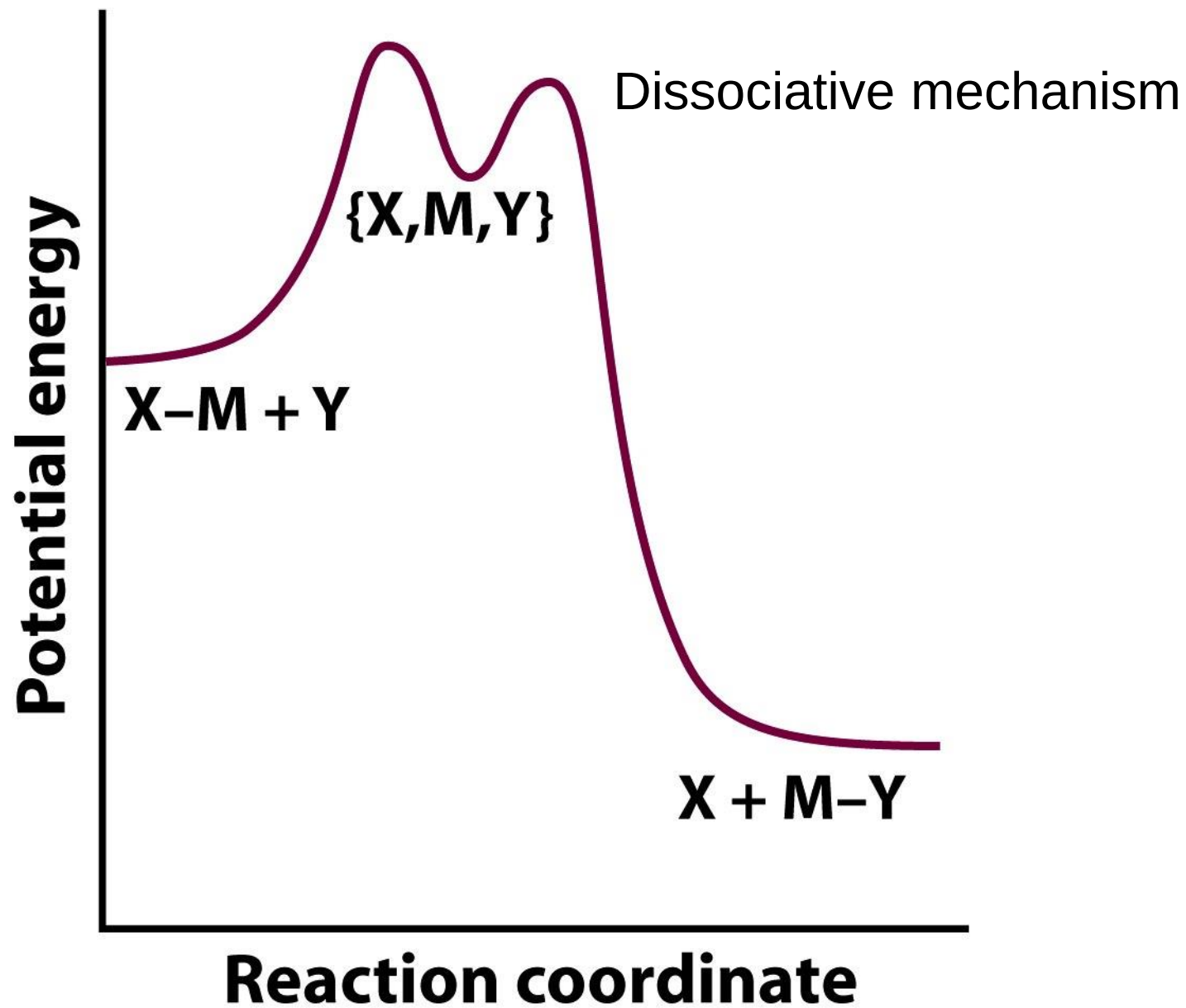
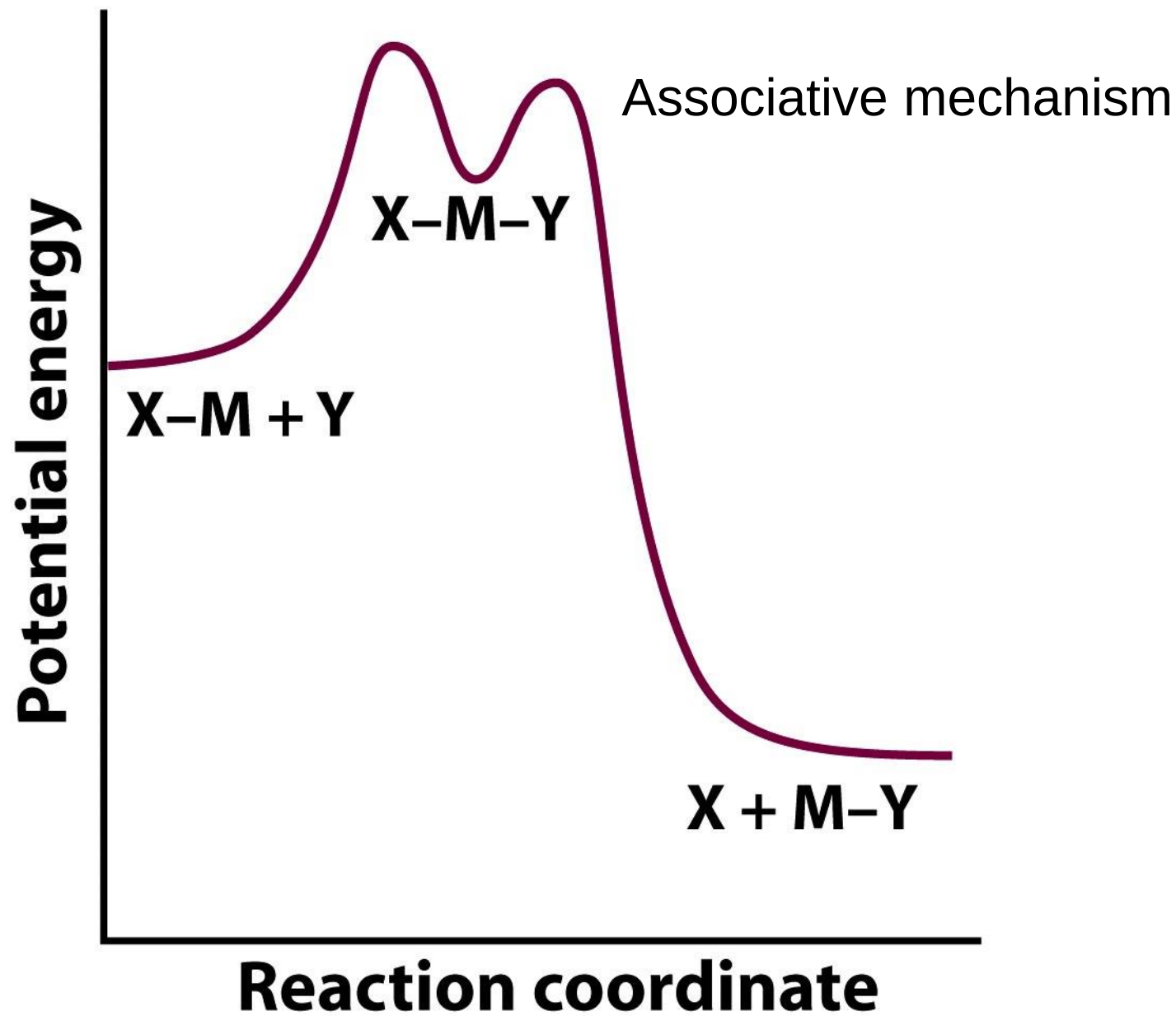
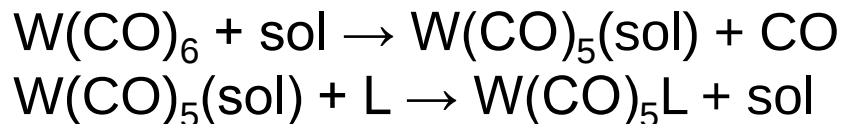
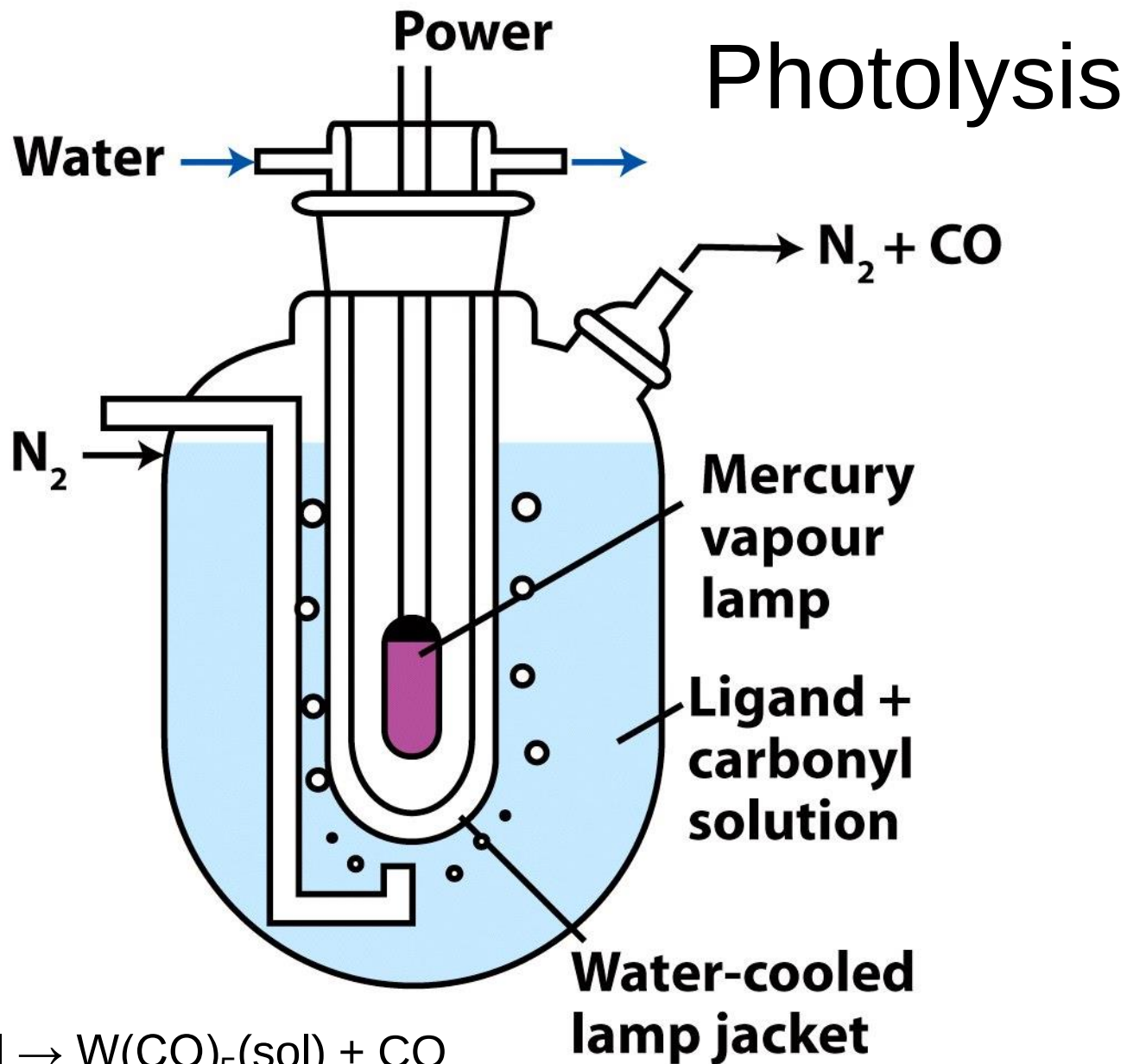
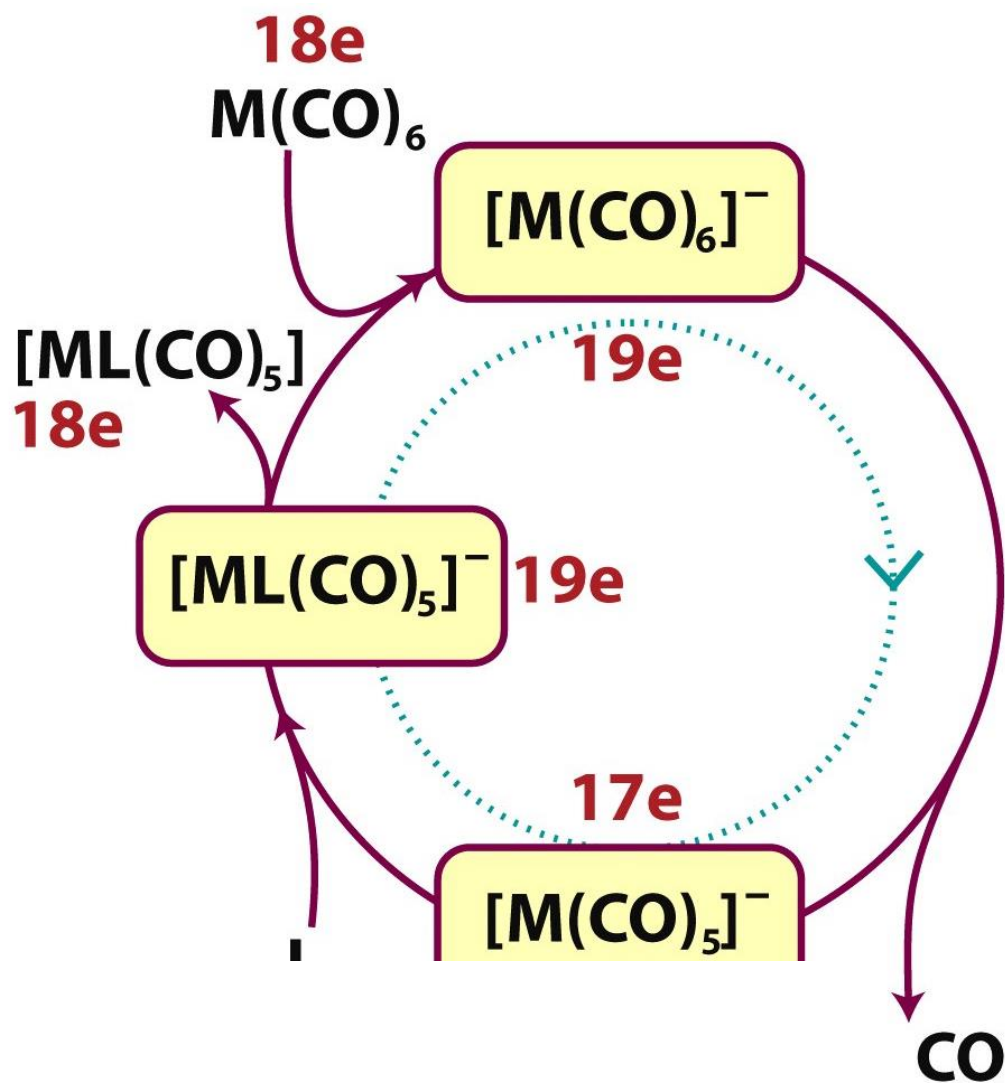








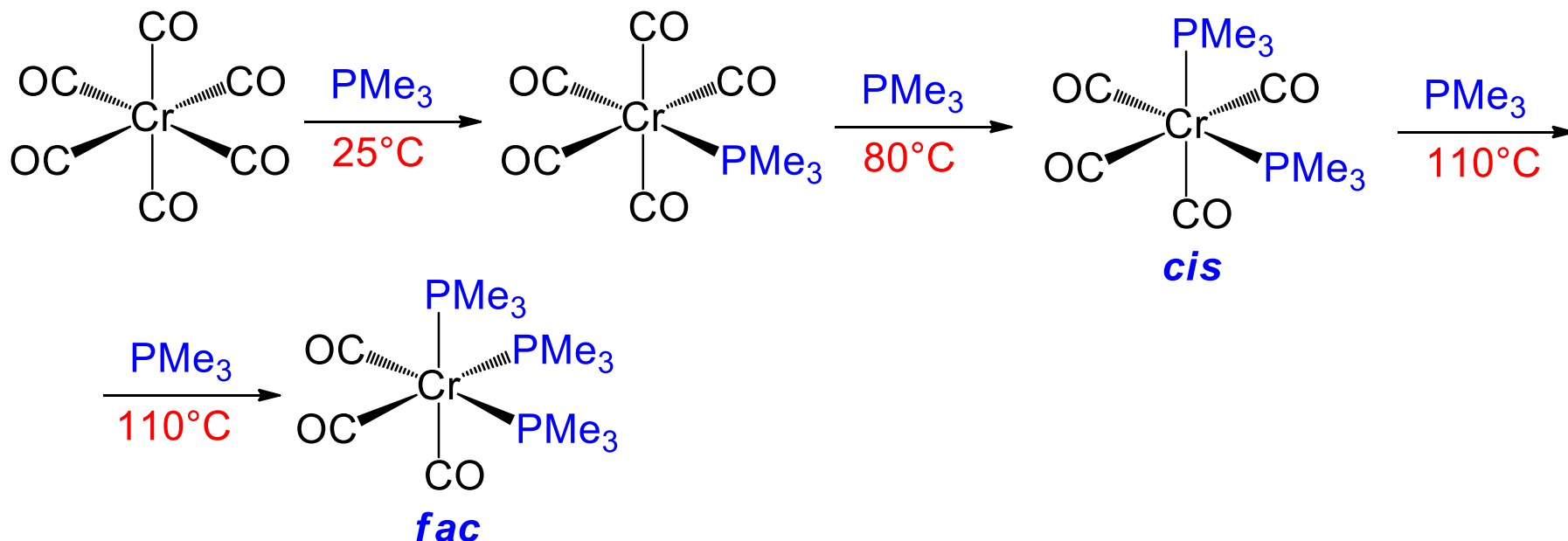
Substitution promoted by a redox process
addition of a catalytic amount of a mono-reducing agent



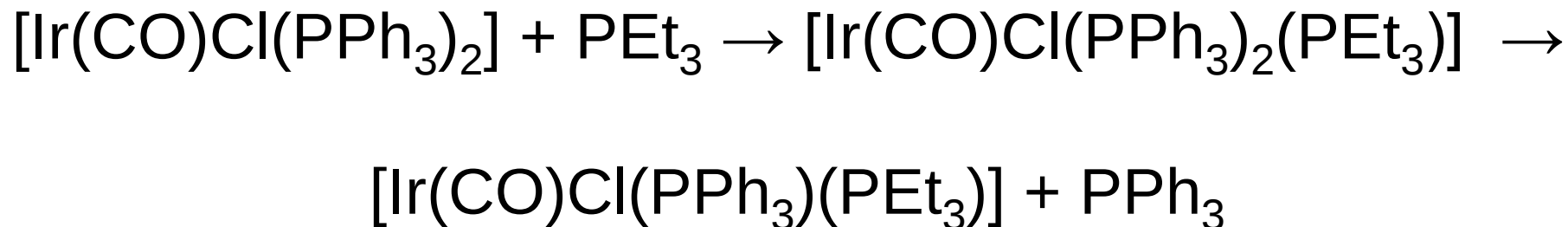
Effect of the Lewis basicity of the ligand

The presence of **more basic** ligands coordinated to the metal center **reduces the rate** of CO substitution.

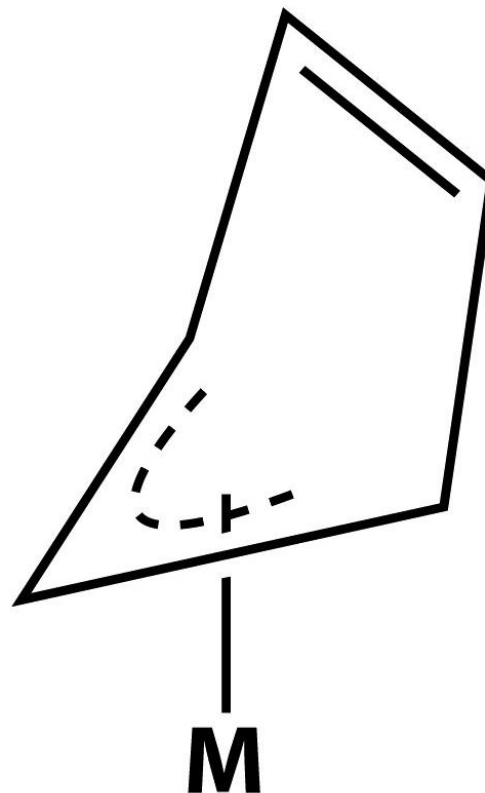
The introduction of 2 or 3 phosphines represent the limit of the substitution.



16e⁻: associative mechanism



Substitutions for 18 electron compounds with associative mechanism

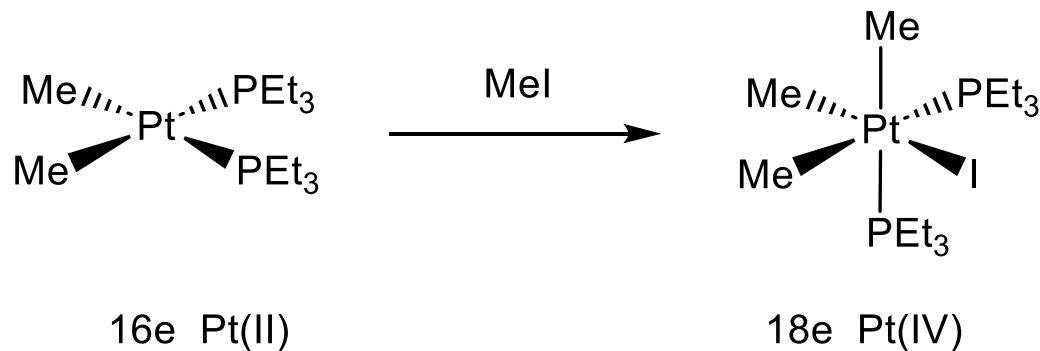


Steric considerations

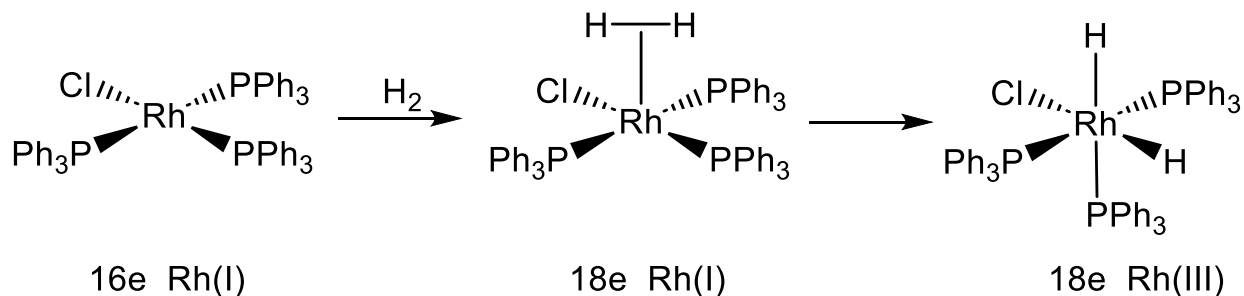
The bulk of other ligands on the metal affects the rate of the substitution reaction:

- Large ligands **INCREASE** the rate of **dissociative** processes
- Large ligands **DECREASE** the rate of **associative** processes

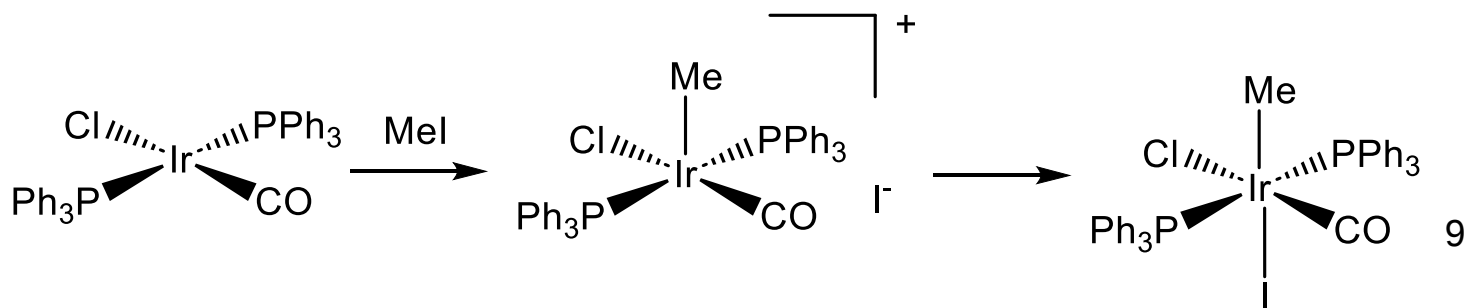
Oxidative Addition



Concerted mechanism

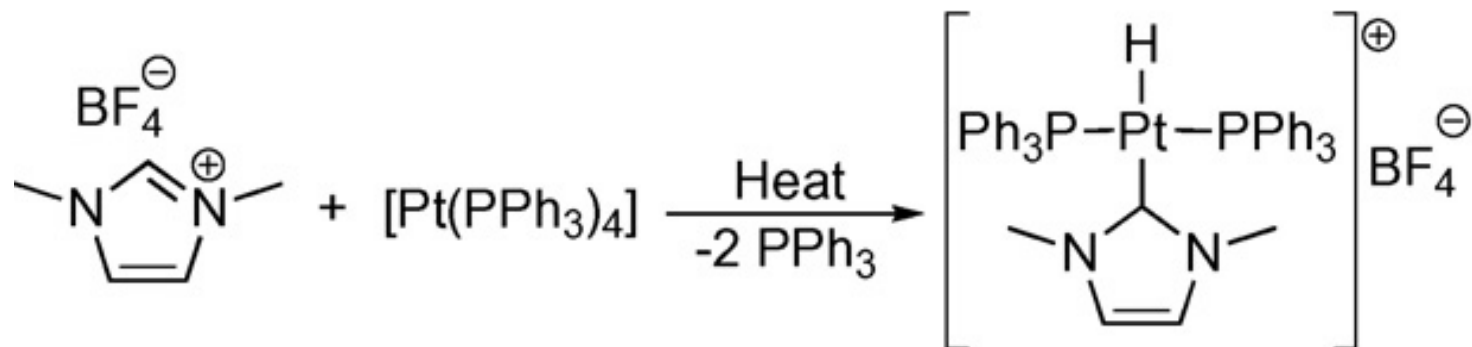


S_N2 mechanism

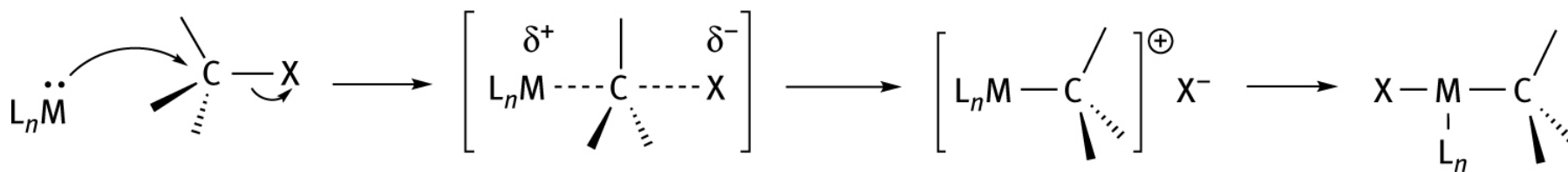


Irregular oxidative addition

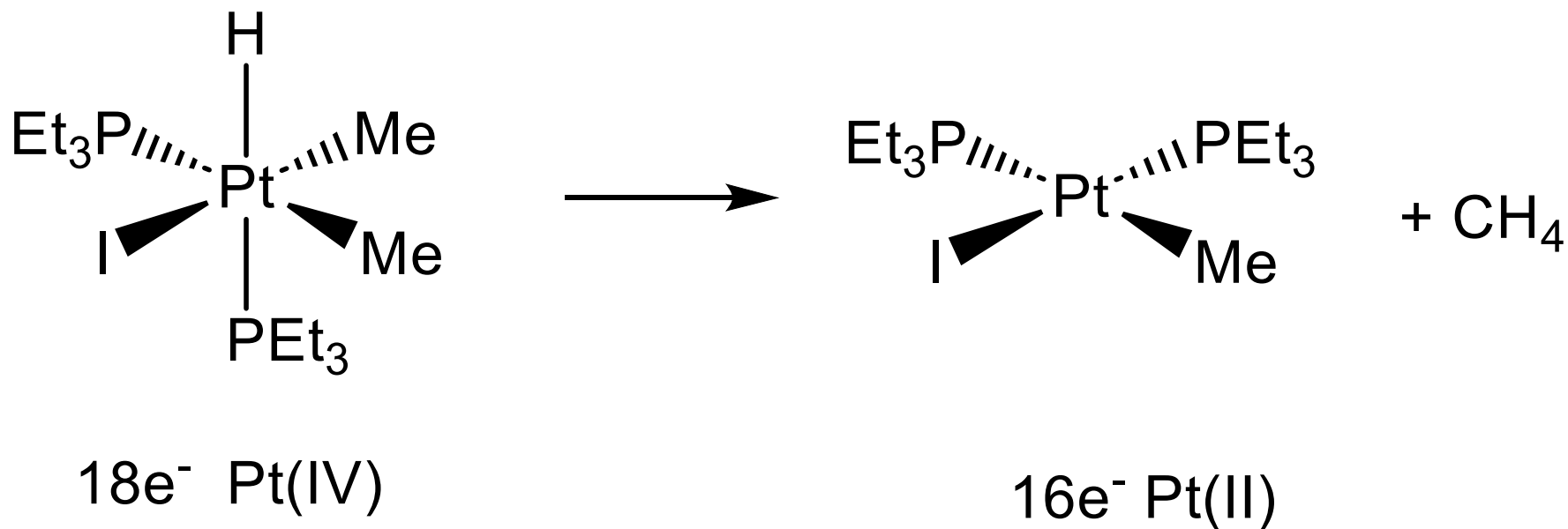
Oxidative addition of imidazolium salts from zero-valent precursors



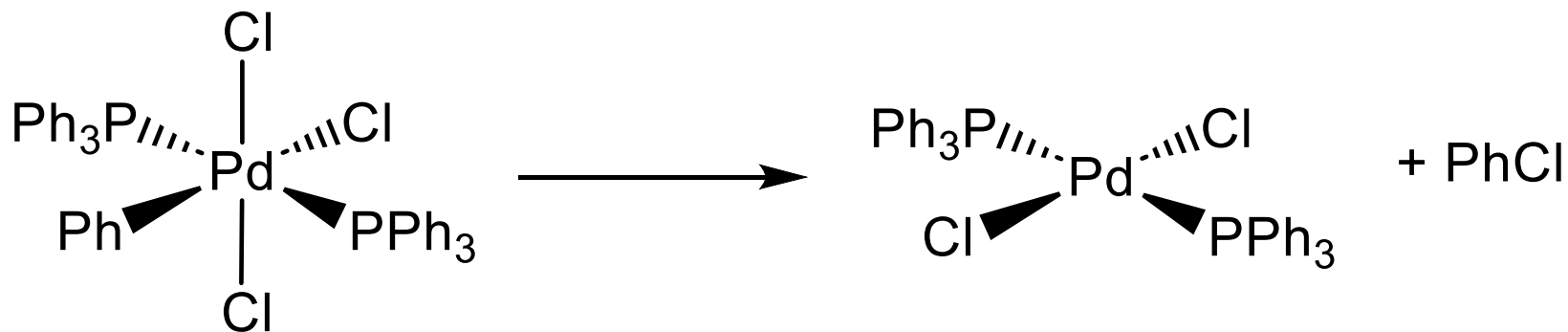
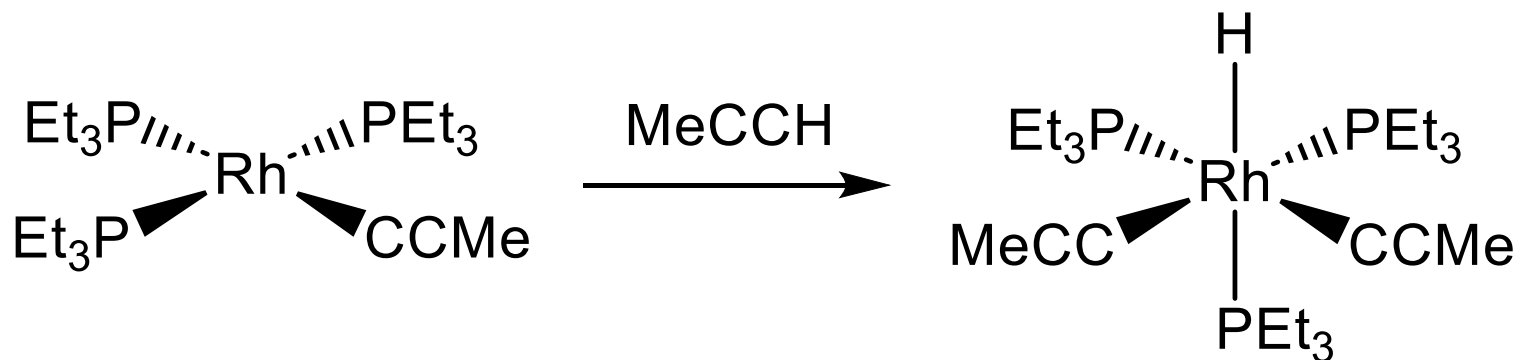
Polar solvents favour polar transition states, therefore a **$S_{\text{N}}2$** mechanism.



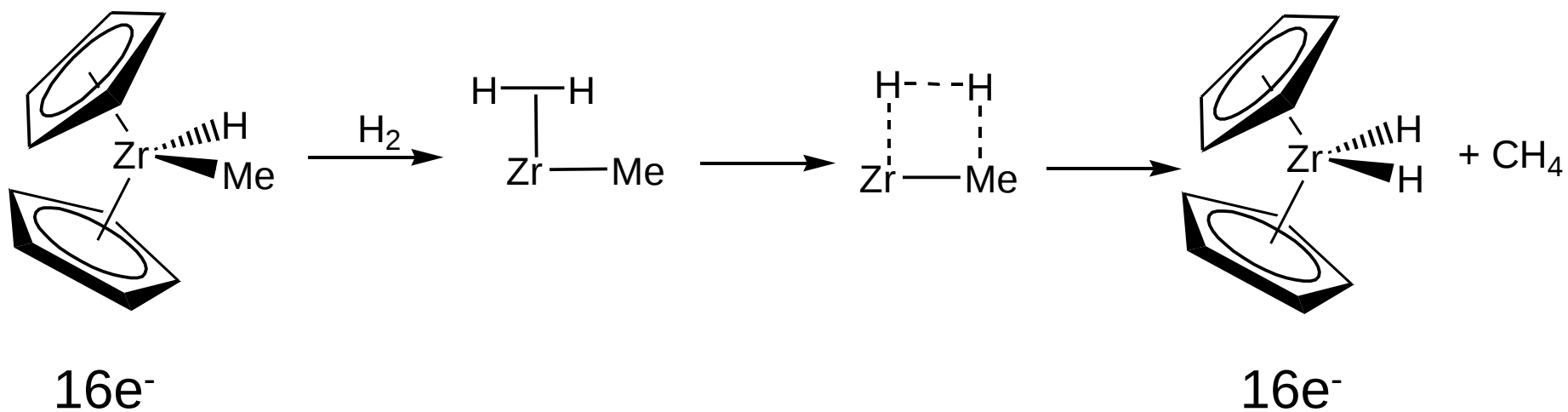
Reductive Elimination



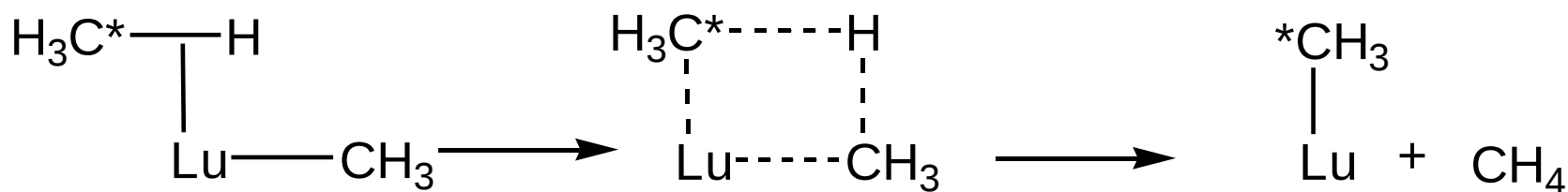
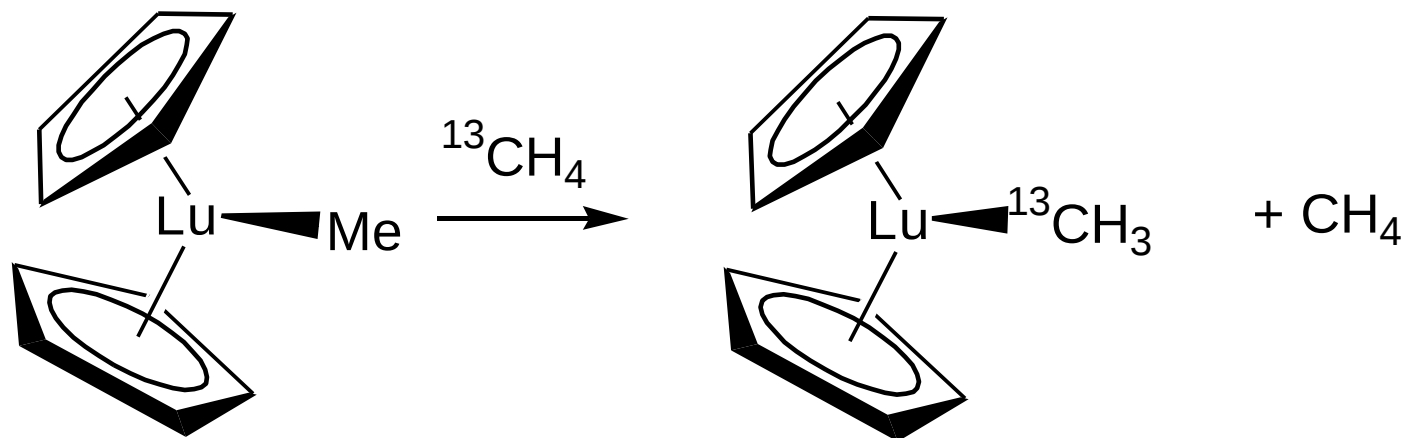
Examples



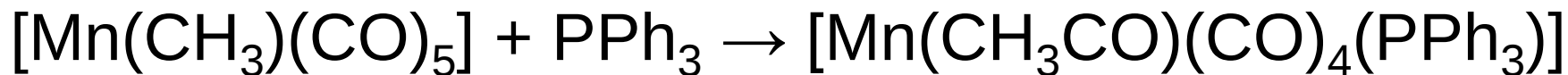
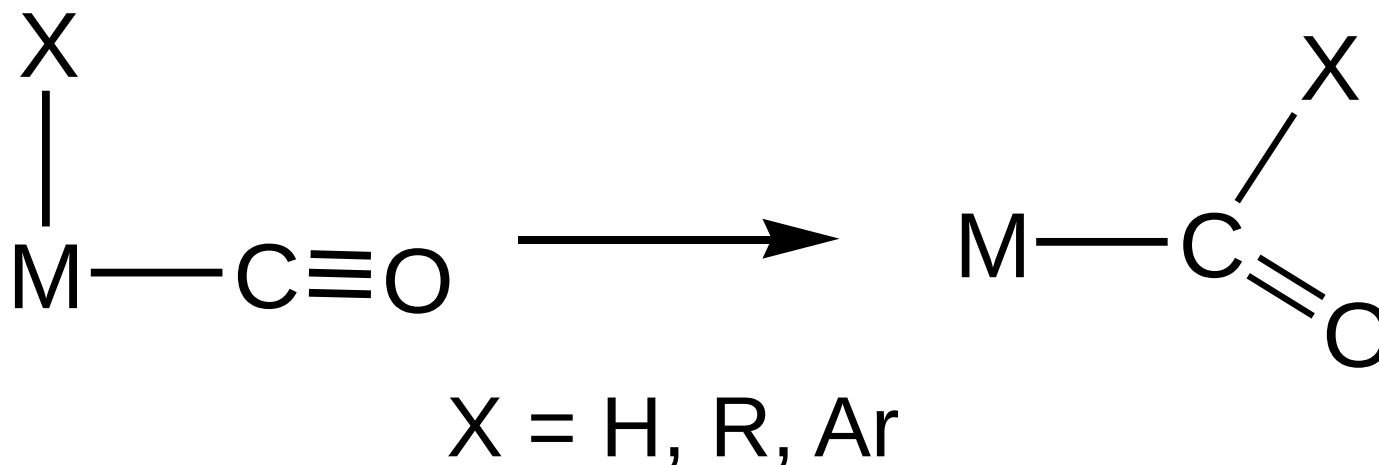
σ -bond metathesis



σ -bond metathesis

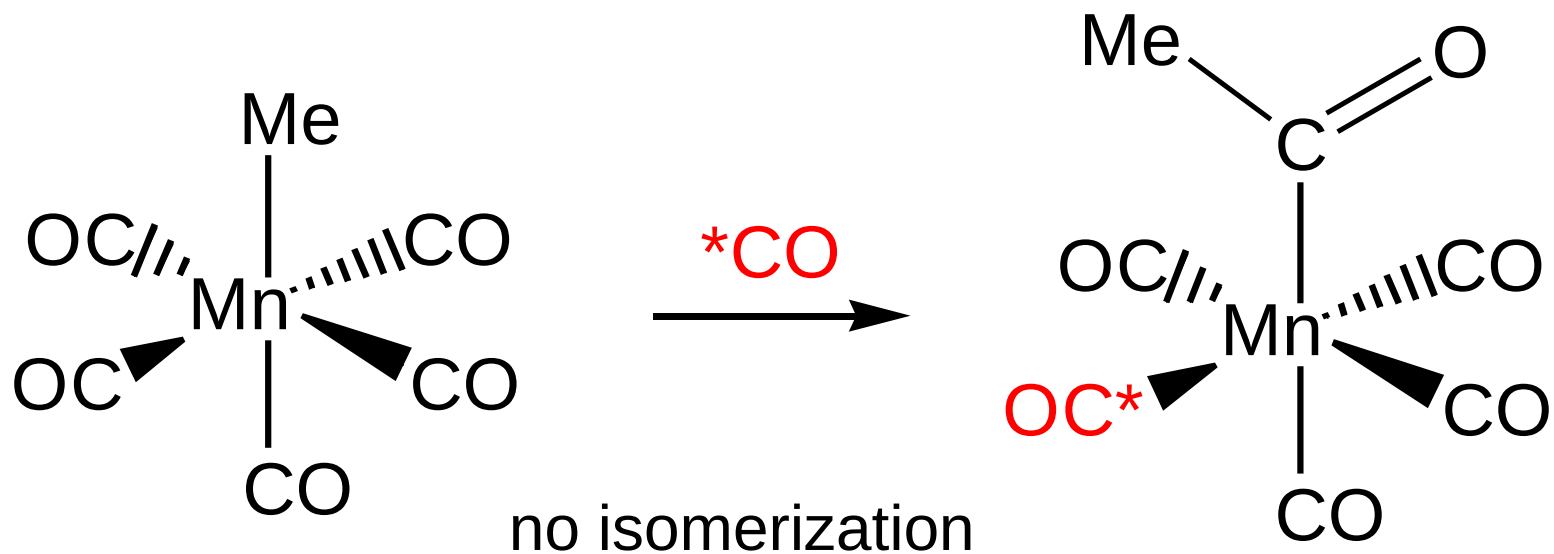


1,1 Migratory Insertion



Migration of X on C or insertion of CO in the M–X bond?

Mechanism of the 1,1 Migratory Insertion



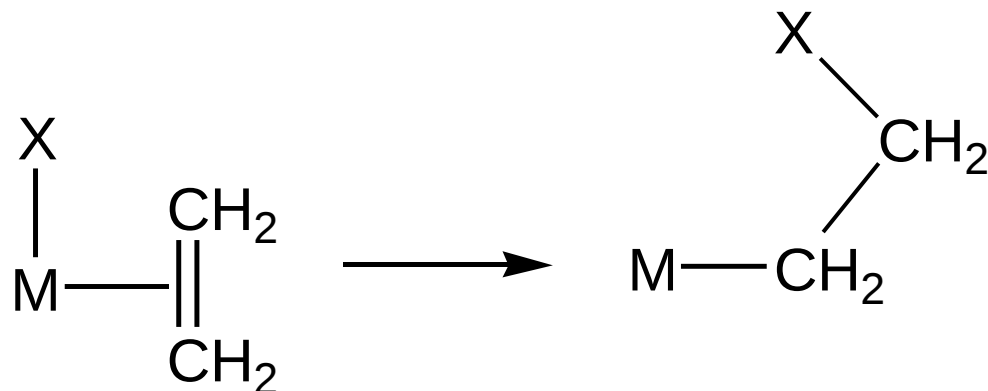
Decarbonylation of $[\text{Mn}(*\text{COCH}_3)(\text{CO})_5]$: only *cis*- $[\text{MnCH}_3(*\text{CO})(\text{CO})_4]$
 Principle of microscopic reversibility!

Study of the decarbonylation of cis- $[\text{Mn}(\text{CH}_3\text{CO})(\text{CO})_4(*\text{CO})]$ to demonstrate the mechanism:

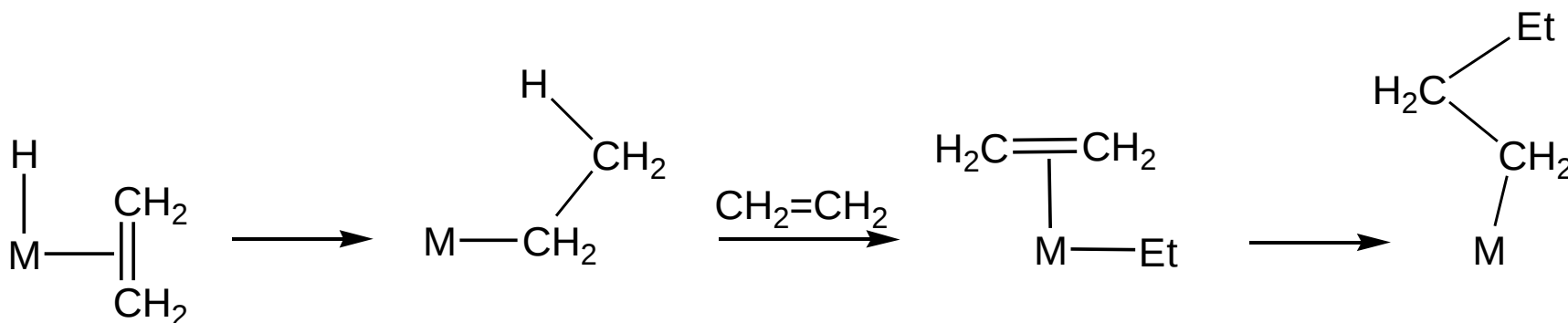
trans- $[\text{Mn}(\text{CH}_3)(\text{CO})_4(*\text{CO})]$ and *cis*- $[\text{Mn}(\text{CH}_3)(\text{CO})_4(*\text{CO})]$ in 1/2 ratio:

METHYL MIGRATION!

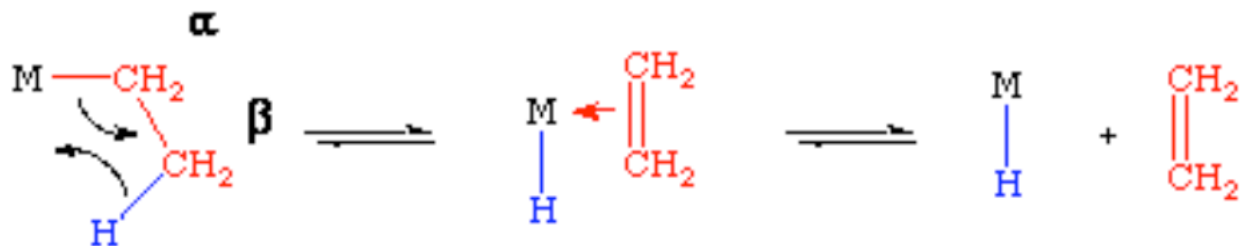
1,2 Insertion *with η^2 ligands*



$X = \text{H, R, Ar}$

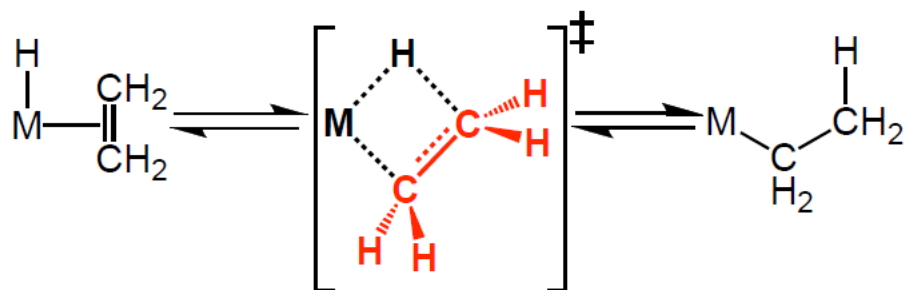


Polyethylene and Polypropylene formation



Beta-hydride Elimination

Mechanism $\longrightarrow$ Four-center transition state inferred

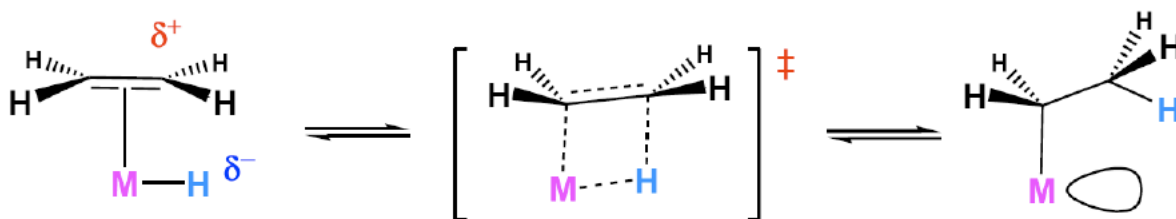


Olefin-insertion – microscopic reverse reaction

critical step in olefin polymerization

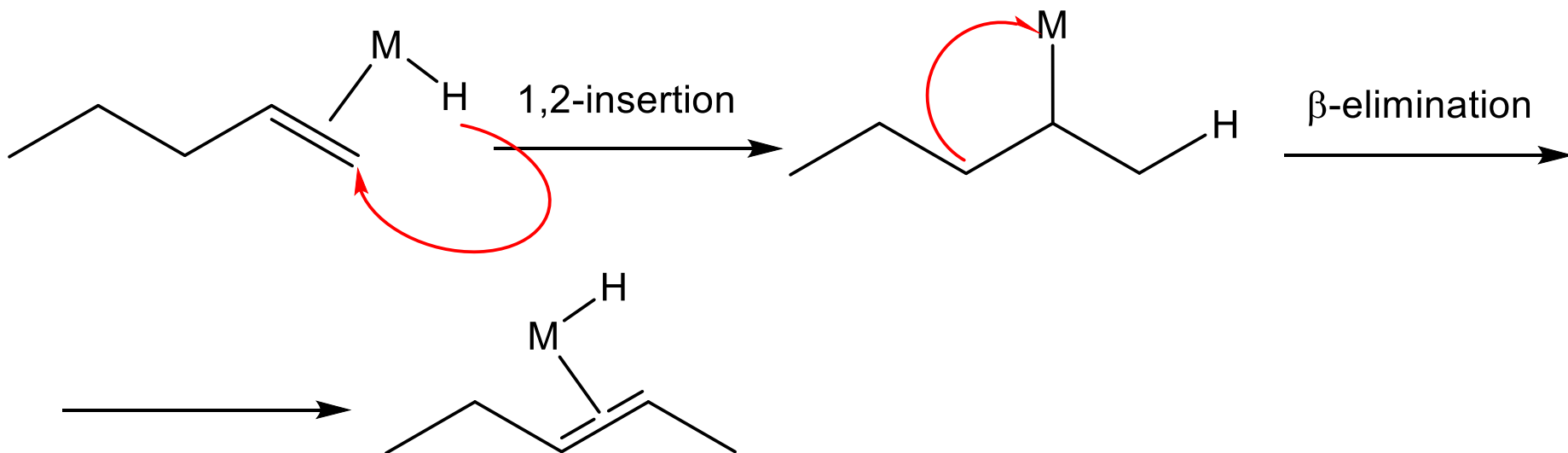
β -hydride elimination is a termination step in olefin polymerization

migratory insertion $\longrightarrow$



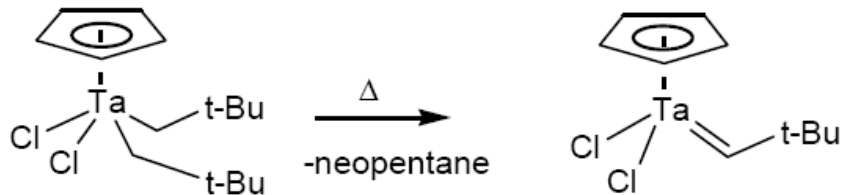
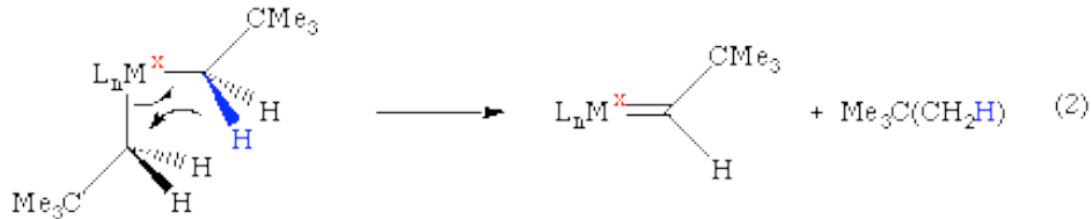
$\longleftarrow$ *β -hydride elimination*

Isomerization of alkenes



α -elimination reaction

Typical for early transition metals. There must be an alkyl group with an H on the C_α (with respect to the metal), normally there are no H on C_β . Usually there are two *cis* alkyl groups.



δ - and γ -eliminations are also frequent $\rightarrow$ formation of metallacycles «cyclometallations»



Described as Oxidative Addition of a remote -CH group

Fluxional Behaviour

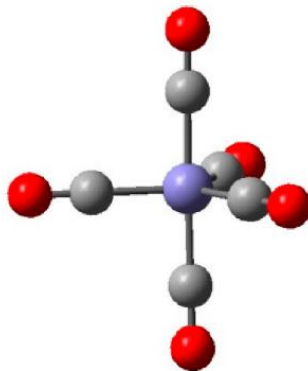
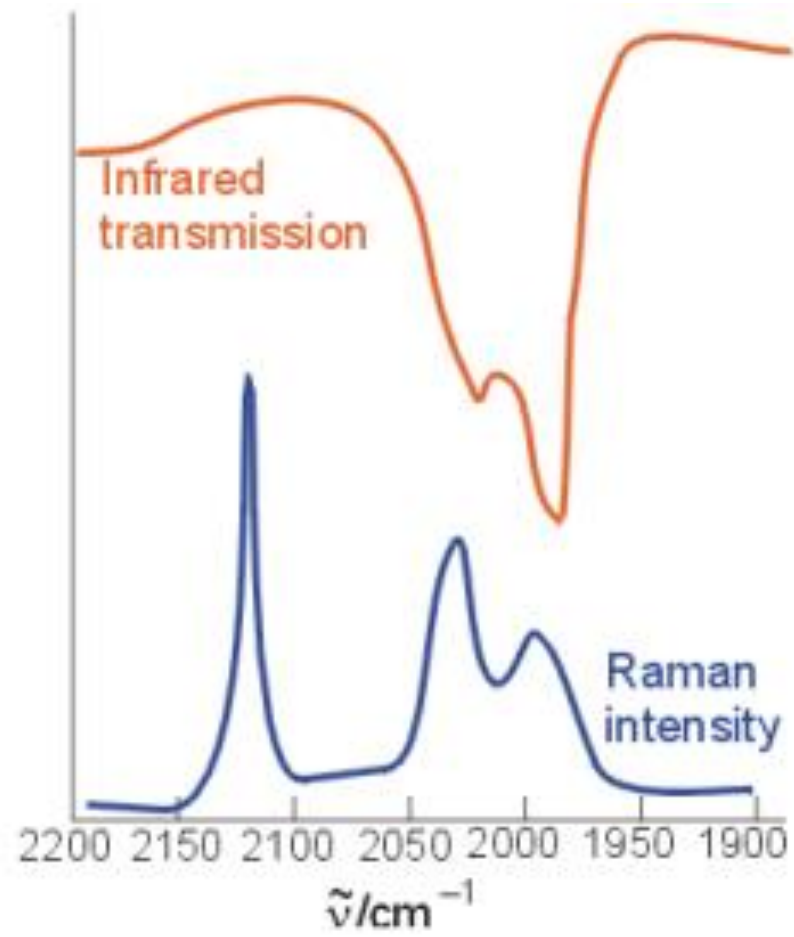


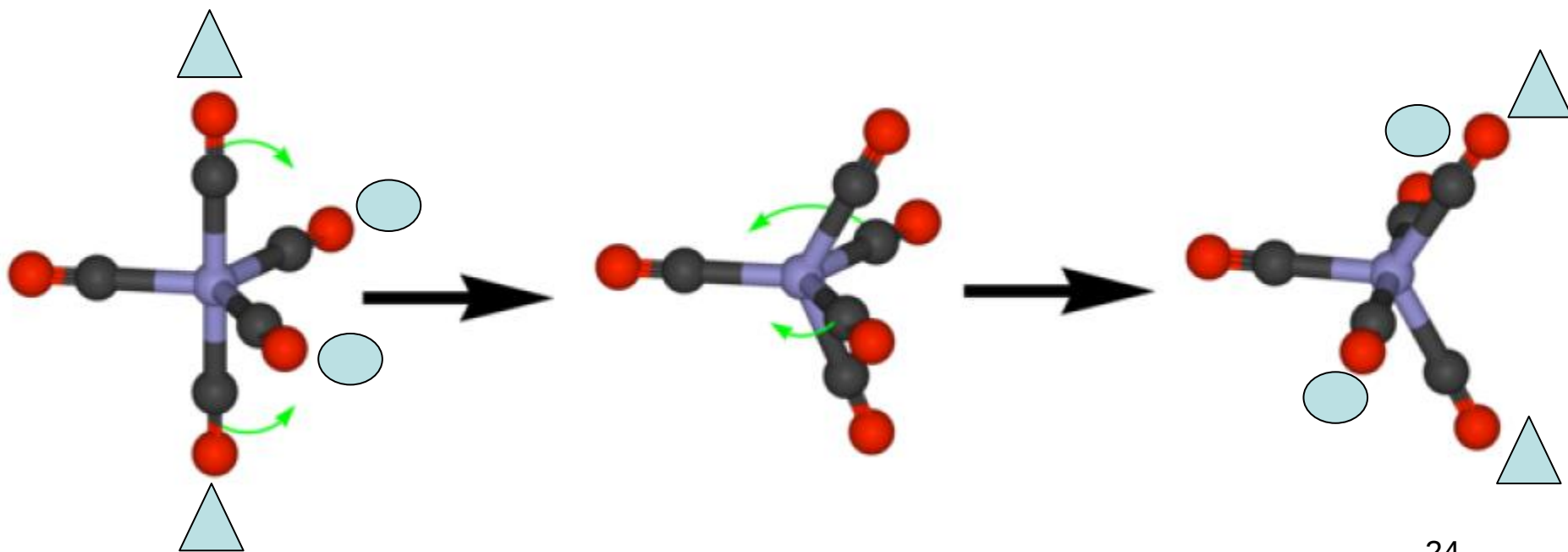
Figure 1. Ball-and-stick model of the D_{3h} -symmetric structure of $\text{Fe}(\text{CO})_5$. Fe, lilac; C, gray; O, red.

Complex	Isomer	Structure	Point group	Number of bands*
$\text{M}(\text{CO})_5$			D_{3h}	2

Characterized by two intense ν_{CO} bands in the IR spectrum at 2034 and 2014 cm^{-1}



The first carbon-13 NMR spectrum of a metal carbonyl was reported in 1958 for iron pentacarbonyl by Cotton, Danti, Waugh, and Fessenden.¹ The result, a single resonance in the carbonyl region, has been shown to be correct by several subsequent investigations;²⁻⁴ in fact the single resonance for $\text{Fe}(\text{CO})_5$ persists to $-160\text{ }^\circ\text{C}$.⁴ Since the structure of iron pentacarbonyl in solution is trigonal-bipyramidal, the carbon-13 NMR spectrum for this complex should contain two signals of relative intensity 2 to 3. Of the possible explanations for the single resonance it is now accepted that the trigonal-bipyramidal structure undergoes a reorientation which is fast on the NMR time scale and exchanges equatorial and axial carbonyl resonances. The most likely mechanism for the exchange of carbonyls is the well-known Berry pseudorotation⁵ shown schematically below.



Fluxional means that the carbonyl groups exchange their positions with one another rapidly.

The capability to detect the molecule in a fixed position is related to the timescale of the applied analytical technique with respect of the rate of the exchange process.

IR has a short time scale ($\sim 10^{-12}$ s)

NMR has a much longer time scale

Diffrazione di raggi X	10^{-18} s
Mössbauer	10^{-18} s
Spettroscopia elettronica UV/Visibile	10^{-15} s
Spettroscopia vibrazionale IR/Raman	10^{-12} s
NMR	c. 10^{-3} – 10^{-6} s
EPR	10^{-6} s

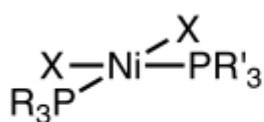
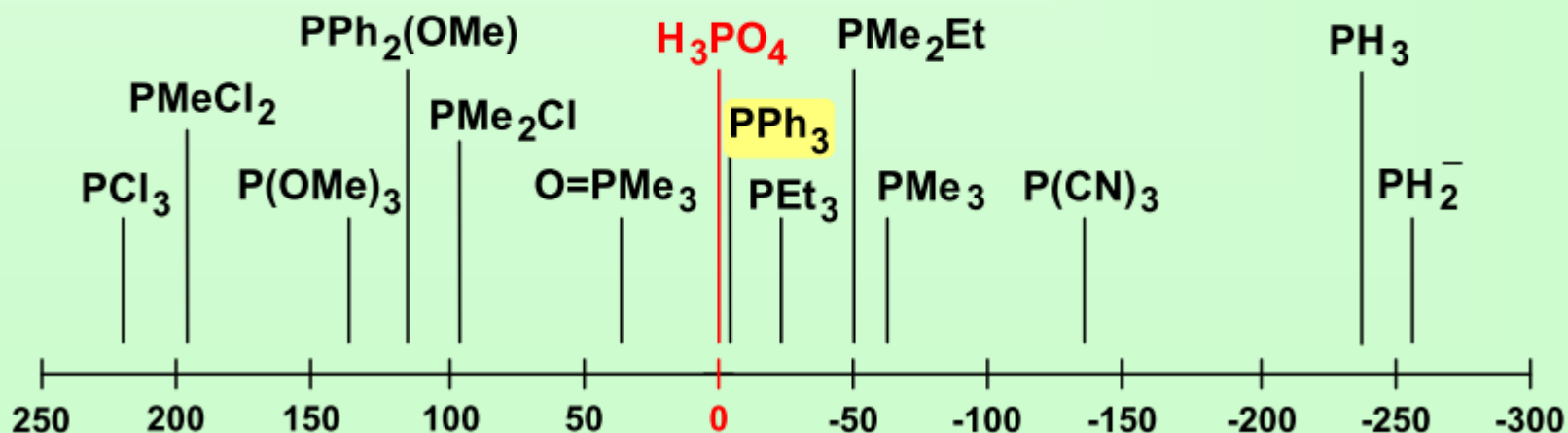
^{31}P NMR very useful for diamagnetic complexes

NMR – ^{31}P characteristics of phosphine complexes

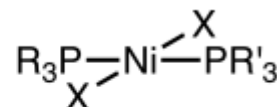
^{31}P NMR shifts: + 245...-163 ppm

Downfield Region

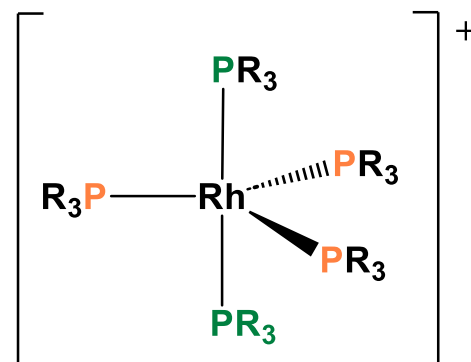
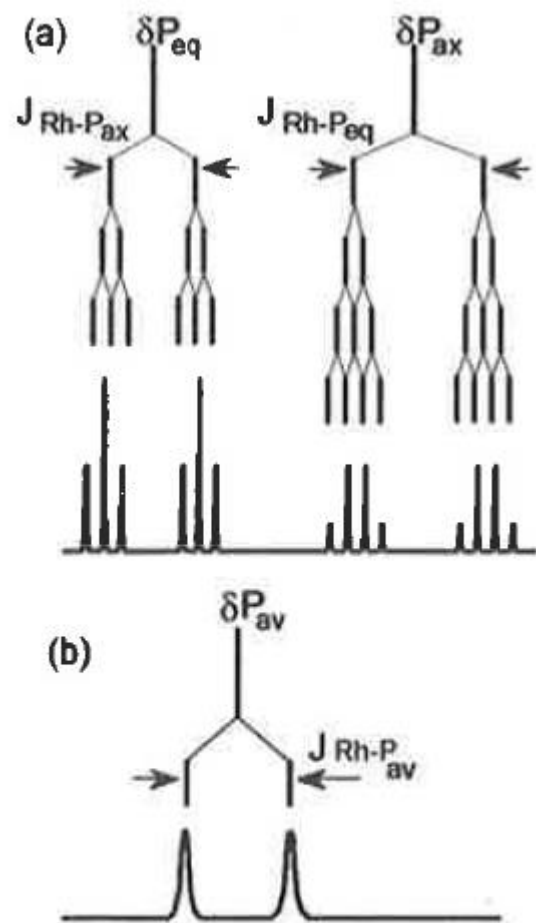
Upfield Region



cis $J_{\text{P-P}}$ 65 Hz



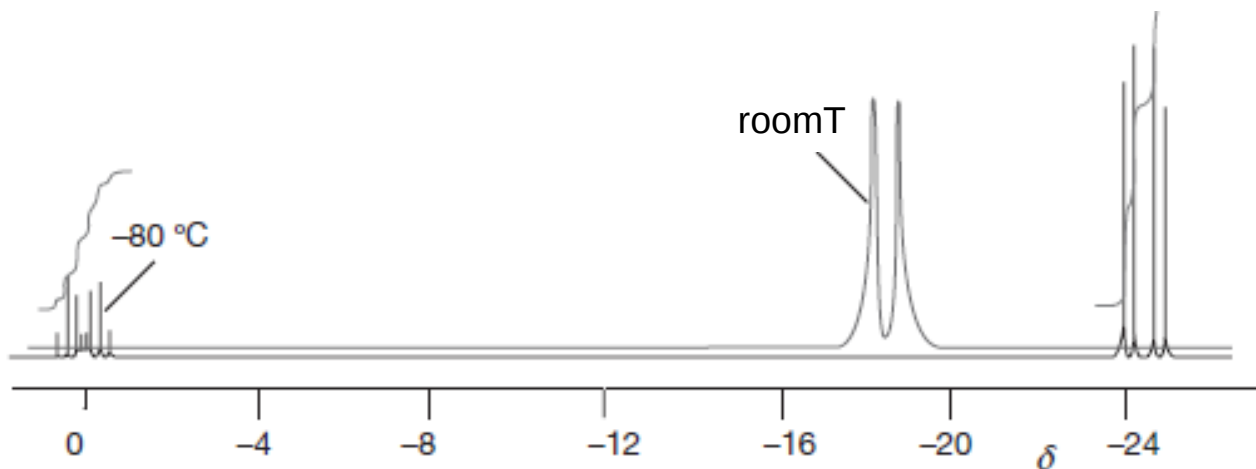
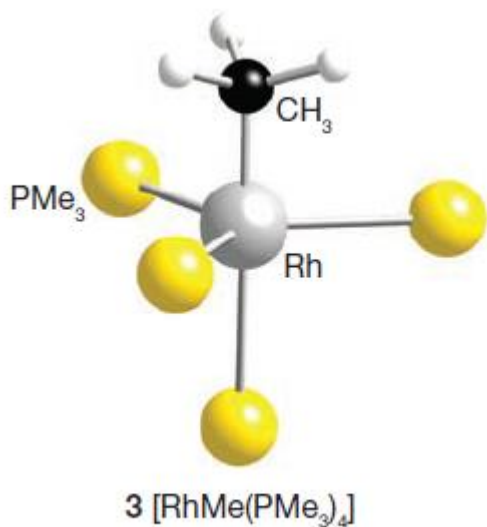
trans $J_{\text{P-P}}$ 300 Hz



$$J(\text{Rh} - \text{P})_{\text{av}} = \frac{2 \times J(\text{Rh} - \text{P}_{\text{ax}}) + 3 \times J(\text{Rh} - \text{P}_{\text{eq}})}{5}$$

$$= \frac{2 \times 140 + 3 \times 210}{5} = 182 \text{ Hz}$$

Fig. 3.36 The predicted NMR patterns for a complex of the type $[\text{Rh}(\text{PR}_3)_5]^+$ at (a) low temperature and (b) room temperature.



Given that the temperature at which the NMR spectra are recorded can be easily varied, often the samples are cooled down at a temperature at which the rate of interconversion becomes slow enough to observe separate resonances. For example in the Figure the ideal ^{31}P NMR spectra of $[\text{RhMe}(\text{PMe}_3)_4]$ at rT and at -80°C are shown. At low T the spectrum consists of a doublet of doublets of relative integration 3 ($\delta = -24$), corresponding to the equatorial P (that couples with the axial ^{31}P and ^{103}Rh), plus a quartet of doublets of relative integration 1, from the axial P (that couples with ^{103}Rh and the three equatorial ^{31}P). At rT the exchange between the PMe_3 groups makes them equivalent and only a doublet is observed (from the coupling with ^{103}Rh).

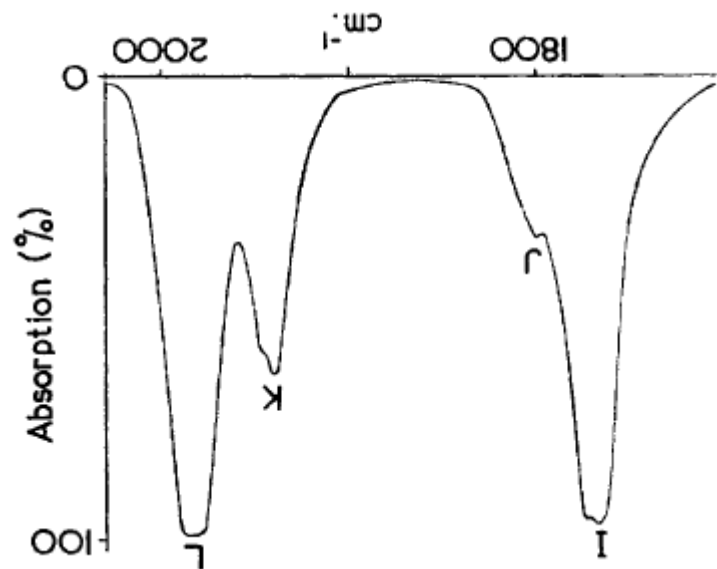
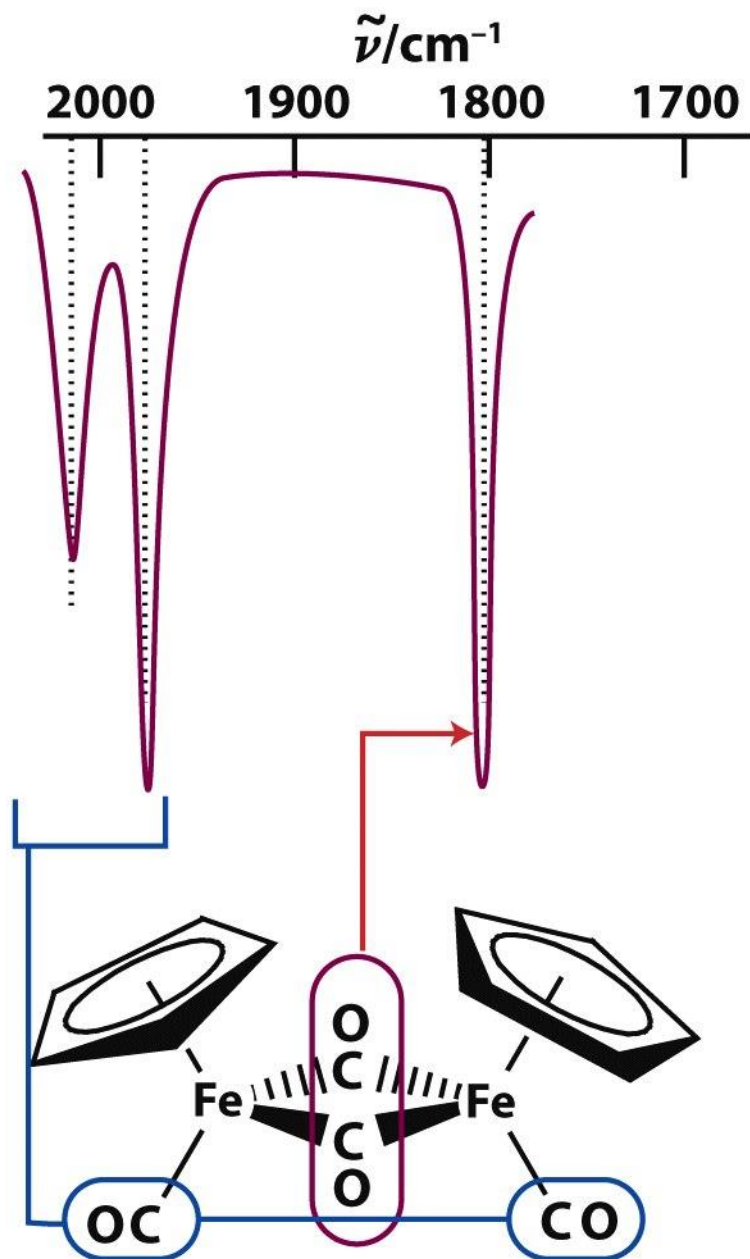


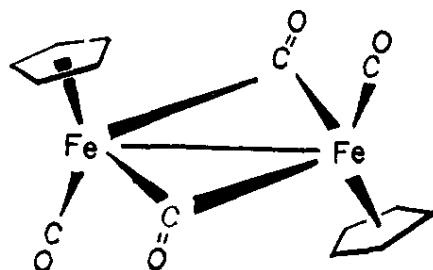
FIGURE 4 The infrared spectrum of $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ in dimethyl sulphoxide solution (1700—2100 cm^{-1} region)

A Definitive Identification of the Structures of Dicyclopentadienyldiiron Tetracarbonyl in Solution

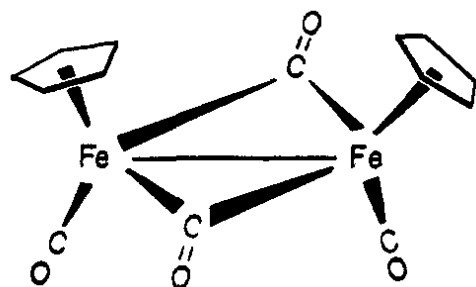
J. G. Bullitt,¹¹ F. A. Cotton, T. J. Marks¹²

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received January 10, 1970

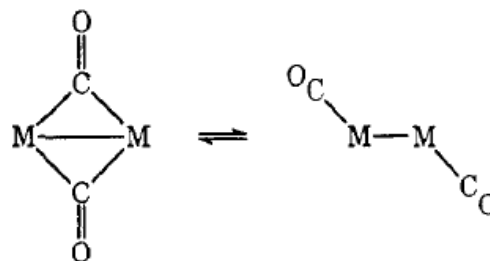


I (C_{2h})



II (C_{2v})

The pmr experiments reported here, as well as other results we shall publish elsewhere, resolve the question of the structure(s) of $(C_5H_5)_2Fe_2(CO)_4$ in solution definitively in favor of Manning's three-structure model. However, the results have, in our opinion, an importance which transcends their role in resolving this specific problem. They provide the first strong proof that bridged-nonbridged structure interconversions, of the type



can occur very rapidly and can therefore form the basis for an extensive and important class of stereochemically nonrigid or fluxional molecules.¹⁰

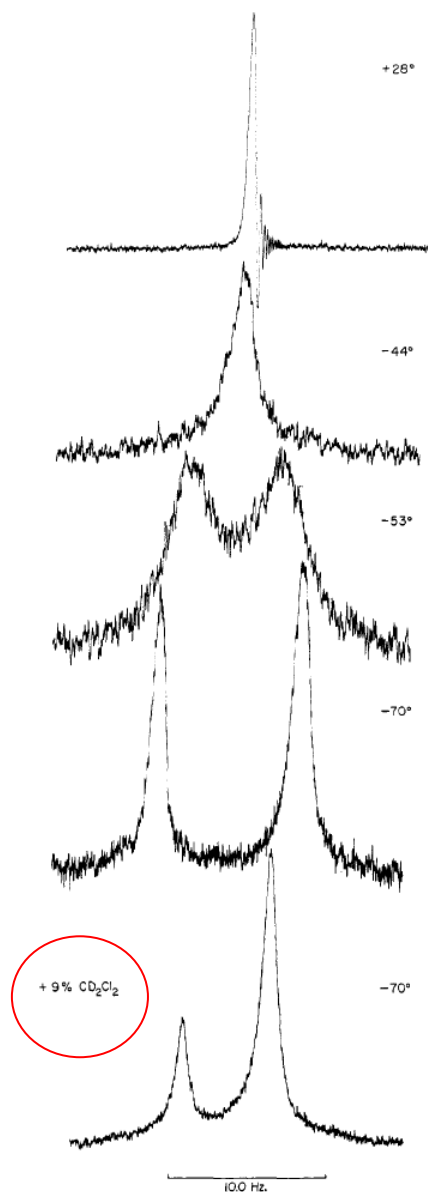
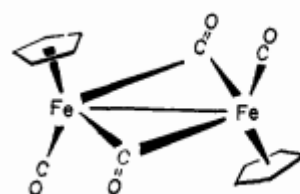


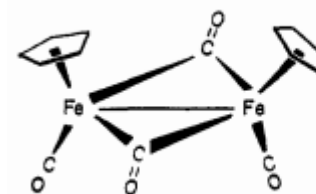
Figure 1. PMR spectra (100 MHz) for $(C_5H_5)_2Fe_2(CO)_4$ at various temperatures. Upper four traces made using $C_5D_5CD_3-CS_2$ (1/3, v/v). Lower trace made using same solvent to which ~9% volume of CD_2Cl_2 was added.

in accord with this, the intensity ratio of the two peaks is substantially affected.

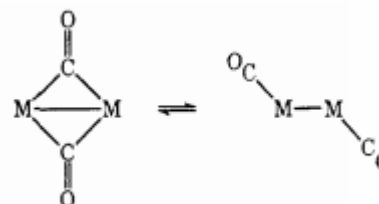
The structures of both the *cis*- and *trans*-isomers of $(\eta^5-Cp)_2Fe_2(CO)_4$ have been confirmed by X-ray crystallography. In solution, both isomers are present, and the terminal and bridging CO ligands undergo intramolecular exchange. Above 308 K, interconversion of the *cis*- and *trans*-forms occurs, and it is proposed that this involves the formation of an unbridged dimer.



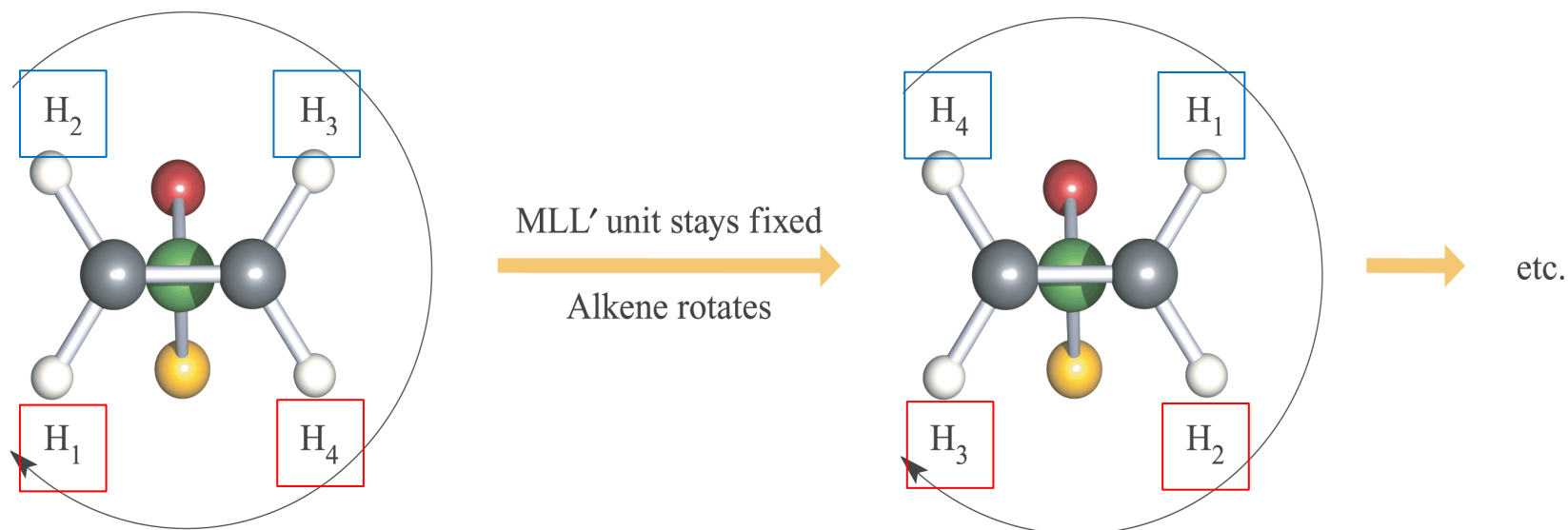
I (C_{2h})



II (C_{2v})

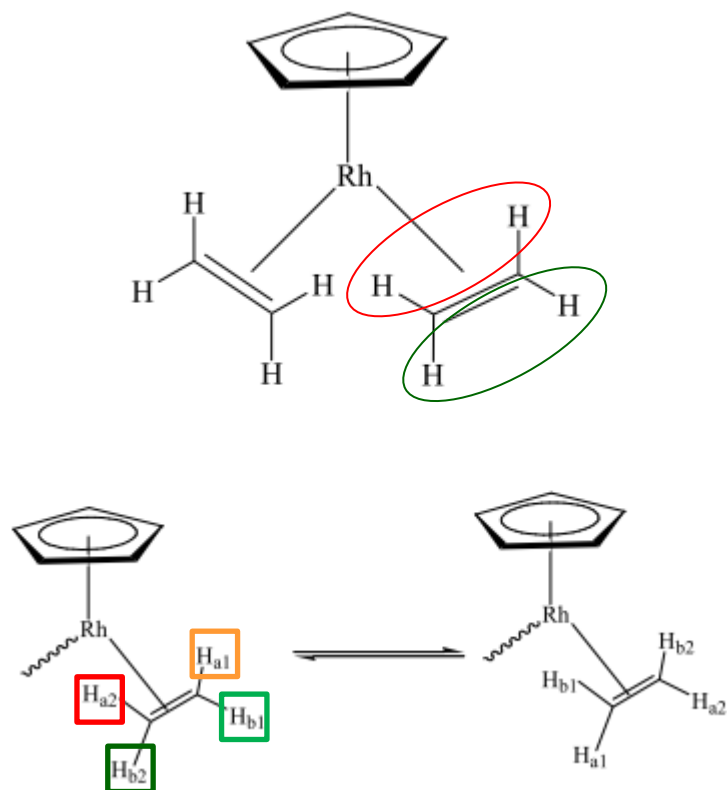
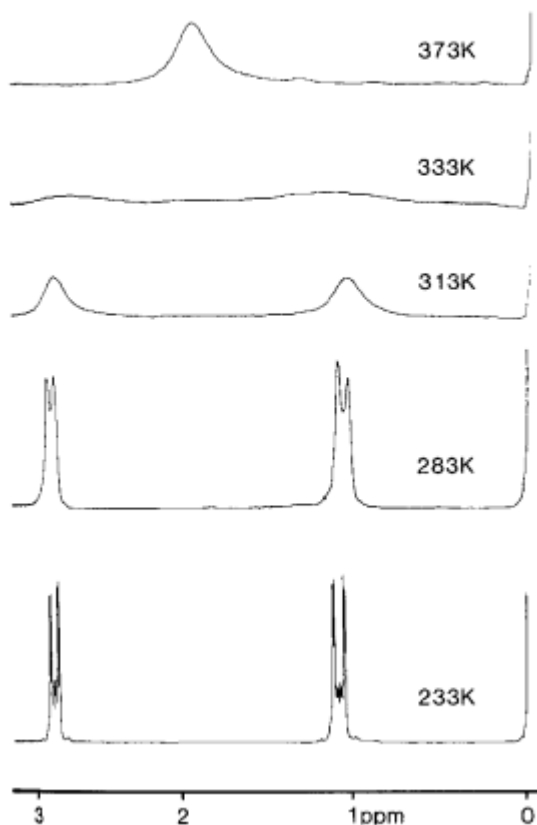


Fluxionality of the η^2 -alkene bond

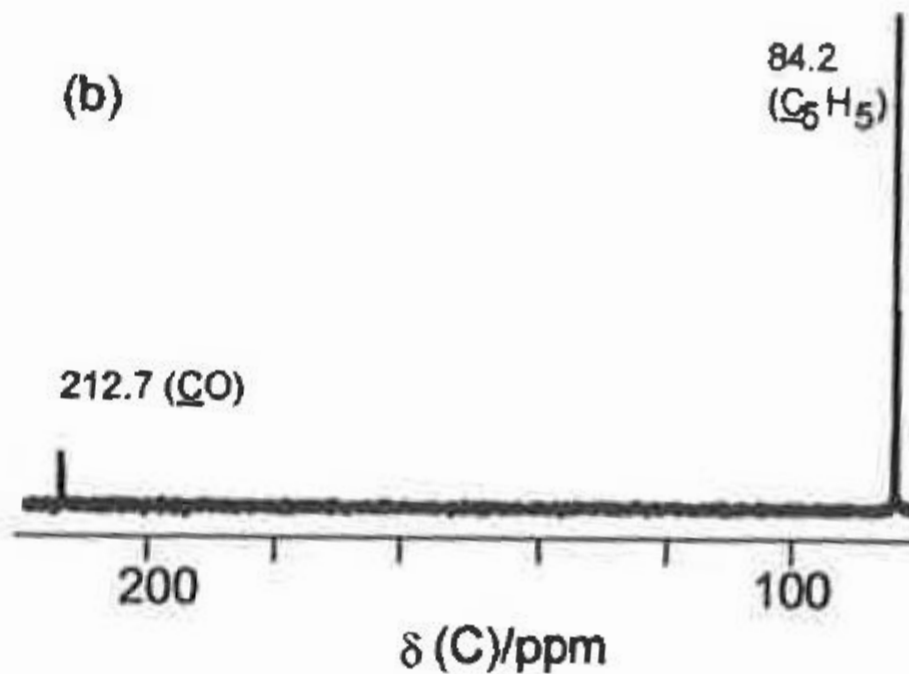
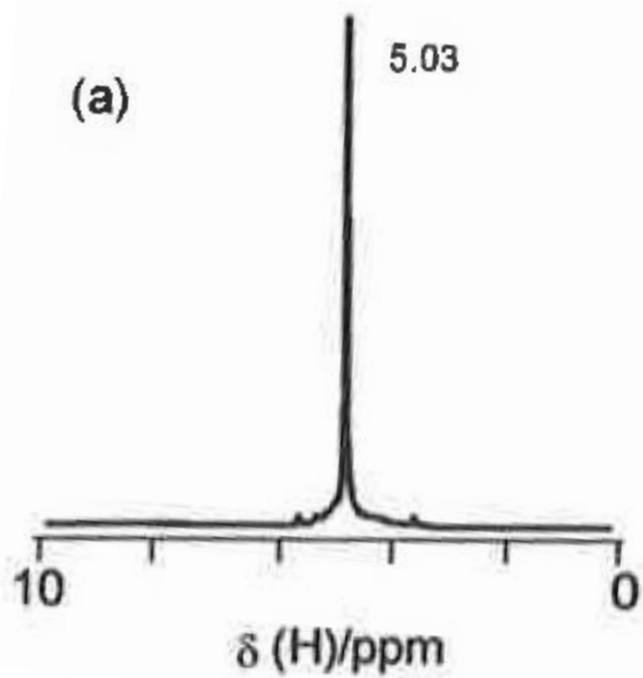
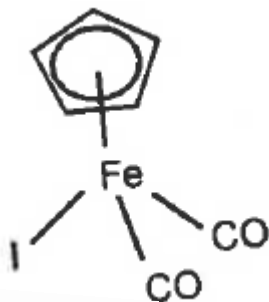


Fluxionality of the η^2 -alkene bond

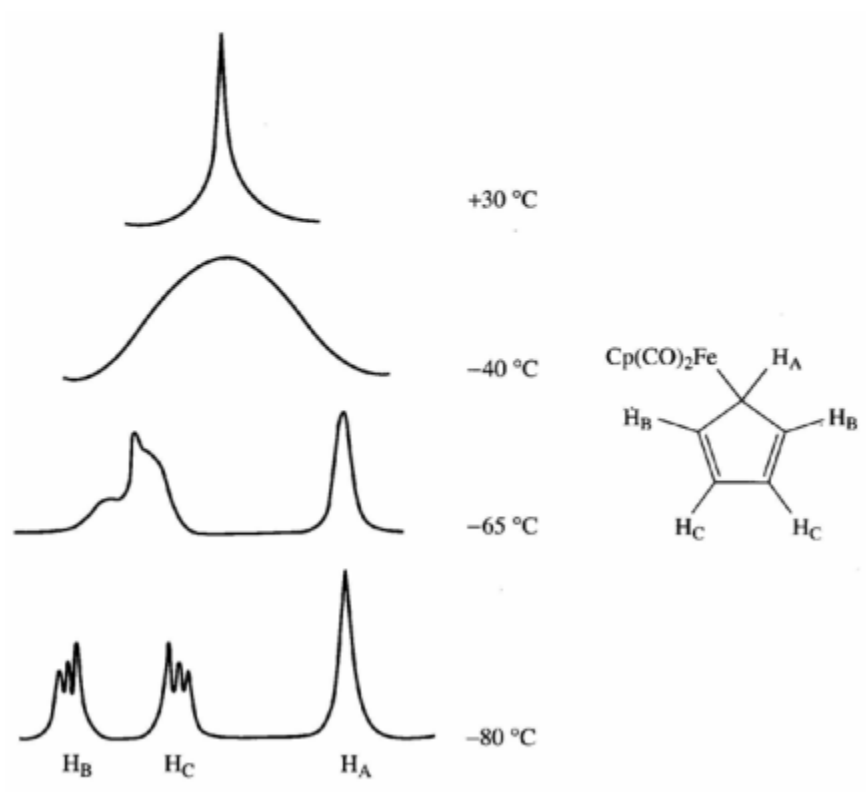
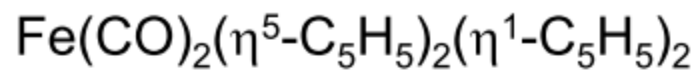
Dynamics in alkene complexes



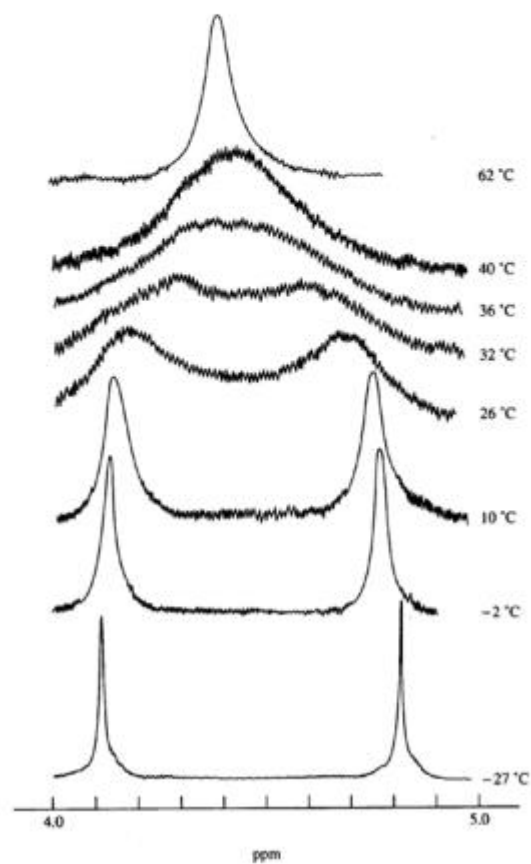
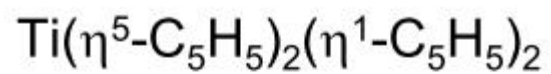
Fluxionality of the η^5 -Cp bond

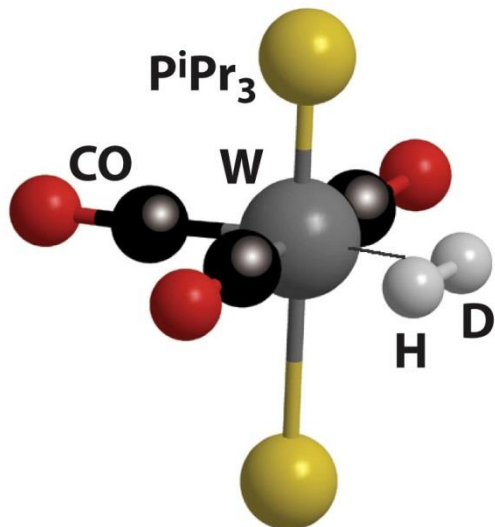


η^1 -Cp Ring-Whizzing

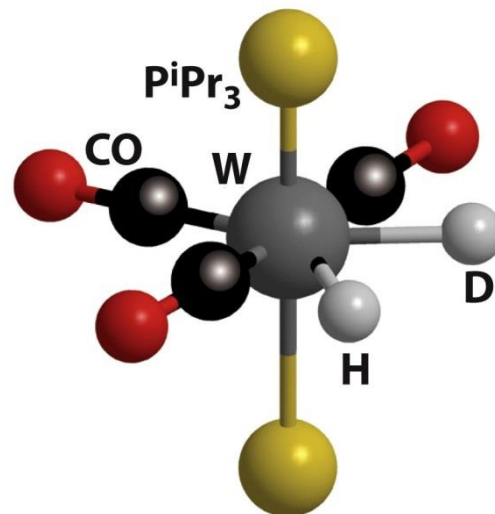


Fluxionality of Cp





NMR: $J_{\text{HD}} = 34 \text{ Hz}$

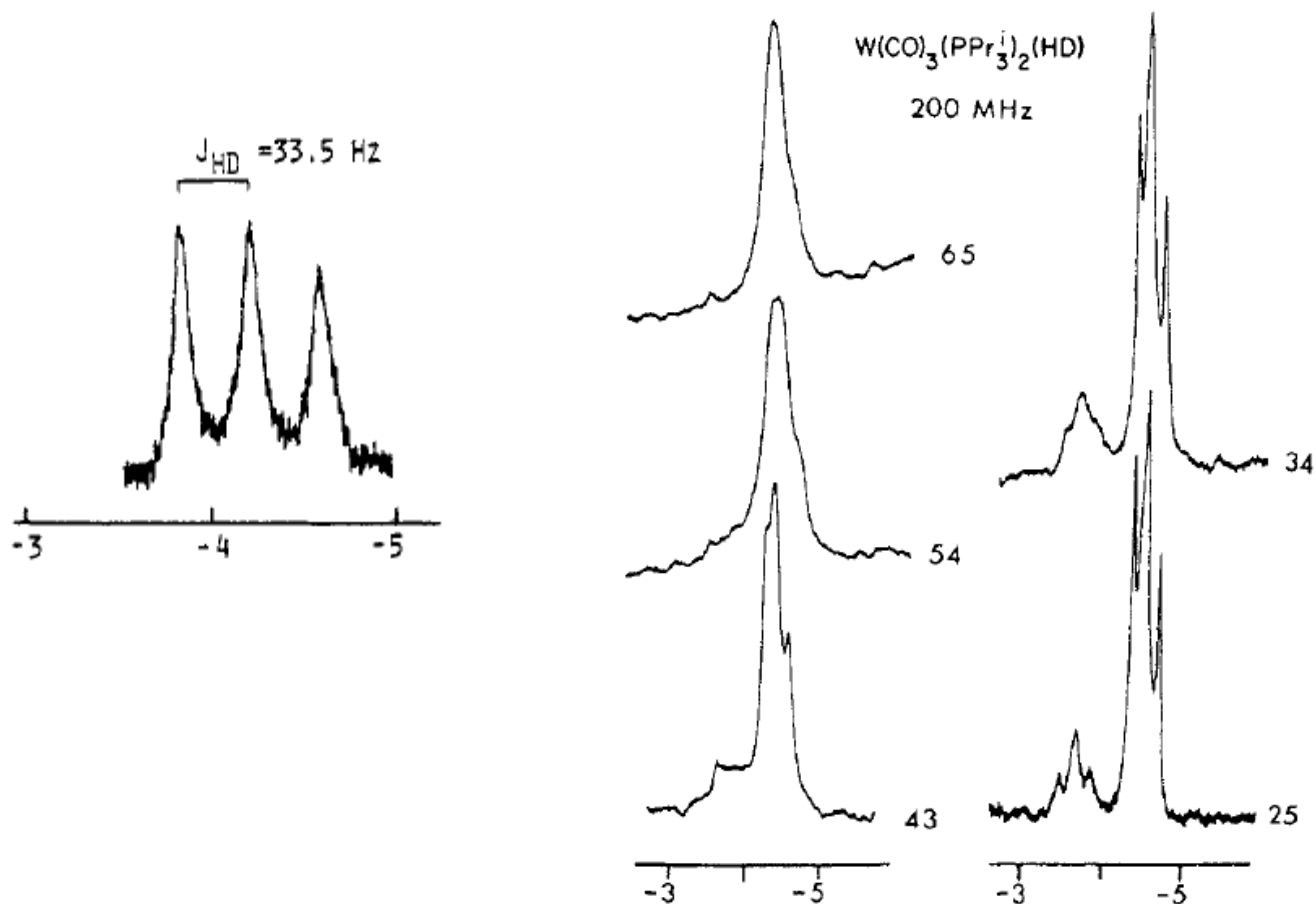


NMR: $J_{\text{HD}} < 2 \text{ Hz}$

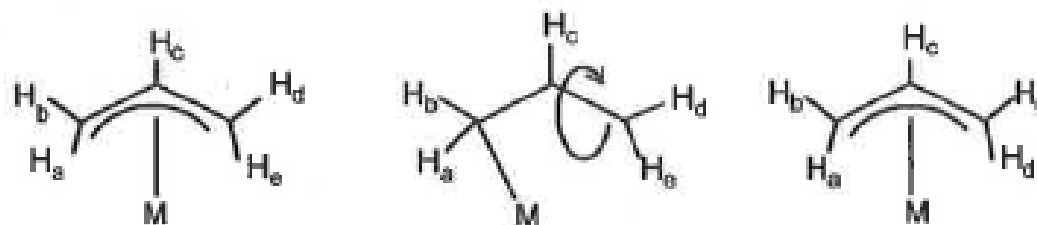
Molecular Hydrogen Complexes of the Transition Metals. 4.
Preparation and Characterization of $\text{M}(\text{CO})_3(\text{PR}_3)_2(\eta^2\text{-H}_2)$ ($\text{M} = \text{Mo}, \text{W}$) and Evidence for Equilibrium Dissociation of the
H–H Bond To Give $\text{MH}_2(\text{CO})_3(\text{PR}_3)_2$

Gregory J. Kubas,* Clifford J. Unkefer, Basil I. Swanson, and Eiichi Fukushima

The ^1H NMR spectrum of the monodeuterated complex $\text{W}(\text{CO})_3(\text{P-}i\text{-Pr}_3)_2(\text{HD})$ provides unequivocal evidence for direct H-H bonding in the $\eta^2\text{-H}_2$ ligand. The signal at -4.2 ppm is split by spin 1 deuterium into a 1:1:1 triplet with $J(\text{HD}) = 33.5$ Hz (Figure 4). This value of J is an order of magnitude larger than that found for compounds containing nonbonded H and D atoms and is 77% of the value of $J(\text{HD})$ for HD gas, 43.2 Hz.²¹ Thus, since the magnitude of the coupling constant is a good measure of the bond order here, the H-D bond is weakened on coordination.



For example, frequently the four protons attached to the terminal carbon atoms in the π -bound allyl ligand C_3H_5 appear as a single resonance because of exchange. The mechanism believed to be responsible for this is a change in bonding mode of the allyl ligand from being π -bound to σ -coordinated followed by a rotation of one end of the ligand around the central C–C bond before the π -bonding mode is reattained. The effect of this is to swap protons that were on the underside of the allyl ligand with those on the top, as shown in Fig. 3.34. There is equal probability that the σ -bond will be formed at either terminal carbon atom and so all four of the protons H_a , H_b , H_d , and H_e will exchange.



Of course this mechanism does not allow the central proton to swap with the terminal ones and therefore a separate signal is observed for this, usually appearing as a quintet due to coupling with the other four protons that are equivalent due to the exchange process.

CARBON MONOXIDE INSERTION REACTIONS
V. THE CARBONYLATION OF METHYLMANGANESE PENTACARBONYL
WITH ^{13}CO

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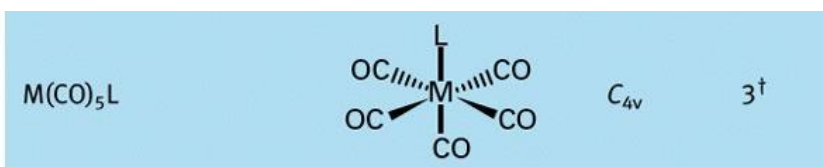
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Heavy isotope substitution reduces frequency of corresponding vibration;
reduced mass, μ , in Hooke's Law, increases

{Force constant k doesn't change; bond strengths change little with isotope substitution.}

Hooke's Law:
$$\bar{\nu} = \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}} ; \mu = \frac{m_x m_y}{m_x + m_y}$$



CARBONYL STRETCHING BANDS OF $LMn(CO)_5^a$

L	$\nu(CO) (cm^{-1})$					
	<i>Radial CO groups</i>			<i>Axial CO groups</i>	<i>Acetyl CO</i>	
	A_1	E	A'	A_1		
CH_3	2110	2012	(1976) ^b	1991 (1949)		
CH_3CO	2115	2011	(1970) ^b	2003 (1963)	1664	(1625)