$\Delta G^{\neq} = 10.5$ kcal/mol (from line shape analysis

IR: ν_{C-H} 2704, 2864 cm^{-1} (~ 2900 - 3000 cm^{-1} for 'free' C-H)

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lecture 7

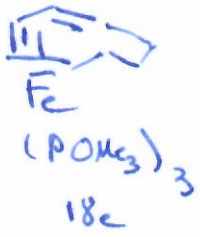
^{1}H-NMR: J_{C-H} : 75-100 Hz

(typical $J_{C(sp^3)-H} \sim 125$ Hz)

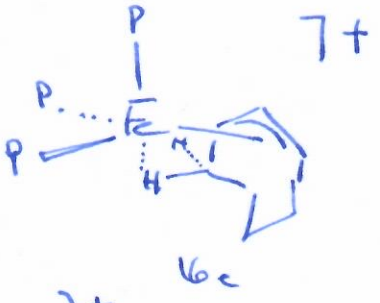
structural data : neutron diffraction

S. Ittel et al

JACS 1980, 102, 981



HBF_4 →



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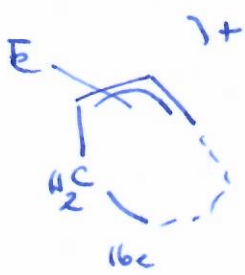
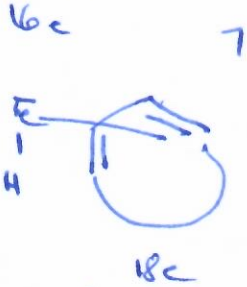
isotopic perturbation of resonance

e.g. J. Shapley JACS 1978, 100, 7726

read! PS#2!





Prod of β-H-elim

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metal carbonyls

homoleptic, only CO ligands

Mond, $Ni(CO)_4$ 1890

read: Ch 4 (5)

bonding 2 interactions

a) σ-donation

HOMO of CO

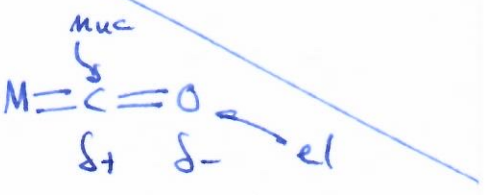
all CO's bind terminal via C

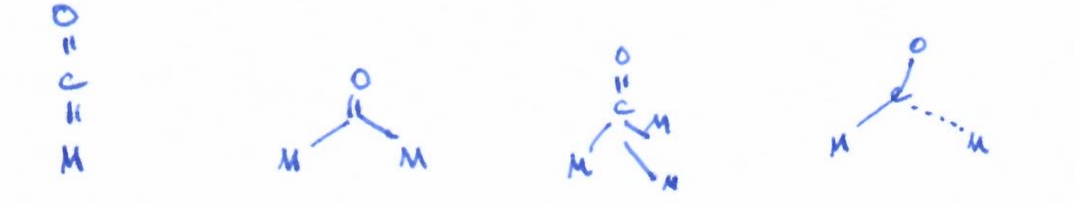
b) π-backbonding

LUMO of CO

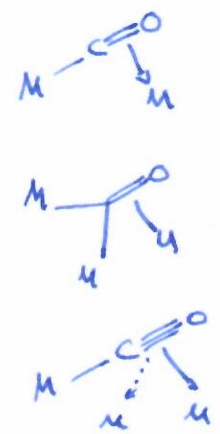
π*, set of 2

c) π-donation





terminal · μ_2-CO · μ_3-CO · semibridging or



$\delta-$

$M - C \equiv O - M'^{+}$

μ-isocarbonyl

IR spectroscopy – ν_{C-O} stretching

	ν_{CO}	
free $|C\equiv O|$	2143 cm^{-1}	only σ-donation
$M=C=O$	2120 – 1830 cm^{-1}	$H_3B \leftarrow CO$ 2164 cm^{-1}
μ_2-CO	1850 – 1750	$[OC-Au-CO]^{+}$ 2211 cm^{-1}
μ_3-CO	1730 – 1620	
$H_2C=O$	~ 1720 cm^{-1}	

↖ all due to π-backbonding

$[Mn(CO)_6]^{+}$ $Cr(CO)_6$ $[V(CO)_6]^{-}$ isoelectronic

2030 cm^{-1} 2000 1860

number of CO stretches depends on <u>symmetry</u>

preparation

$$Ni(s) + 4\,CO \longrightarrow Ni(CO)_4$$
(Fe)

$$CrCl_3 + Al + CO \xrightarrow[140°C,\ 300\ bar]{C_6H_6,\ AlCl_3} Cr(CO)_6$$

Reactivity:

- ligand substitution $Cr(CO)_6 \xrightarrow[\Delta]{CH_3CN} Cr(CO)_3(CH_3CN)_3$ 18e carbonyl D, I_d
- addition of nucleophiles $Cr(CO)_6 + RLi \rightarrow (OC)_5Cr{=}C(R)(O^{\ominus}Li)$ 17e carbonyl A, I_a
- insertions $M(R)(CO) \xrightarrow{L} M(L)(C(O)R)$