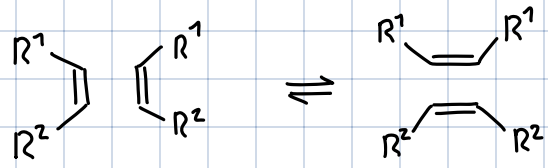
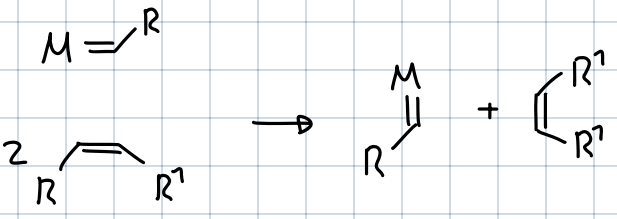
06.12.

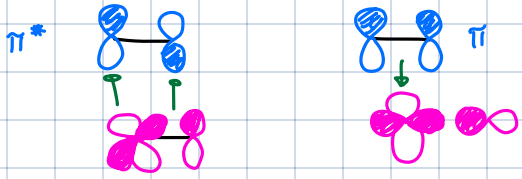
Olefin Metathesis

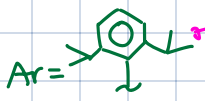


By

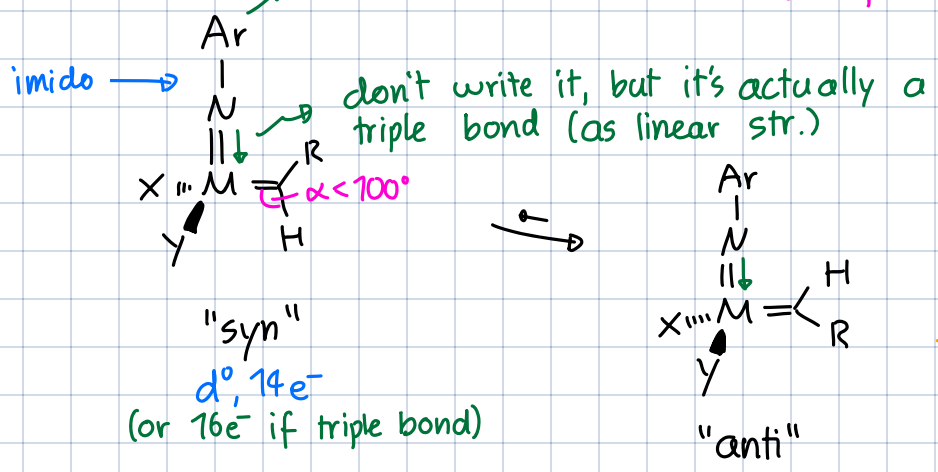


Orbital int.:





pointing away from metal center
⇒ for M looks like small ligand, but from outside looks large



don't write it, but it's actually a triple bond (as linear str.)

M = W, Mo

X, Y = mono-anionic ligand

↳ Schrock alkylidene, high ox. state d° catalyst

↳ Observe $200 < \delta_C < 350$ ppm

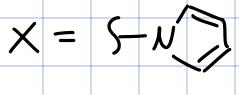
$^1J_{C-H}$ (syn) < 120 Hz → result of CH bond stretch

$^1J_{C-H}$ (anti) ≈ 140 Hz

Reactivity for X=Y=OR in olefin metathesis:

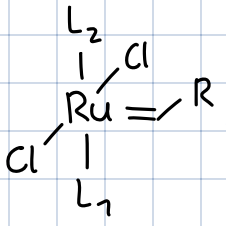
R = $^tBu_{F_0}$ < $^tBu_{F_3}$ < $^tBu_{F_6}$ < $^tBu_{F_9}$

But best cats are with X ≠ Y:

X =  , Y = O-Ar

Grubbs or Grubbs-Hoveyda cat.

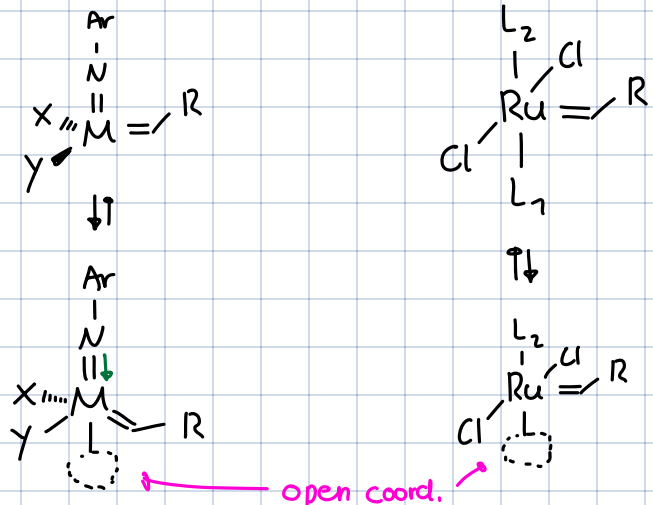
$L_1 = PCy_3$
$L_2 = PCy_3$ in G-I
$= NHC$ in G-II → diff cats



→ Ru^{II} or Ru^{IV} ? → Formalism, can discuss!
But behaves a lot like Ru^{II} ⇒ $\not\subset^{R}$ "L-type"

↓

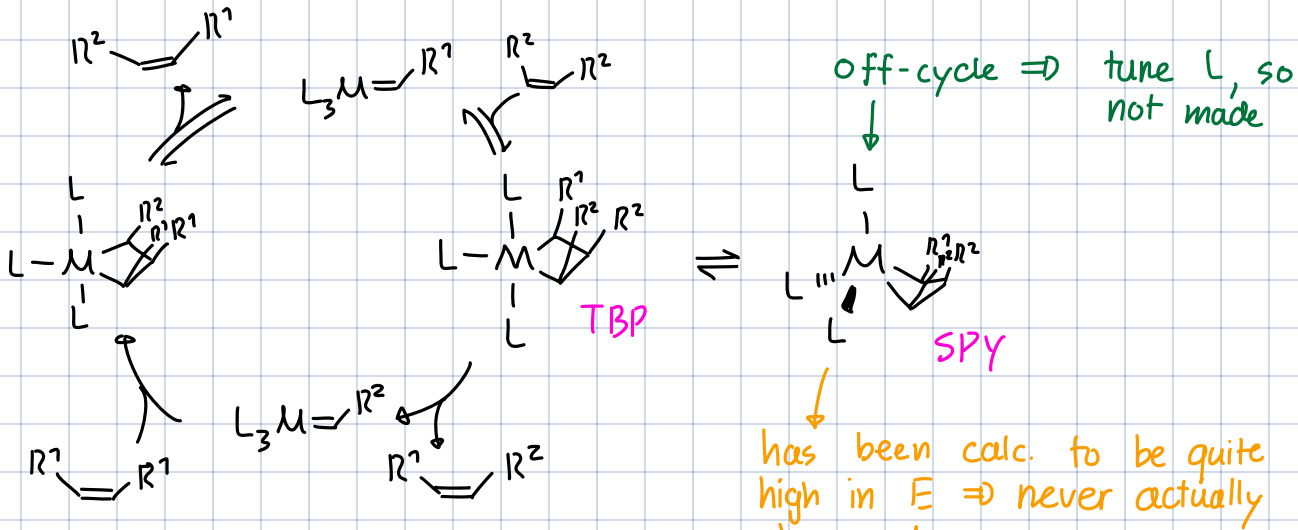
To get active sites:



d^0
12e⁻ (imido = X_2)
14e⁻ (imido = LX_2)

d^6
14e⁻

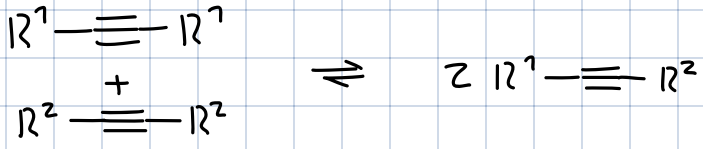
Mechanism:



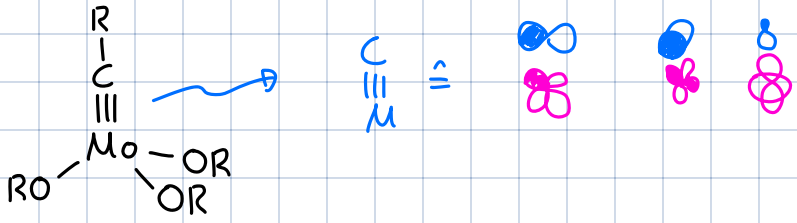
off-cycle ⇒ tune L, so not made

has been calc. to be quite high in E ⇒ never actually observed

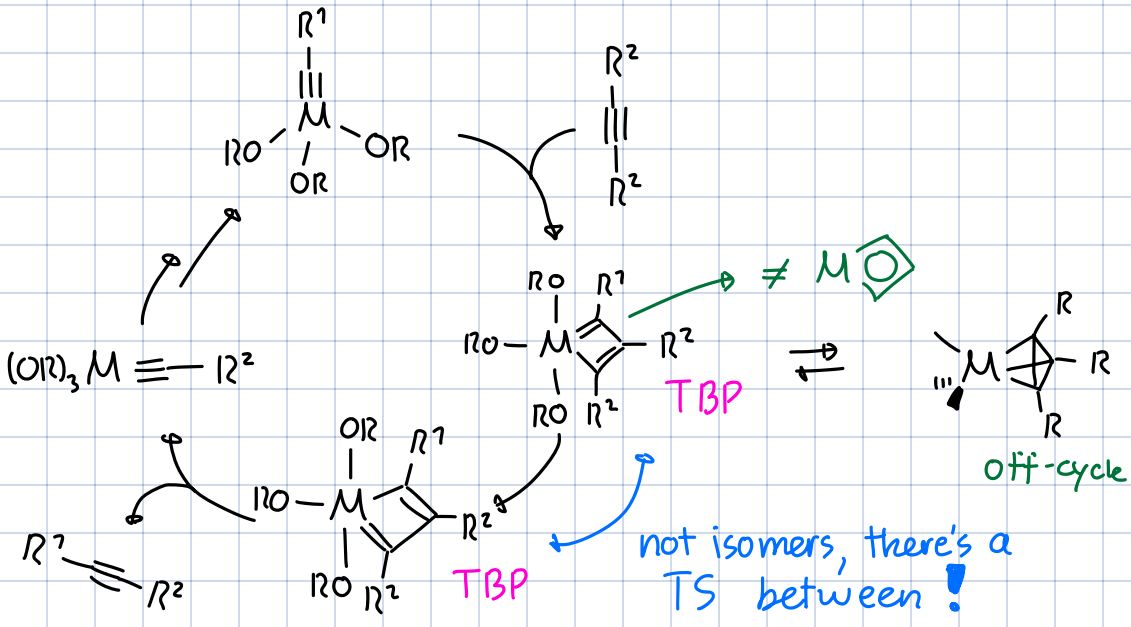
Can we do the same with alkynes?

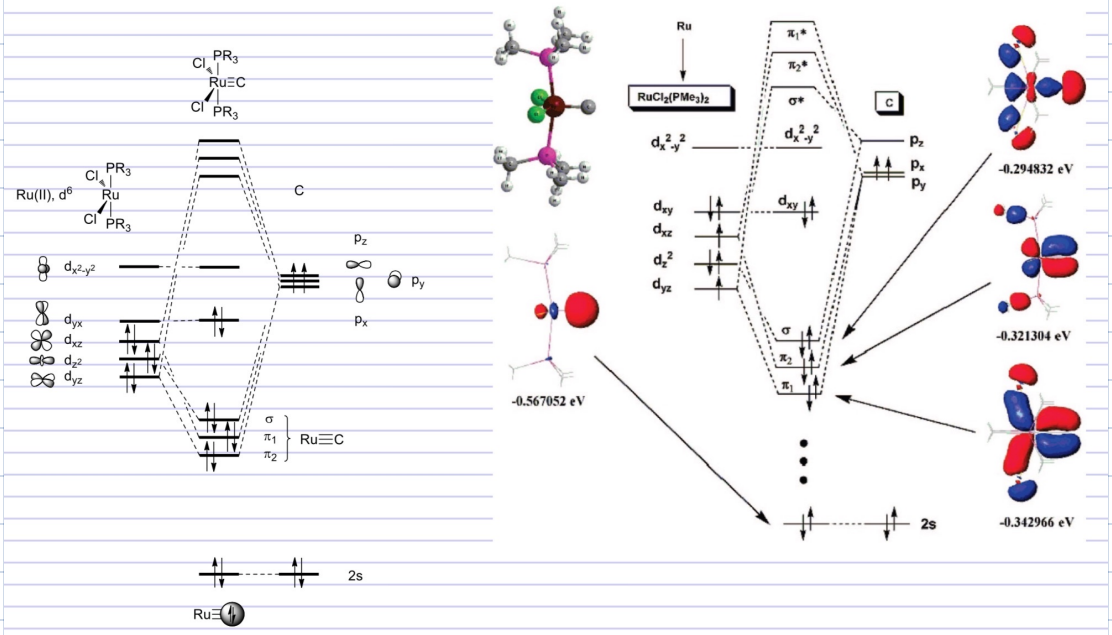


↳ No Ru cat, but a lot of Mo can do it:

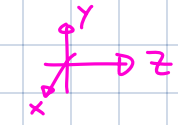


same mech.:

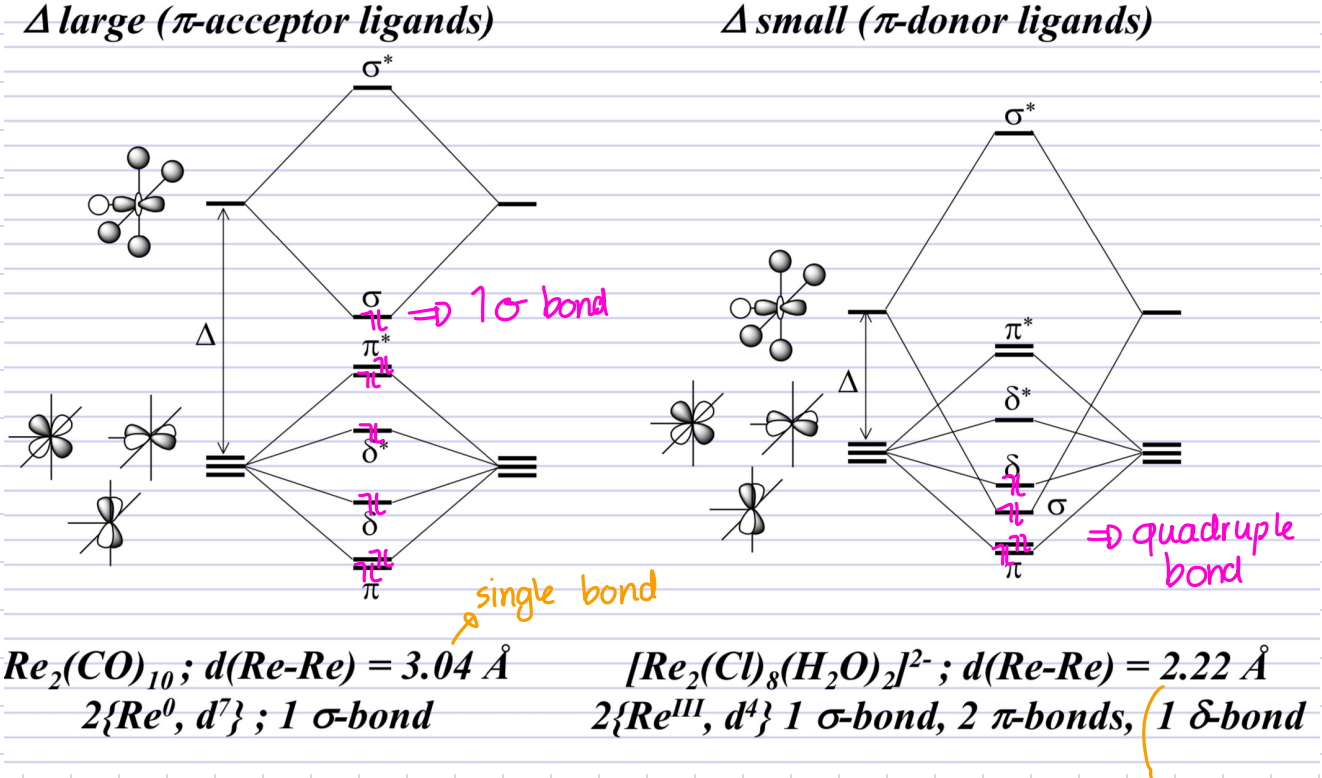




Metal carbon multiple bonds



M – Me	M–M		σ
M = CH_2	M = M		π_1
M ≡ CH	M ≡ M		π_2
M ≣ C	M ≣ M		δ



$Re_2(CO)_{10}$; d(Re-Re) = 3.04 Å
$2\{Re^0, d^7\}$; 1 σ-bond

$[Re_2(Cl)_8(H_2O)_2]^{2-}$; d(Re-Re) = 2.22 Å
$2\{Re^{III}, d^4\}$ 1 σ-bond, 2 π-bonds, 1 δ-bond

very short (4- bond)

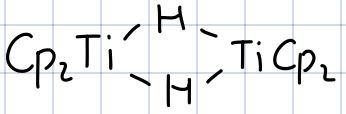
Metal Hydrides → Hydrogenation key interm.

$(CO)_4 Co H$

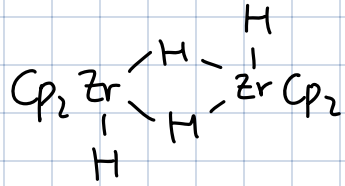
$Cp^*_2 M H$

$Cp^*_2 M H_2$

$Cp^*_2 M H_3$

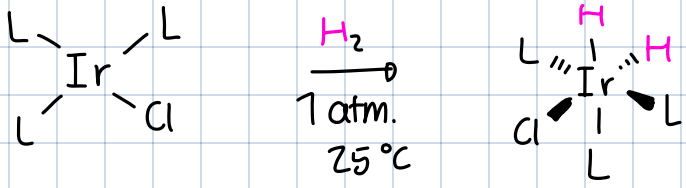


bridging H



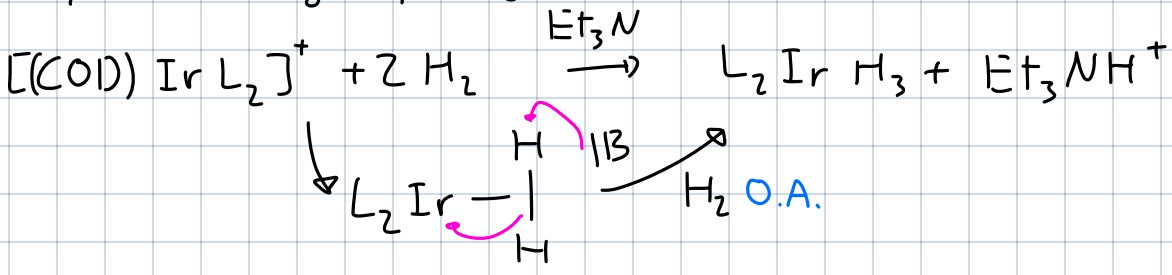
Synthesis

1. Oxidative Addition

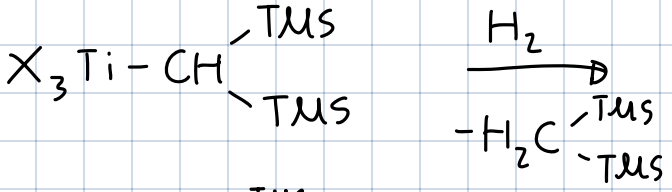


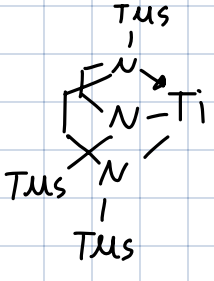
$L = PPh_3$

2. Heterolytic cleavage of H_2



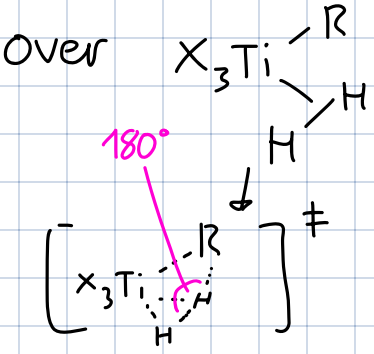
3. σ-Bond metathesis





TMS = $SiMe_3$

Over



4. Homolytic addition

$$Co_2(CO)_8 + H_2 \xrightarrow{\Delta} 2\ Co(CO)_4 + H_2 \rightarrow H\,Co(CO)_4$$

5. Protonation

$$Mn(CO)_5^- \overset{H^+}{\rightleftharpoons} H\text{-}Mn(CO)_5$$

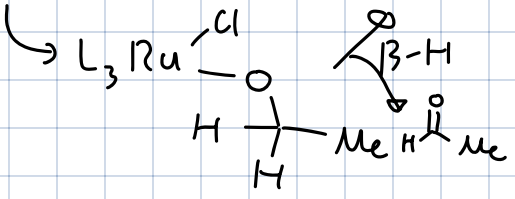
$$L_2Ni \overset{H^+}{\rightleftharpoons} L_2Ni^{II}\text{-}H^{+} \qquad L = P(OEt)_3$$

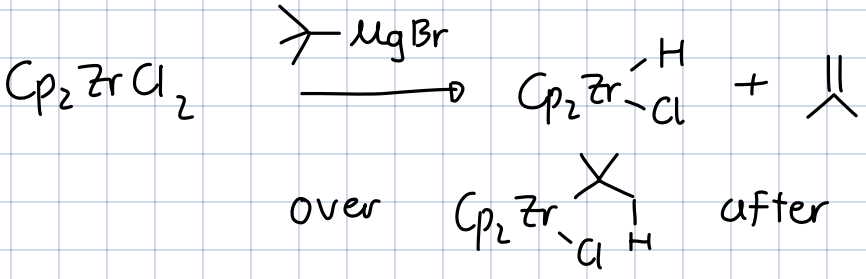
6. Reduction

$$W^{VI}Cl_6 + NaBH_4 + 2\ Cp\text{-}H \rightarrow Cp_2W^{IV}H_2$$

7. β-H elim.

$L_3RuCl_2 \xrightarrow{EtOH} L_3Ru(H)(Cl)$ $\quad L = PPh_3$





Reactivity

π-acc. like CO can stabilize ⇒ acidic

$L_nM\text{-}H \rightarrow L_nM^- + H^+$ Acidity, pK_a

$L_nM\text{-}H \rightarrow L_nM^{\cdot} + H^{\cdot}$ BDE $\quad 3d < 4d < 5d$

$L_nM\text{-}H \rightarrow L_nM^+ + H^-$ Hydricity

Hydricity vs. acidity is mainly ligand driven

linear relation

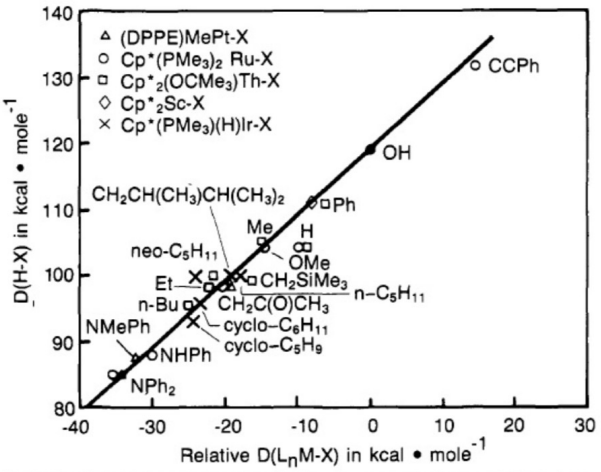


Figure 7. Cumulative plot of H–X vs. relative L_nM–X bond strengths discussed in this manuscript. Data for (DPPE)MePt–X (△), $Cp^*(PMe_3)_2Ru$–X (○), Cp^*_2Sc–X (◇), $Cp^*_2(OCMe_3)Th$–X (□), and $Cp^*(PMe_3)(H)Ir$–X (×) depicted for X = singly bonded first row main group substituents along with the arbitrary line (slope = 1.00; intercept = 119.0 kcal·mol^{-1}) described in Figure 5. Scale definitions for (DPPE)MePtX, $Cp^*(PMe_3)_2RuX$, and $Cp^*_2(OCMe_3)ThX$ data as described in Figures 5 and 6. To put the Sc–X data on these axes the Sc–C bond in Cp^*_2Sc–Ph has been defined as –8.1 kcal·mol^{-1}; similarly, the Ir–C bond in $Cp^*(PMe_3)(H)Ir$-*cyclo*-C_6H_{11} has been assigned an arbitrary value of –21 kcal·mol^{-1}. Good 1:1 correlation of H–X and L_nM–X bond strengths is noted.

Brnydza et al. J. Am. Chem. Soc. 1987, 109, 1444-1456.

Spectroscopy

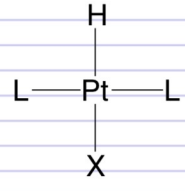
IR: $1600 < \nu(M-H) < 2200\ cm^{-1}$

↳ low μ_{M-H} ≙ low intensity

^{1}H-NMR: very broad range for chem. shift

$30 < \delta_{M-H} < -30$ ppm

↳ Driven by spin orbit coupling (not discussed)



L = $P(CH_2C_6H_5)_3$

X	δ(H)	^{1}J(P,H)/Hz
ClO_4	–26.5	1518
NO_3	–24.4	1330
Cl	–17.9	1290
NCO	–18.1	1050
SH	–11.0	992
CN	–8.7	776

↳ trans effect ⇒ modulate bond length and thus orb. int. & SO coupling

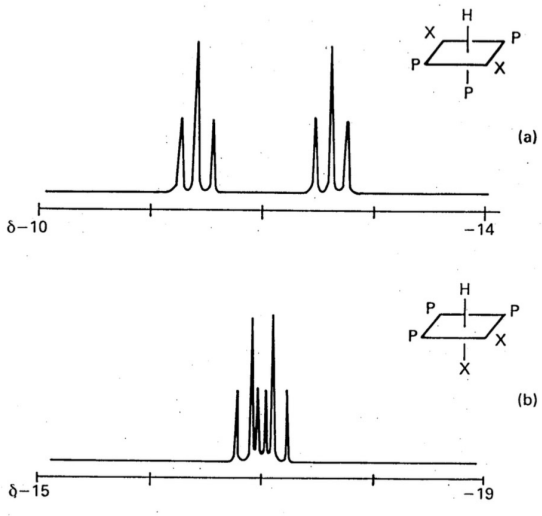


Fig. 2.10 — The hydride regions of the ^1H spectra of two metal hydrides showing coupling to two equivalent and one unique ^{31}P nucleus. The parameters used are typical of the geometries shown: (a) δ−12, ^2J(H–P)=14, 14, and 120 Hz; (b) δ−17, ^1J(H–P)=13, 13, and 19 Hz. Note that in spectrum (b) the two triplets overlap (simulations).

$\rightsquigarrow$ $J_{H-P,trans} < J_{H-P,cis}$!

New type of bond: σ-complex where H_2 binds to M: $M-\overset{H}{\underset{H}{|}}$ but H-H bond remains intact

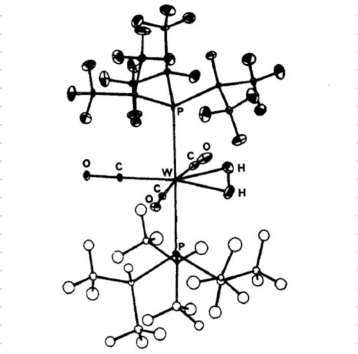


Figure 1. Structure of $W(CO)_3(PPr^i_3)_2(H_2)$ (neutron, 30 K). (Disorder is present in C–H positions of lower phosphine.)

Kubas et al. J. Am. Chem. Soc. 1984, *106*, 451-452.
G. J. Kubas *Acc. Chem. Res.* 1988, *21*, 120-128.
R.E. Crabtree *Acc. Chem. Res.* 1990, *23*, 95-101.

How does H_2 interact with the ML_5 fragment?