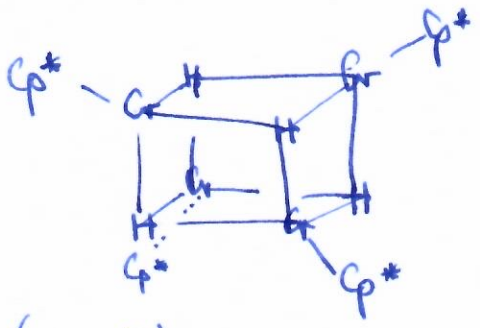


H_2 (30 atm) ⟶ ?

neutron diffraction

$Cp^*_4Cr_4H_7$!?

$(\mu_3\text{-}H)$, Cr^{III} → paramagnet

→ synthesis

$Co_2(CO)_8 \xrightarrow{Na} Na[Co(CO)_4] \xrightarrow{H^+} HCo(CO)_4$ ↑↓

$Mn_2(CO)_{10} \xrightarrow{H_2} 2\ HMn(CO)_5$

$MoCl_5 + 2\ NaCp + NaBH_4 \longrightarrow Cp_2Mo^{IV}H_2$

$Cp^*_2Sm\text{-}R \xrightarrow[-\ R\text{-}H]{H_2} [Cp^*_2Sm\text{-}H]_2$ 'hydrogenolysis' (σ-bond metathesis)

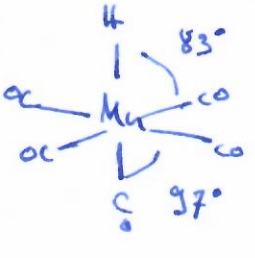
---

properties, spectroscopy

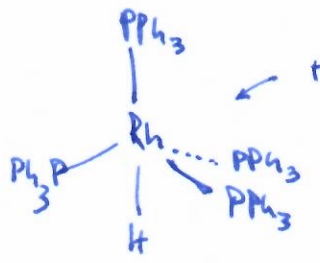
H-H 0.74 Å → r_{cov}: 0.37 Å M-H: 1.5 – 1.7 Å

M-H distances by neutron diffraction: R. Bau Inorg. Chim. Acta 1997, 259, 27

stereochemically active?



vs

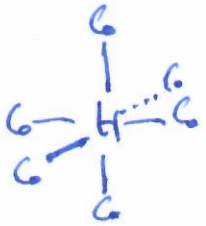


regular tetrahedron

^1H-NMR: δ = 0 → −40 ppm

bal, interstitial hydride

$[HCo_6(CO)_{15}]^-$



$\delta(^1H)$: 23.2 ppm

IR:

$\nu_{M\text{-}H} \sim 1550 - 2200\ cm^{-1}$ (terminal) D-substitution

$\nu_{M\text{-}(\mu H)} \sim 1000 - 1500\ cm^{-1}$ (bridging) $\nu_{M\text{-}D} \approx \frac{1}{\sqrt{2}}\nu_{M\text{-}H}$

$D_{M-H} \geq 60$ kcal/mol

<u>reactivity</u> → hydrides can be <u>acidic</u>

Review: R.H. Morris Chem. Rev 2016, <u>116</u>, 8588

	pK_a (in H_2O)
$HCo(CO)_4$	< 0, 'strong'
$H_2Fe(CO)_4$	4.0
$HMn(CO)_5$	7.1

2) <u>insertion</u>

3) H-atom transfer

(PCET – proton coupled electron transfer)

Sweeney & Halpern
JACS 1977, <u>99</u>, 8335

$M-H + CCl_4 \rightarrow M-Cl + HCCl_3$

test rxn for metal hydrides

4) hydride transfer (H^-)

$L_nM-H \rightleftharpoons L_nM^+ + H^- \quad \Delta G^\circ_{H^-} = ?$

hydricity

	$\Delta G^\circ_{H^-}$	in CH_3CN
$CpFe(CO)_2H$	61.7	weakest
$Co(dppe)_2H$	49.9	
$[W(CO)_5H]^-$	40.0	
$Rh(dmpe)_2H$	26.6	strongest

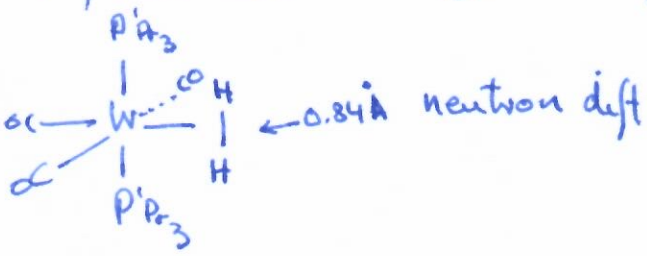
rev. A.M. Appel et al. Chem Rev 2016, <u>116</u>, 8655

$L_nM-H + CO_2 \rightarrow HCO_2^- + L_nM^+$

'formate'

'dihydrogen complexes'

1984, G. Kubas JACS 1984, 106, 451



← 0.84 Å neutron diff

a σ-complex