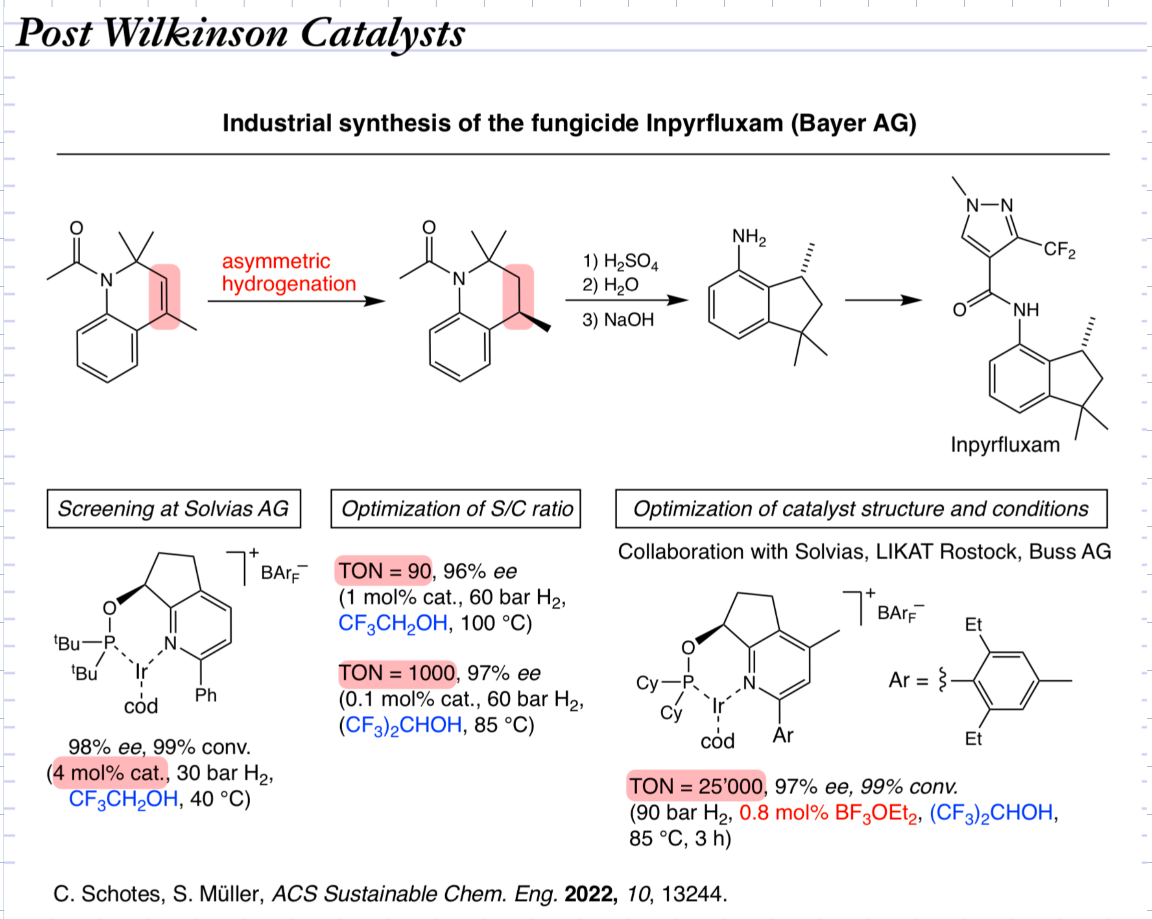
Post Wilkinson Catalysts

50 bar H_2
CH_2Cl_2
23 °C

99% (*R*,*R*,*R*)-Tocopheryl acetate

S. Bell, B. Wüstenberg, S. Kaiser, F. Menges, T. Netscher, A. Pfaltz, *Science* **2006**, *311*, 642.

Example where sth. more active than Wilkinson's cat is needed



Post Wilkinson Catalysts

Industrial synthesis of the fungicide Inpyrfluxam (Bayer AG)

asymmetric hydrogenation

1) H_2SO_4
2) H_2O
3) NaOH

Inpyrfluxam

Screening at Solvias AG

98% *ee*, 99% conv.
(4 mol% cat., 30 bar H_2, CF_3CH_2OH, 40 °C)

Optimization of S/C ratio

TON = 90, 96% *ee*
(1 mol% cat., 60 bar H_2, CF_3CH_2OH, 100 °C)

TON = 1000, 97% *ee*
(0.1 mol% cat., 60 bar H_2, $(CF_3)_2CHOH$, 85 °C)

Optimization of catalyst structure and conditions

Collaboration with Solvias, LIKAT Rostock, Buss AG

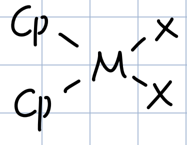
TON = 25'000, 97% *ee, 99% conv.*
(90 bar H_2, 0.8 mol% BF_3OEt_2, $(CF_3)_2CHOH$, 85 °C, 3 h)

C. Schotes, S. Müller, *ACS Sustainable Chem. Eng.* **2022,** *10*, 13244.

So far always the el. step. oxidative addition was present in the catalyst → Get to a new area?

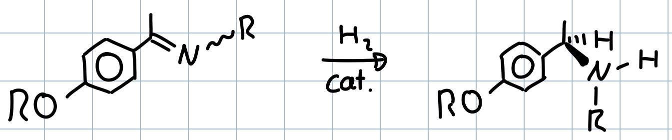
σ-BM could be an alternative

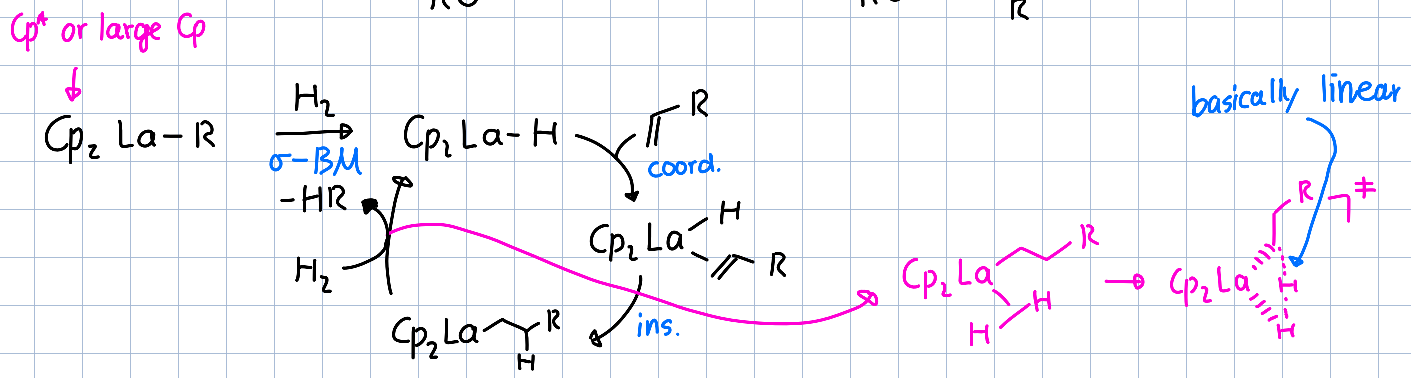
⇒ Bent metallocenes with the 3 free FMOs that allow to activate:



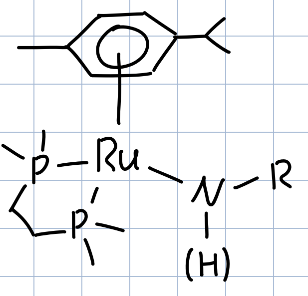
→ typical Cp_2ZrCl_2
Cp_2TiCl_2

→ Using early TM instead of Wilkinson, we can gen. chiral amines:

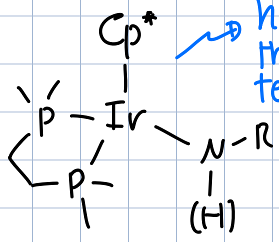




Hydrogenation of ketone (Noyori)

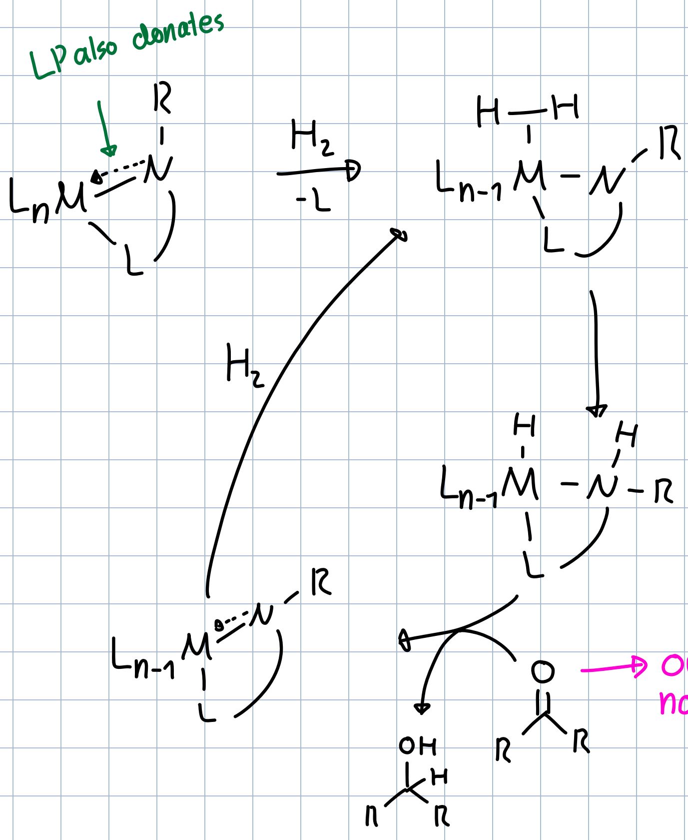


or isoel. could have

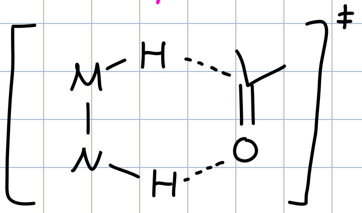


have to think in terms of el. str!

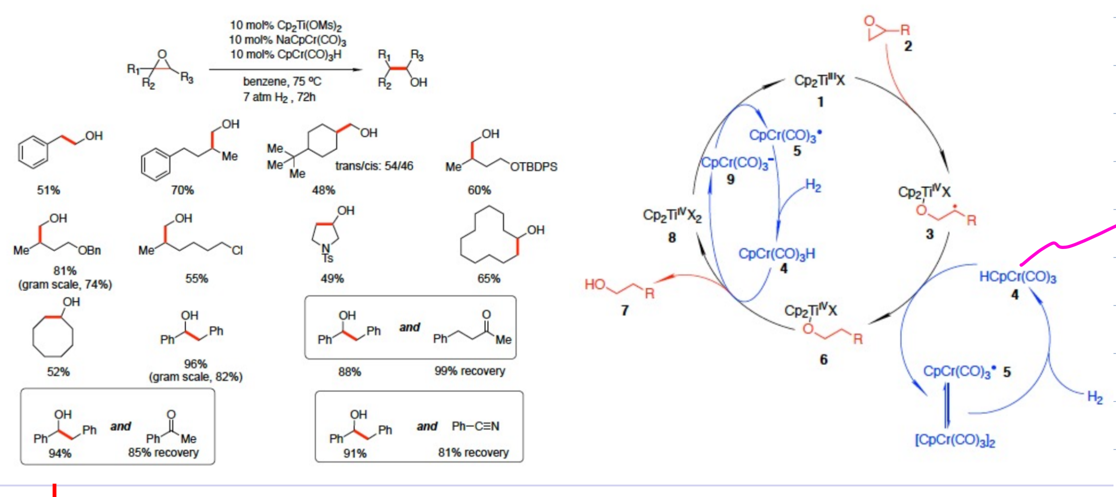
Mechanism:



outer sphere rxn, metal is not directly involved!



Application hydrogenation

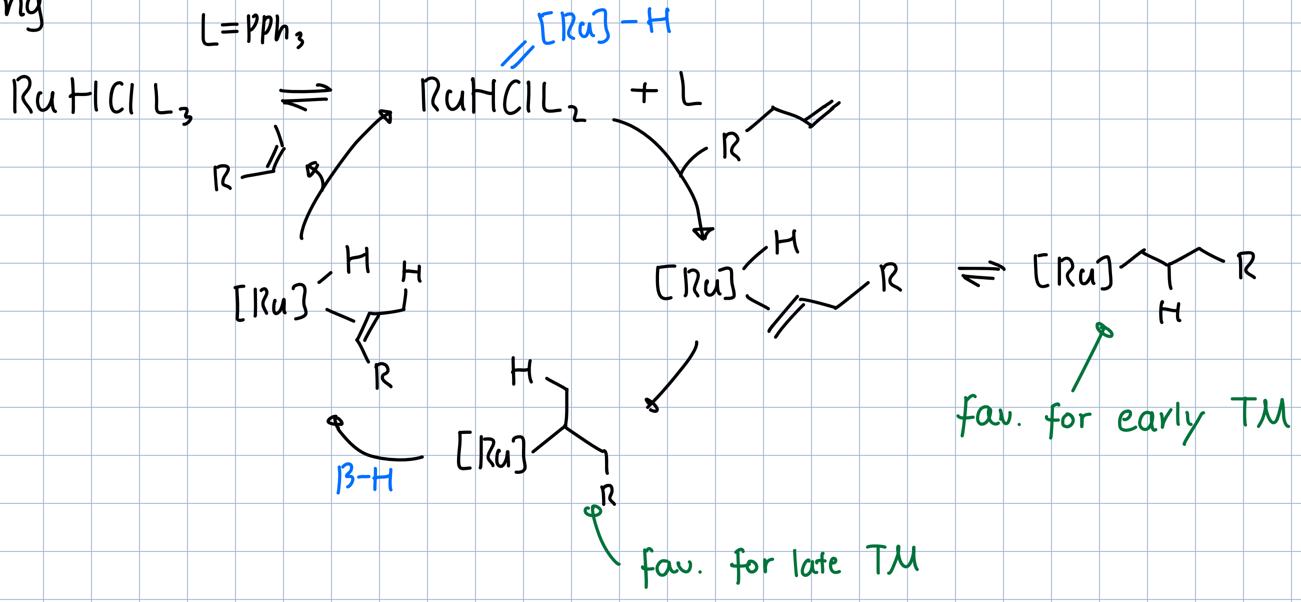


BDE mostly driven by metal (yields $H^•$)

Yao et al. Science, 2019, 364, 764-767.

Isomerization via M-H

Can also use this type of complexes to isomerize via chain-walking



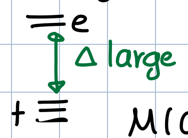
⇒ If we starve our rxn of H_2, DBs will start to move around

Carbonylation

CO chemistry → Carbonylation, Hydroformylation, Fischer-Tropsch

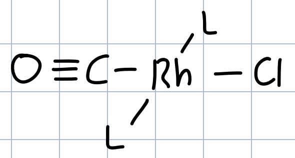
Metal-carbonyl
↳ $L_nM-C\equiv O$: CO is strong π-acc. and σ-donor ligand

⇒ large splitting d-orb.:



$M(CO)_6$
↳ M = Cr, Mo, W
→ d^6 ⇒ $18e^-$

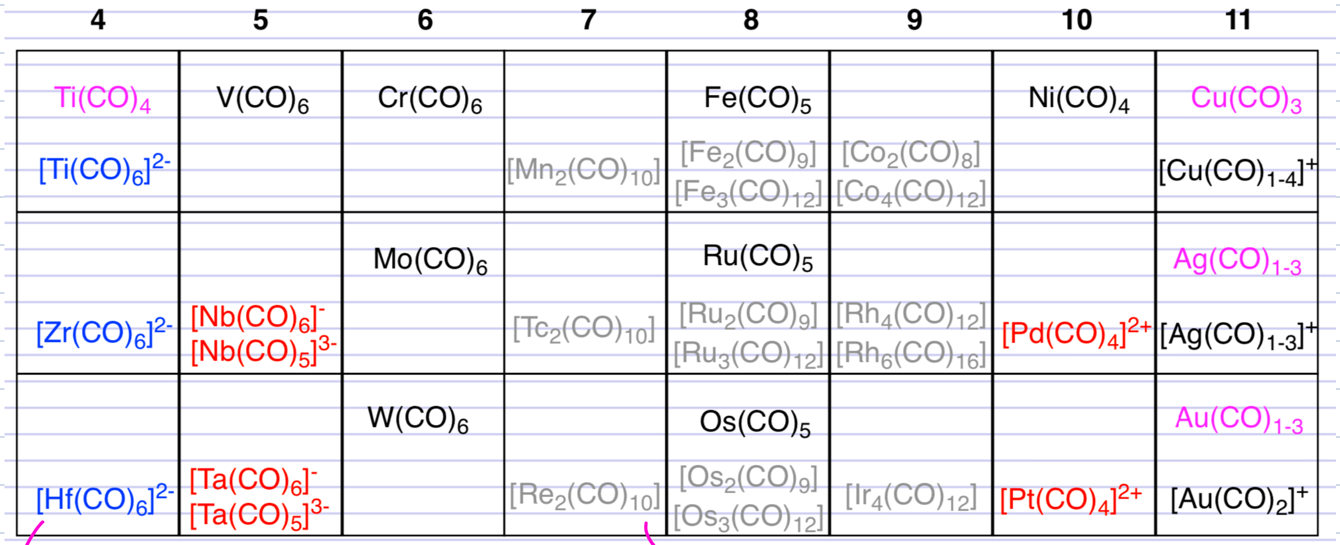
"Wilkinson two" → replace L with CO: ($L = PPh_3$)



$O\equiv C-Rh(L)_2-Cl$

⇒ used for hydroformylation

A lot of carbonyls known across the PTE:

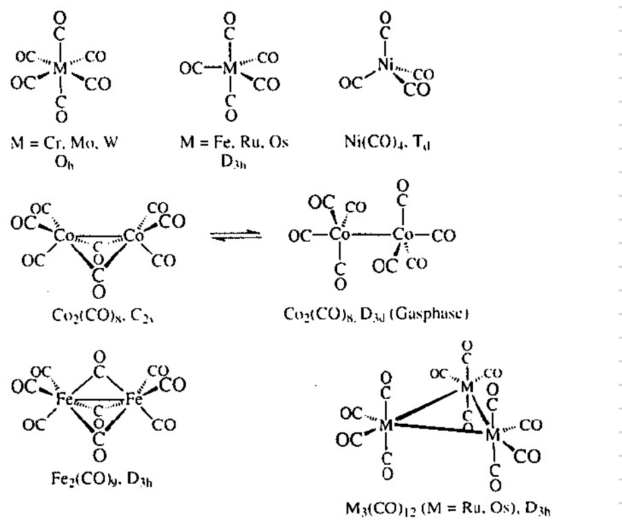


4	5	6	7	8	9	10	11
$Ti(CO)_4$ $[Ti(CO)_6]^{2-}$	$V(CO)_6$	$Cr(CO)_6$	$[Mn_2(CO)_{10}]$	$Fe(CO)_5$ $[Fe_2(CO)_9]$ $[Fe_3(CO)_{12}]$	$[Co_2(CO)_8]$ $[Co_4(CO)_{12}]$	$Ni(CO)_4$	$Cu(CO)_3$ $[Cu(CO)_{1-4}]^+$
$[Zr(CO)_6]^{2-}$	$[Nb(CO)_6]^-$ $[Nb(CO)_5]^{3-}$	$Mo(CO)_6$	$[Tc_2(CO)_{10}]$	$Ru(CO)_5$ $[Ru_2(CO)_9]$ $[Ru_3(CO)_{12}]$	$[Rh_4(CO)_{12}]$ $[Rh_6(CO)_{16}]$	$[Pd(CO)_4]^{2+}$	$Ag(CO)_{1-3}$ $[Ag(CO)_{1-3}]^+$
$[Hf(CO)_6]^{2-}$	$[Ta(CO)_6]^-$ $[Ta(CO)_5]^{3-}$	$W(CO)_6$	$[Re_2(CO)_{10}]$	$Os(CO)_5$ $[Os_2(CO)_9]$ $[Os_3(CO)_{12}]$	$[Ir_4(CO)_{12}]$	$[Pt(CO)_4]^{2+}$	$Au(CO)_{1-3}$ $[Au(CO)_2]^+$

$M(CO)_x$ (magenta) = only isolated in Ar matrix

→ metals are electropositive ⇒ neg. charge donated to π-acc. CO ligands

dimer, as there's a free e^- in group 7 $M(CO)_5$



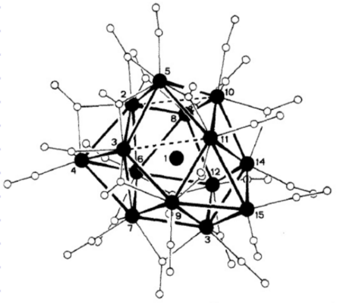
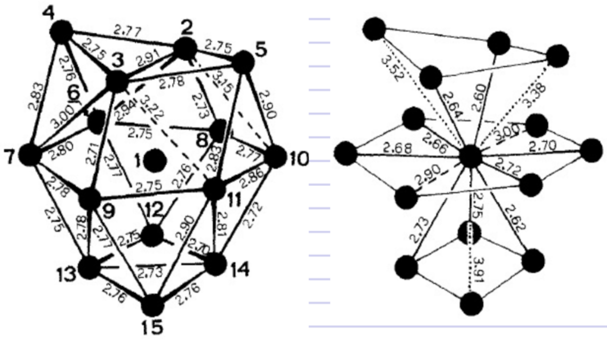


Figure 3. A view of the anion $[Rh_{15}(CO)_{27}]^{3-}$ showing the carbonyls' stereochemistry.



Paolo Chini – 1974

Synthesis

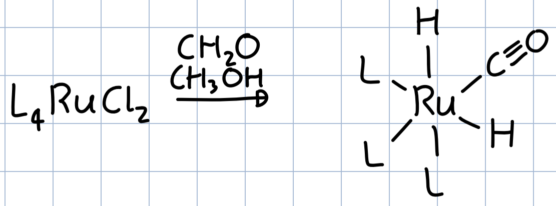
$$\text{Metal} + CO \xrightarrow{\Delta} M(CO)_x$$

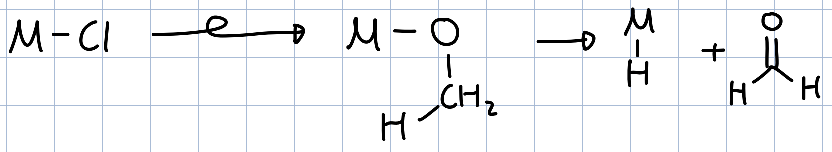
Ni: 1 atm, 80°C
Co: 20-30 bar, 150°C

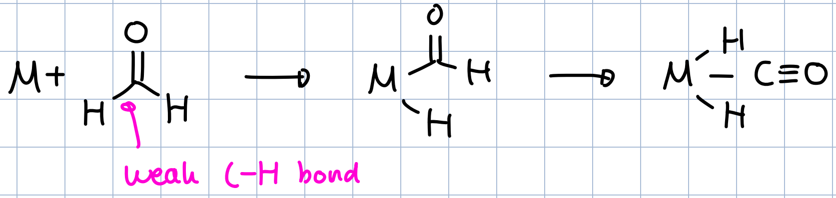
→ kinetics not the same

Reductive carbonylation: $Re_2O_7 + 17\,CO \rightarrow Re_2(CO)_{10} + 7\,CO_2$
$3\,CrCl_2 + 2\,Al + 18\,CO \rightarrow 3\,Cr(CO)_6 + Al_2Cl_6$

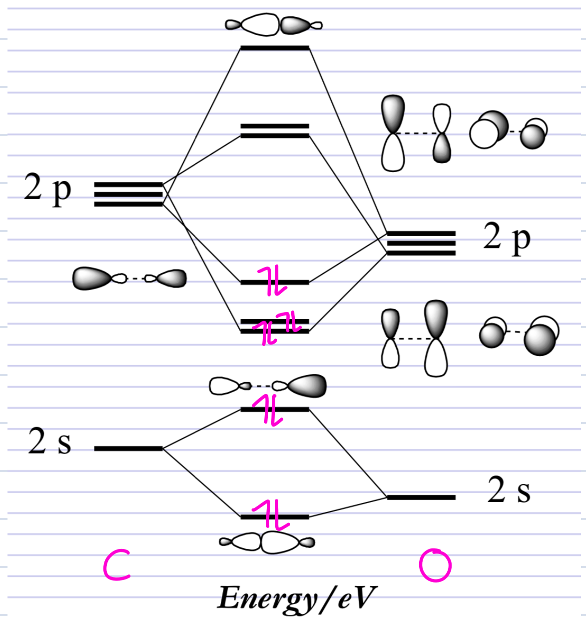
Decarbonylation: (L = PPh_3)







MO-diag. of CO:



$^{\ominus}|C\equiv O^{\oplus}$

↓

barely seen in IR, as no dipole moment, as EN pushes δ-charges other way around

Also CO pretty much insol. in polar solvents!