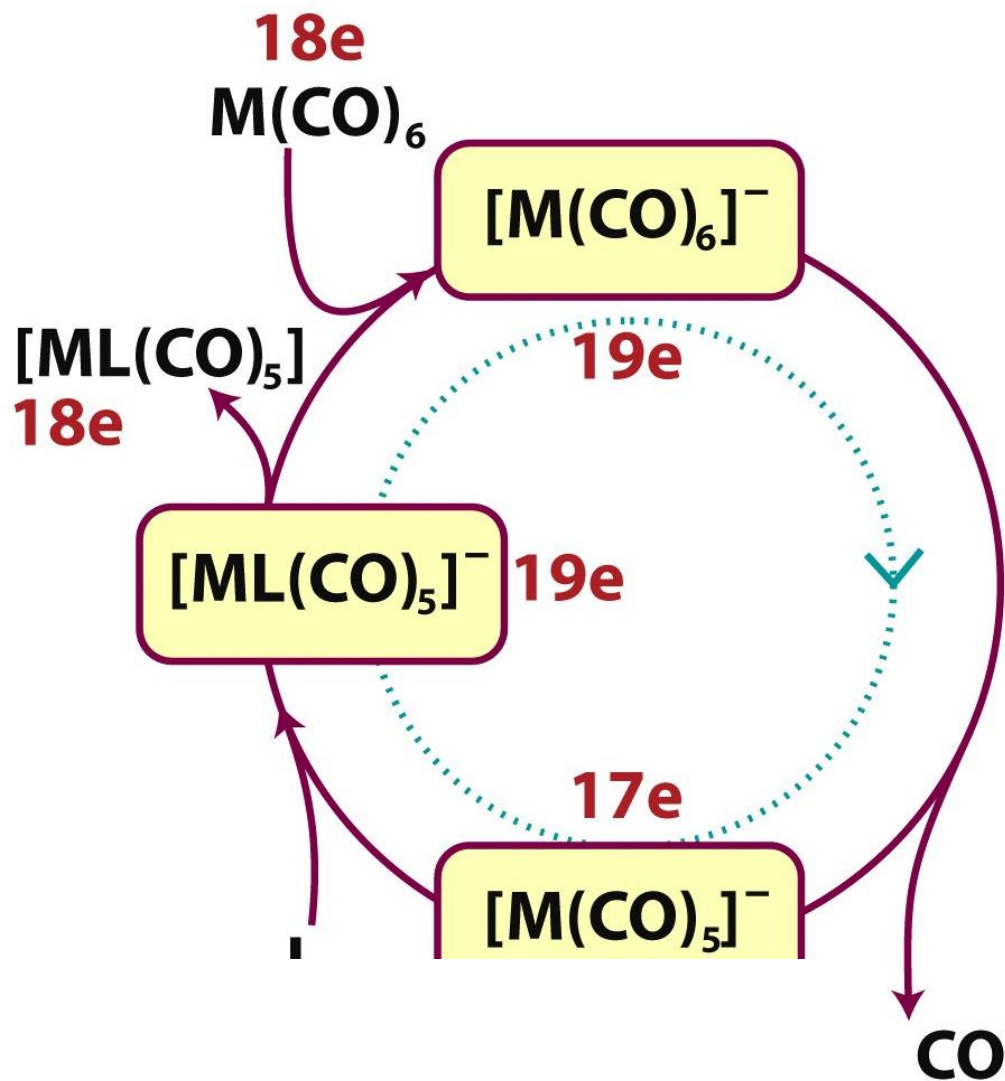


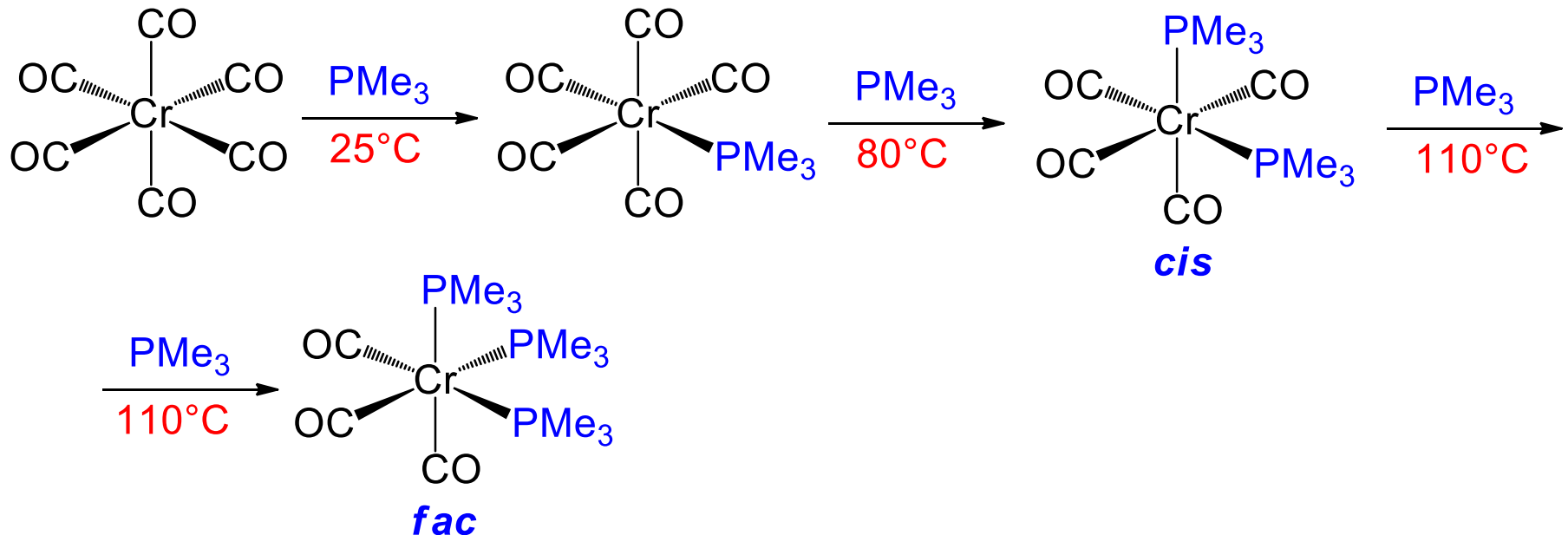
Sostituzione indotta da un processo redox  
*aggiunta di quantità catalitica di un riducente  
monoelettronico*



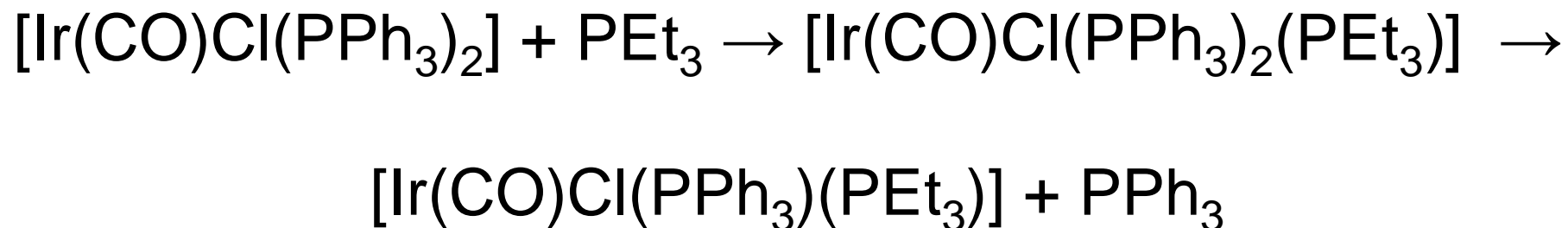
## Effect of the Lewis basicity of the ligand

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

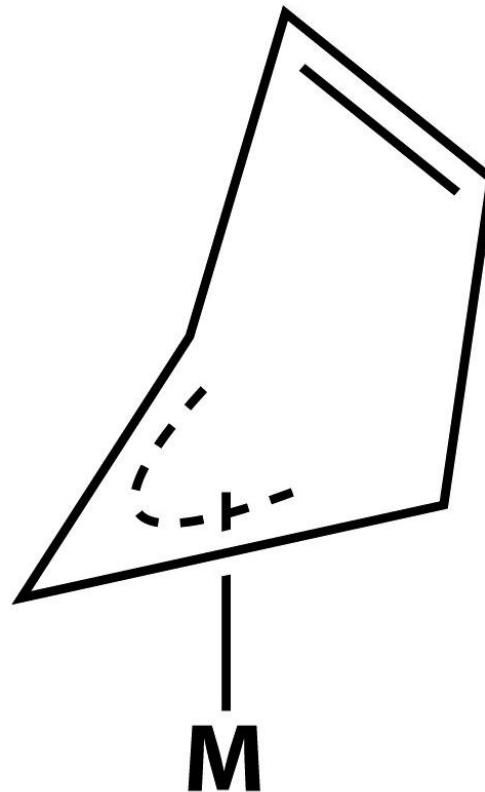
The introduction of 2 or 3 phosphines represent the limit of the substitution.



## 16e: meccanismo associativo



# Sostituzioni con meccanismo associativo in complessi con 18 elettroni



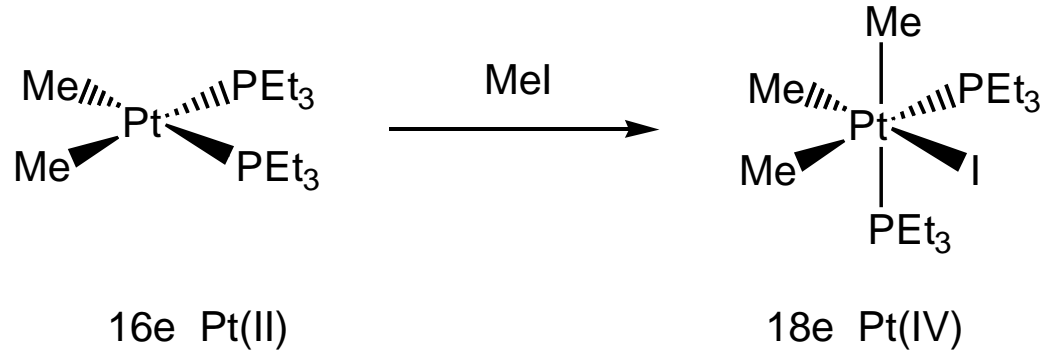
## **Steric** considerations

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

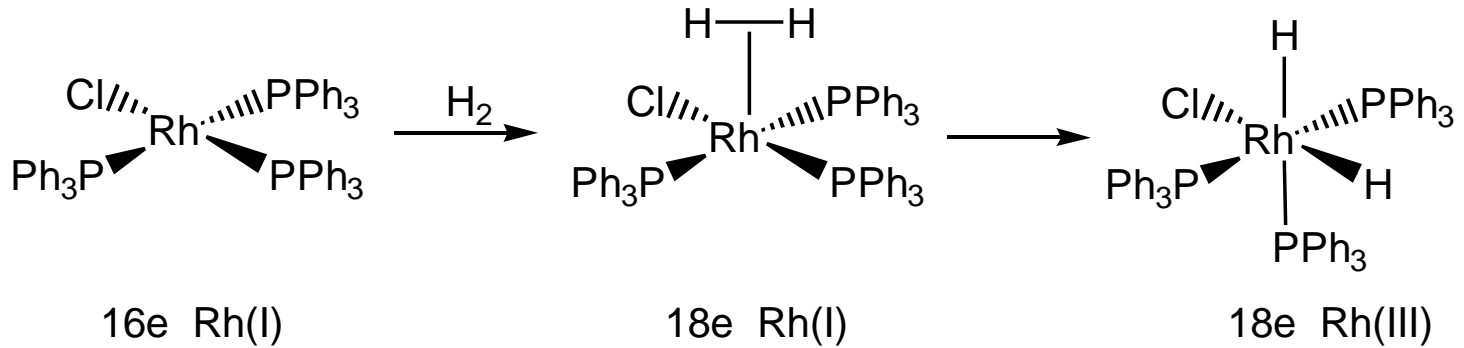
- Large ligands **ENHANCE** the rate of **dissociative** processes
- Large ligand **DECREASE** the rate of **associative** processes



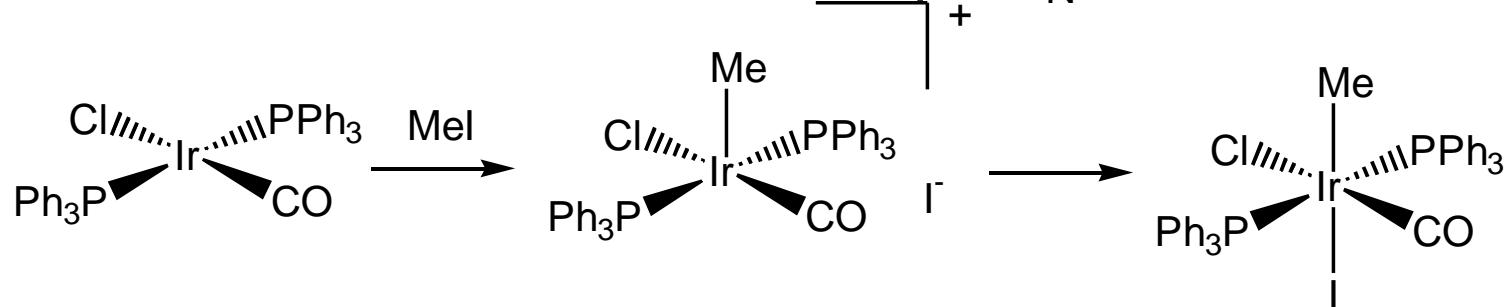
# Addizione ossidativa



## Meccanismo concertato

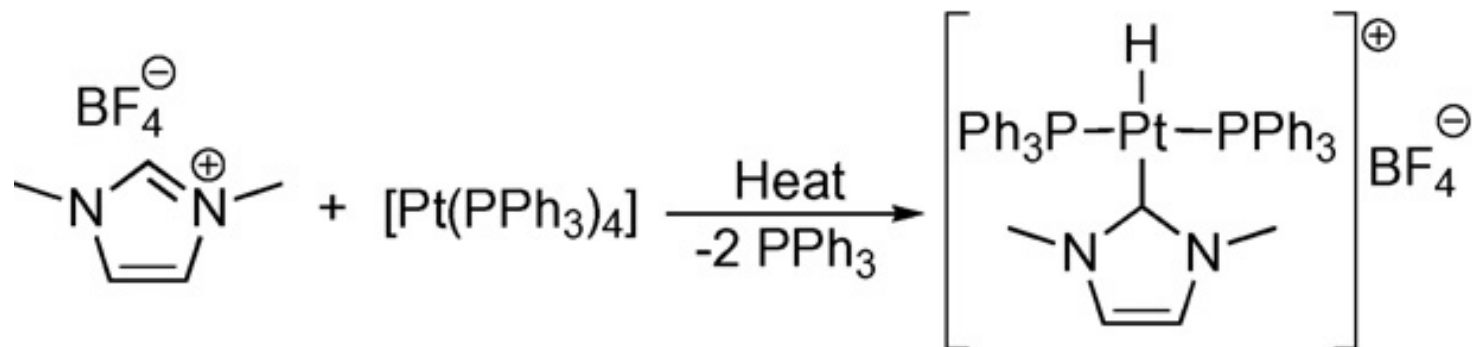


## Meccanismo di tipo S<sub>N</sub>2

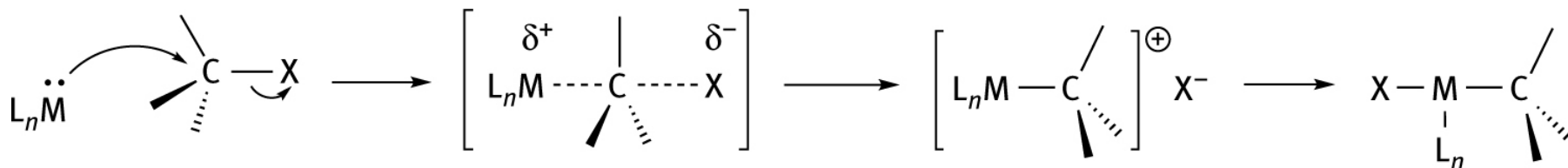


# Caso anomalo di addizione ossidativa

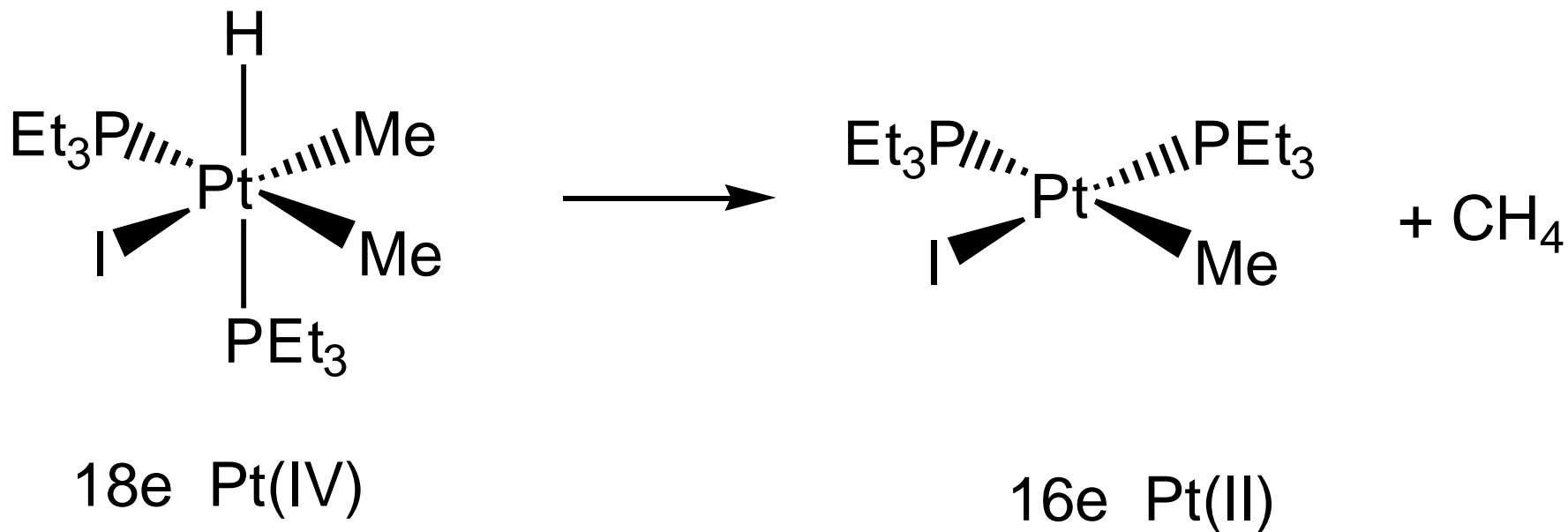
*addizione ossidativa di sali di imidazolio su precursori zerovalenti*



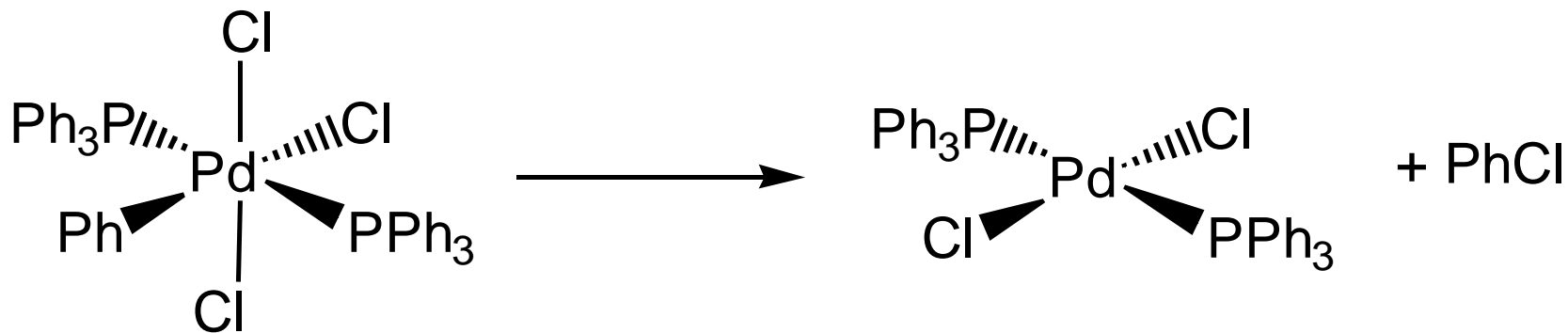
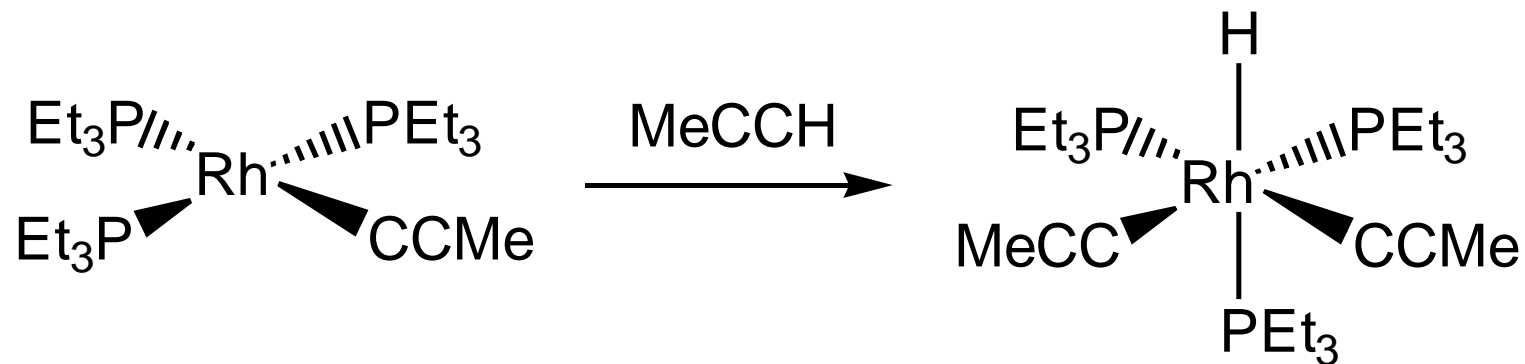
**Solventi polari favoriscono stati di transizione polari, quindi il meccanismo via  $S_N2$ .**



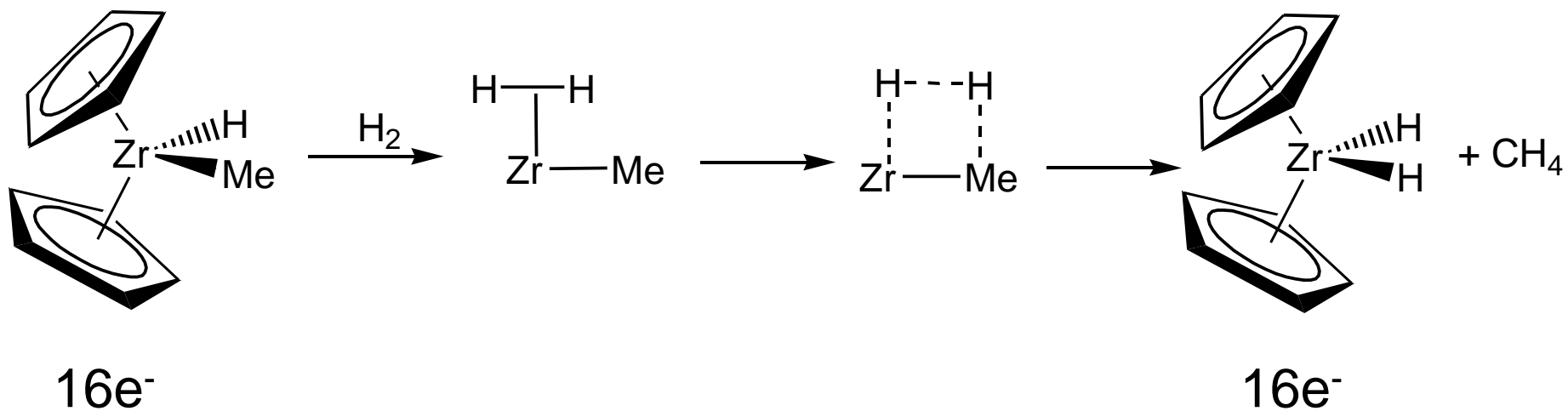
# Eliminazione riduttiva



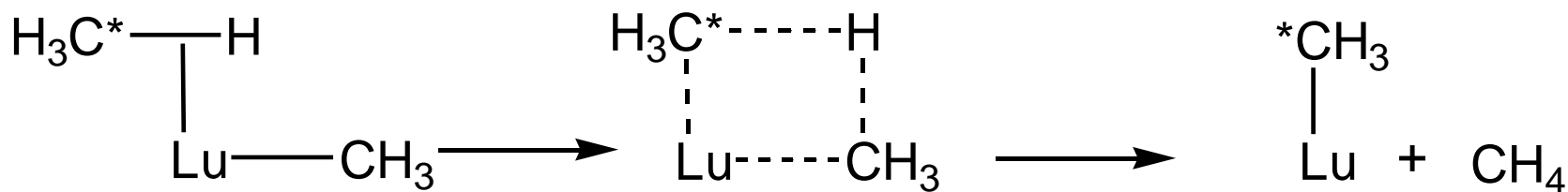
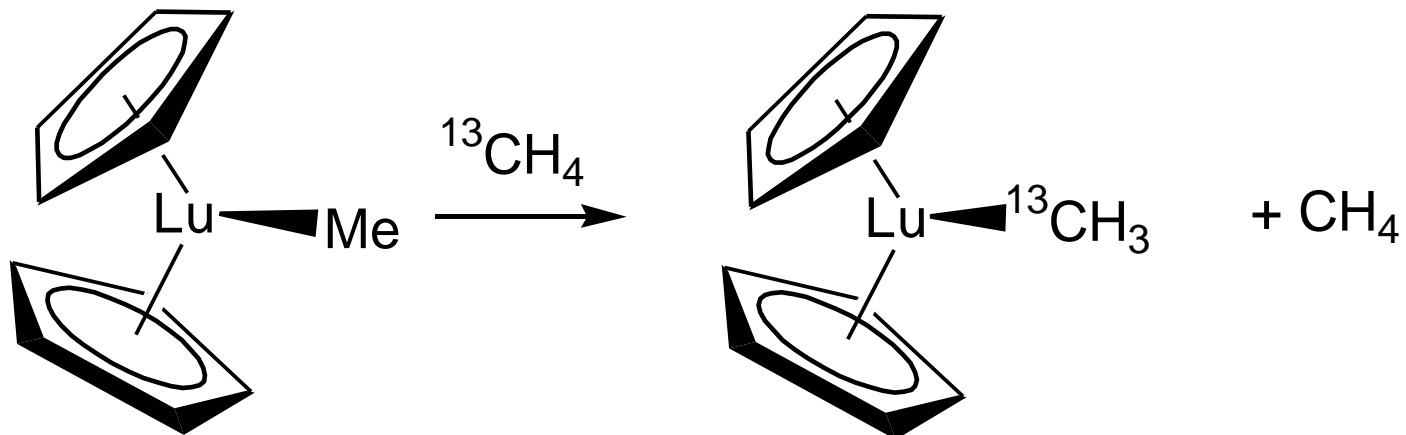
# Esempi



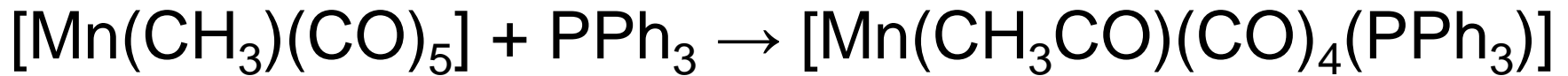
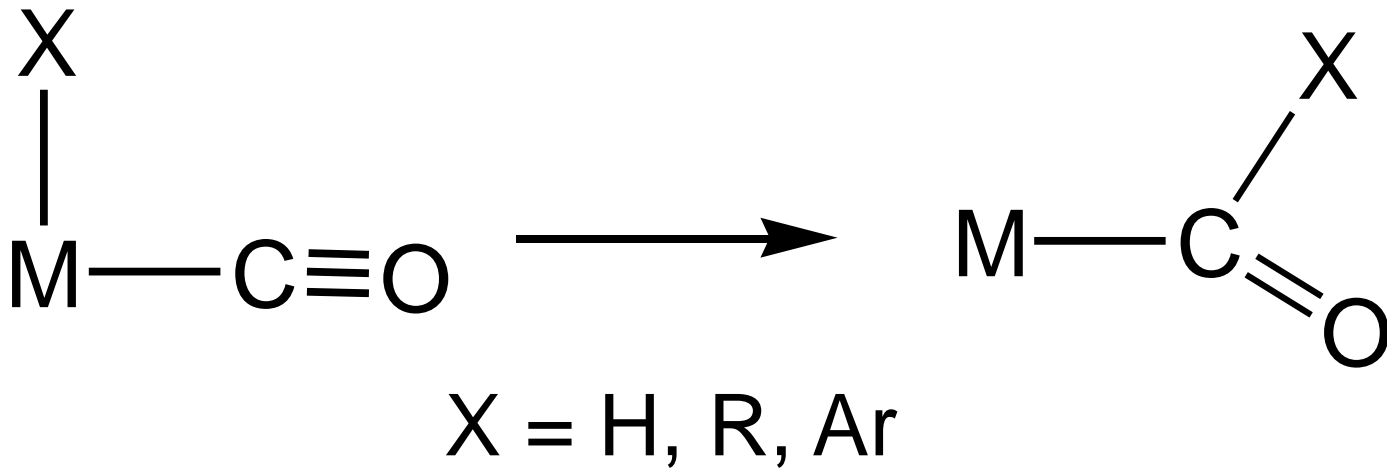
# Metatesi di legame $\sigma$



# Metatesi di legame $\sigma$

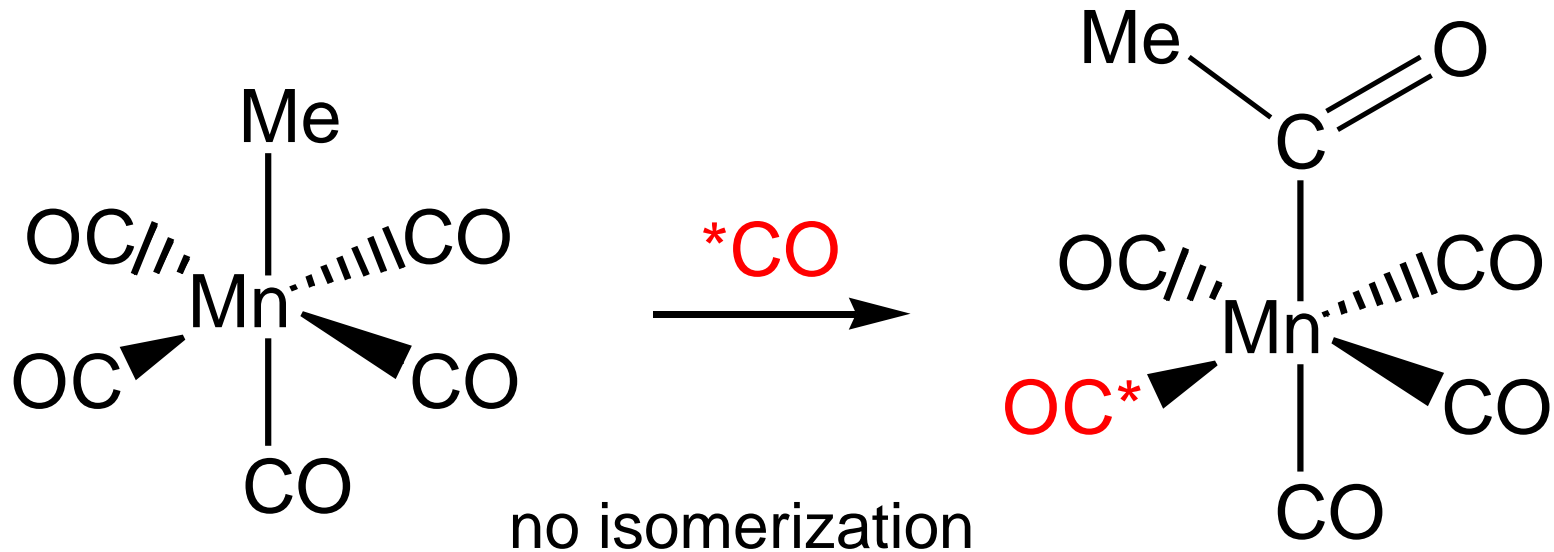


# Inserzione migratoria 1,1



*Migrazione di X su C o inserzione di CO nel legame M-X?*

# Meccanismo dell'inserzione migratoria 1,1



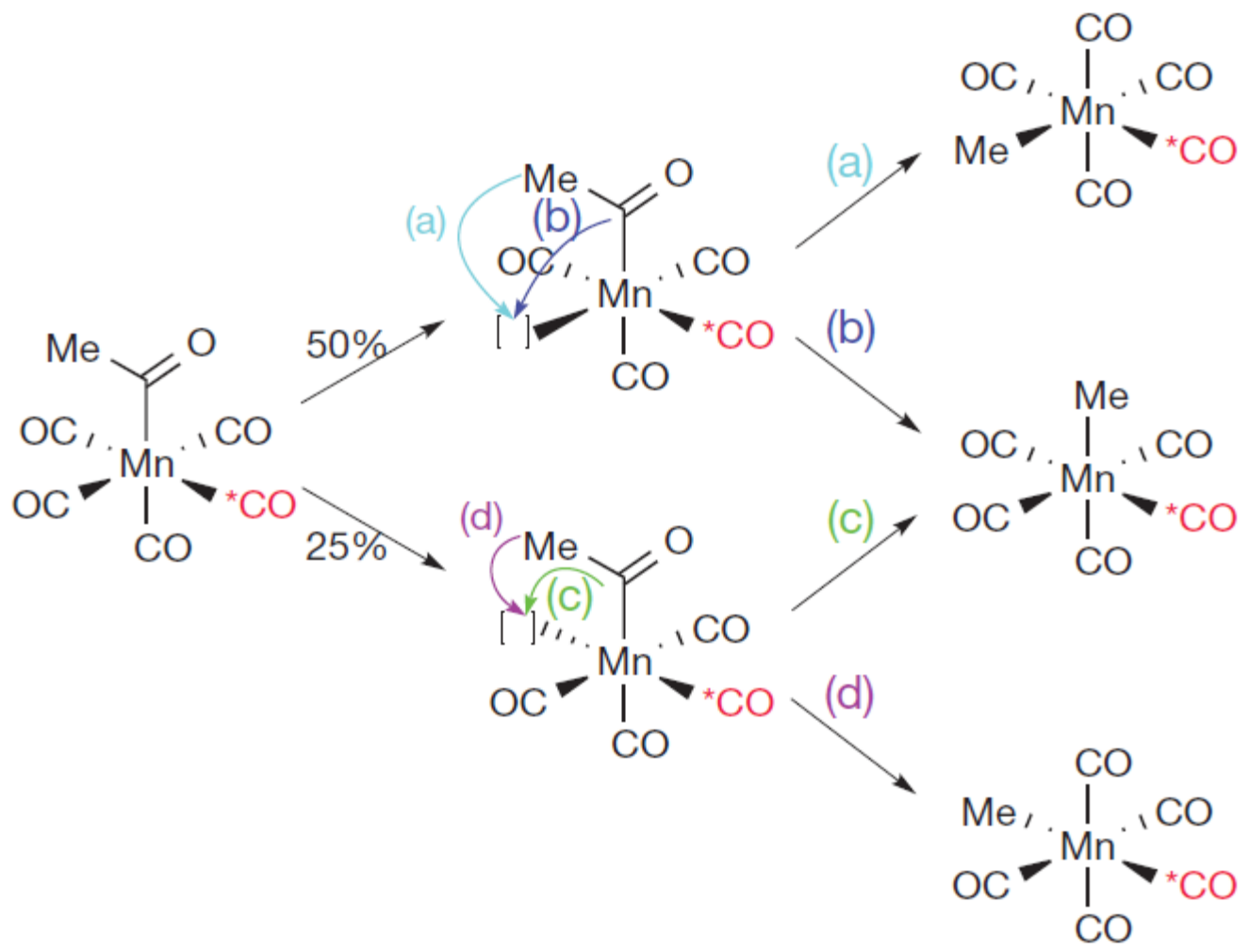
Decarbonylation of  $[\text{Mn}(*\text{COCH}_3)(\text{CO})_5]$  only *cis*- $[\text{MnCH}_3(*\text{CO})(\text{CO})_4]$ :  
Principle of microscopic reversibility!

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

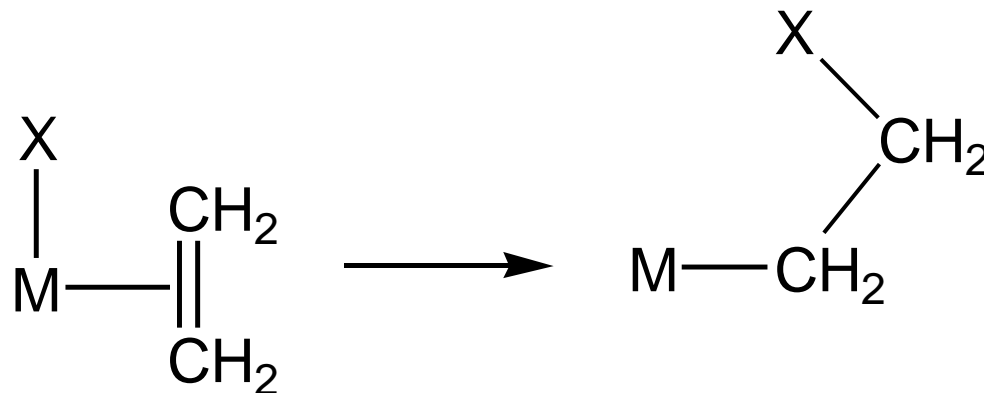
*trans*- $[\text{Mn}(\text{CH}_3)(\text{CO})_4(*\text{CO})]$  and *cis*- $[\text{Mn}(\text{CH}_3)(\text{CO})_4(*\text{CO})]$  in 1:2 ratio:

**METYL MIGRATION!**

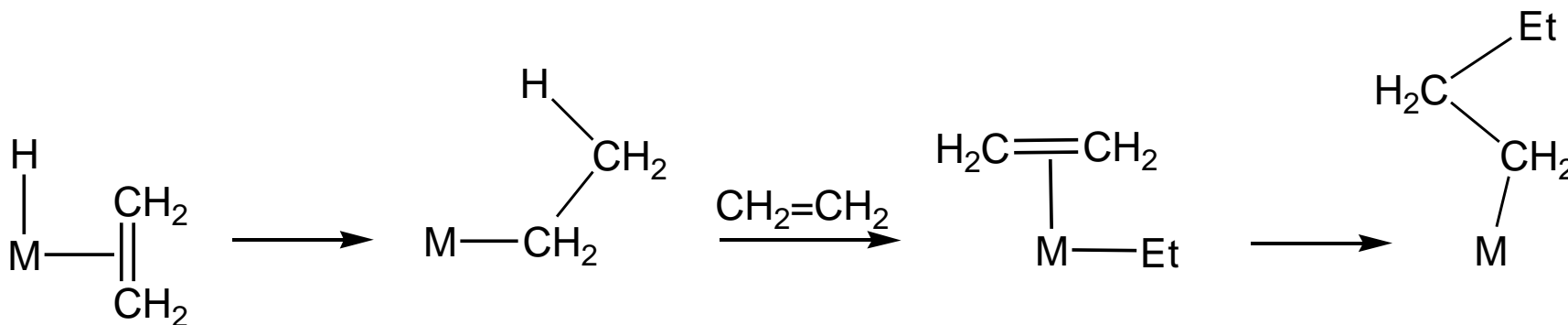




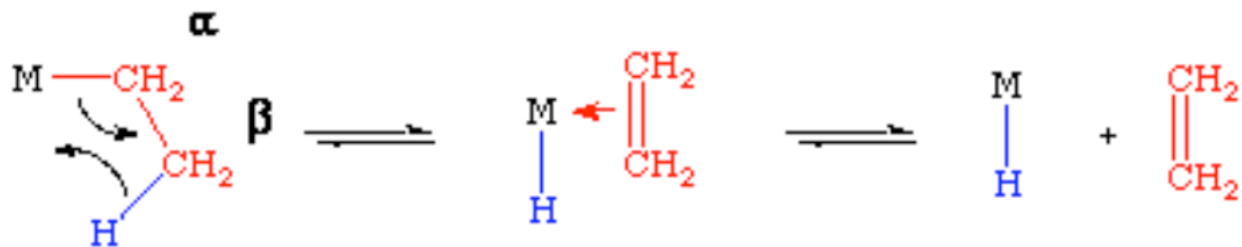
# Inserzione 1,2 *con leganti coordinati $\eta^2$*



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

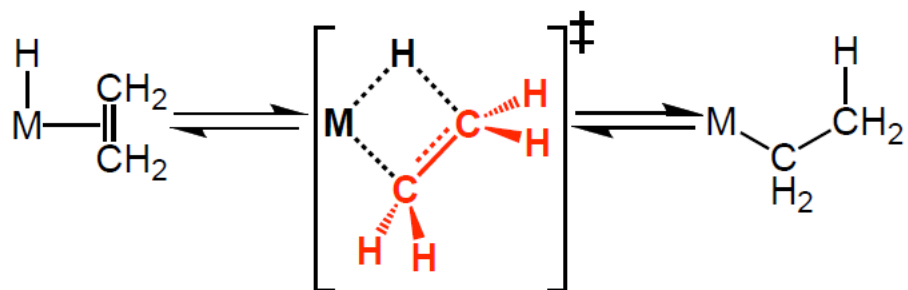


Formazione di polietilene



## Beta-hydride Elimination

Mechanism  $\longrightarrow$  Four-center transition state inferred

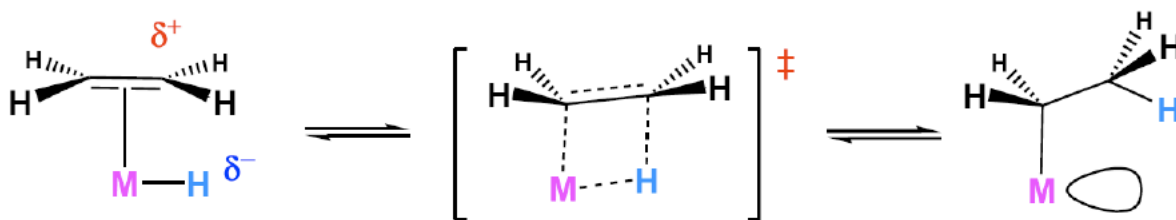


*Olefin-insertion* – microscopic reverse reaction

critical step in olefin polymerization

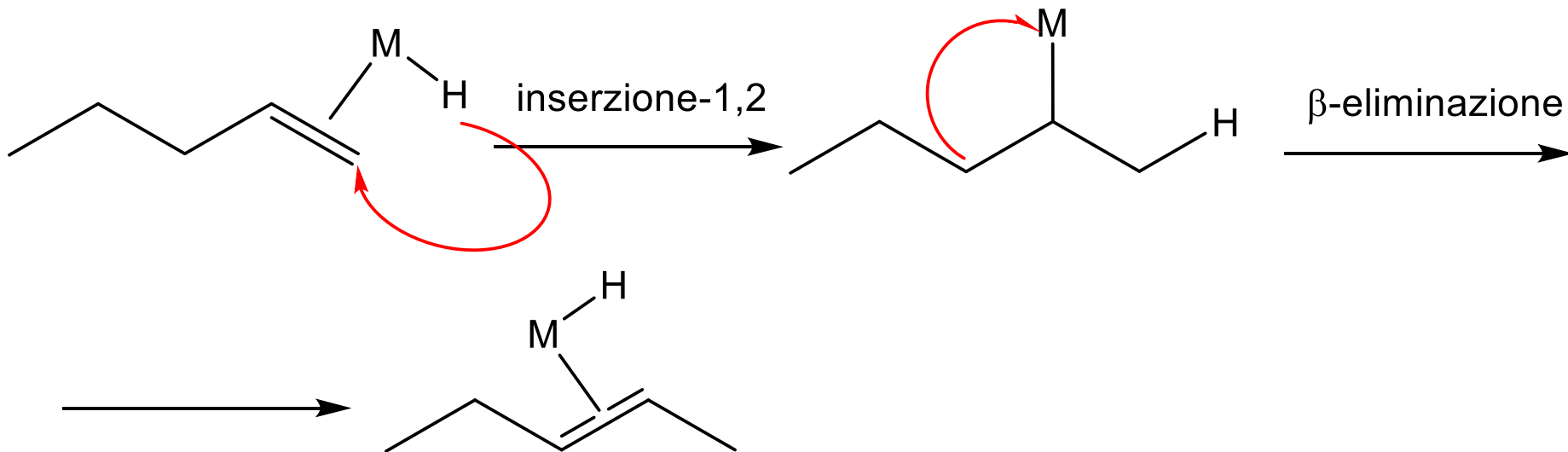
*$\beta$ -hydride elimination is a termination step in olefin polymerization*

*migratory insertion*  $\longrightarrow$



$\longleftarrow$   *$\beta$ -hydride elimination*

# Isomerizzazione di alcheni

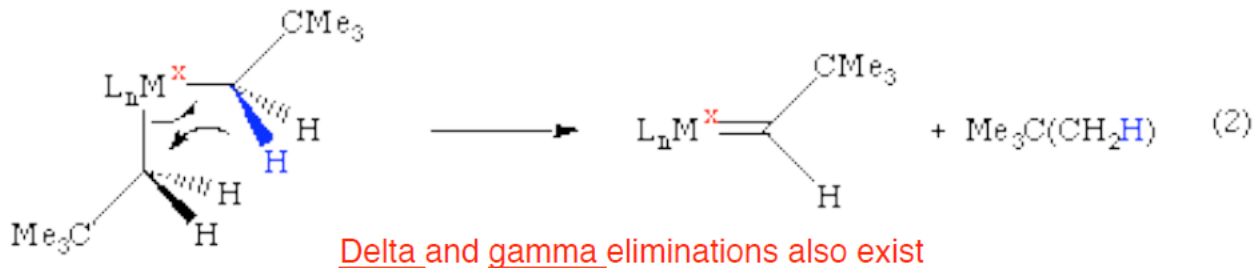
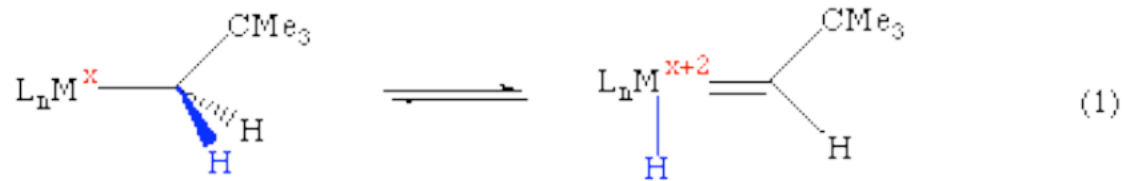


# La reazione di $\alpha$ -eliminazione

E' tipica di complessi con i **metalli di transizione di inizio serie**.

Richiede che sul complesso vi sia un alchile con almeno un atomo di idrogeno sul **C  $\alpha$**  rispetto al metallo.

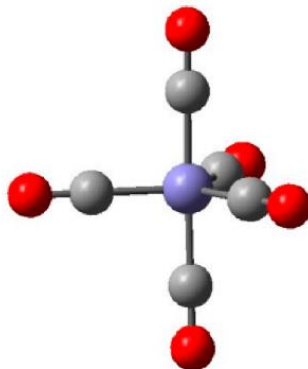
Solitamente si hanno due gruppi alchilici in **cis** tra di loro.



Delta e gamma eliminazioni anche comuni...formazione di metallaccoli «ciclometallazioni»

## Fluxional Behaviour (e.g. $\text{Fe}(\text{CO})_5$ )

---



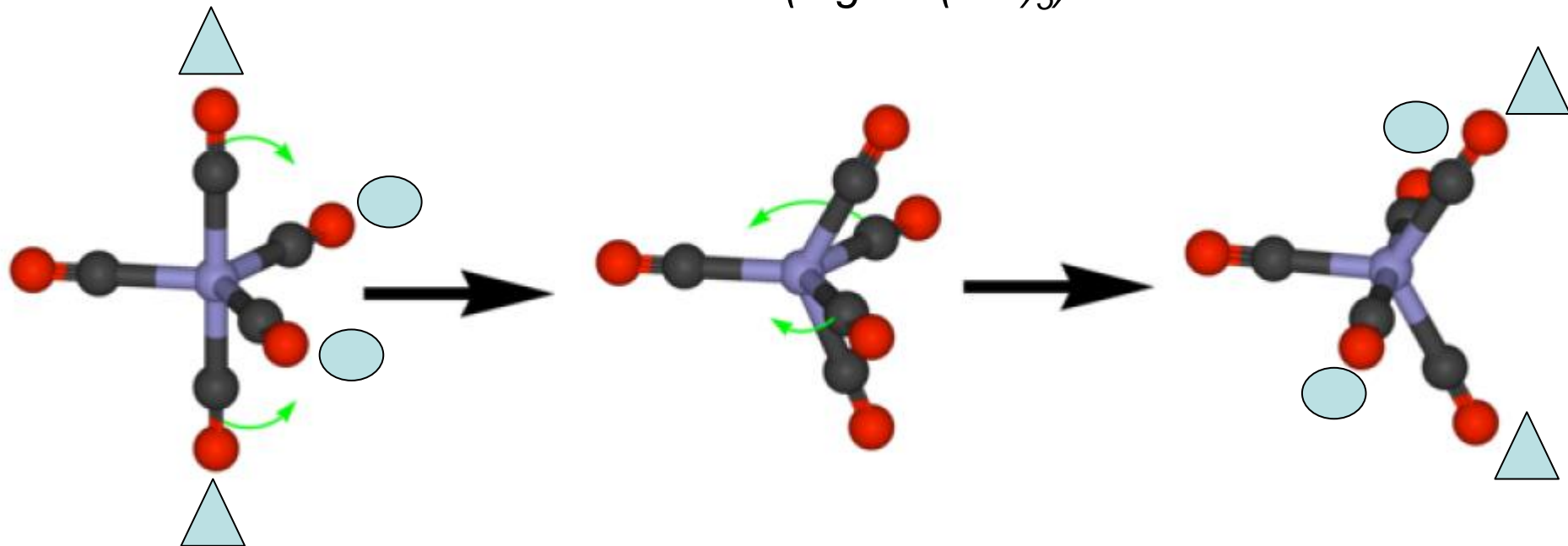
**Figure 1.** Ball-and-stick model of the  $D_{3h}$ -symmetric structure of  $\text{Fe}(\text{CO})_5$ . Fe, lilac; C, gray; O, red.

---

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

Characterized by two intense  $\nu_{\text{C-O}}$  bands in the IR spectrum at 2034 and 2014  $\text{cm}^{-1}$

## Fluxional Behaviour (e.g. $\text{Fe}(\text{CO})_5$ )



The first carbon-13 NMR spectrum of a metal carbonyl was reported in 1958 for iron pentacarbonyl by Cotton, Danti, Waugh, and Fessenden.<sup>1</sup> The result, a single resonance in the carbonyl region, has been shown to be correct by several subsequent investigations;<sup>2-4</sup> in fact the single resonance for  $\text{Fe}(\text{CO})_5$  persists to  $-160\text{ }^\circ\text{C}$ .<sup>4</sup> 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 pseudorotation<sup>5</sup> shown schematically below.

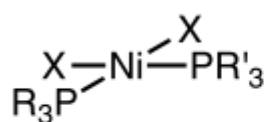
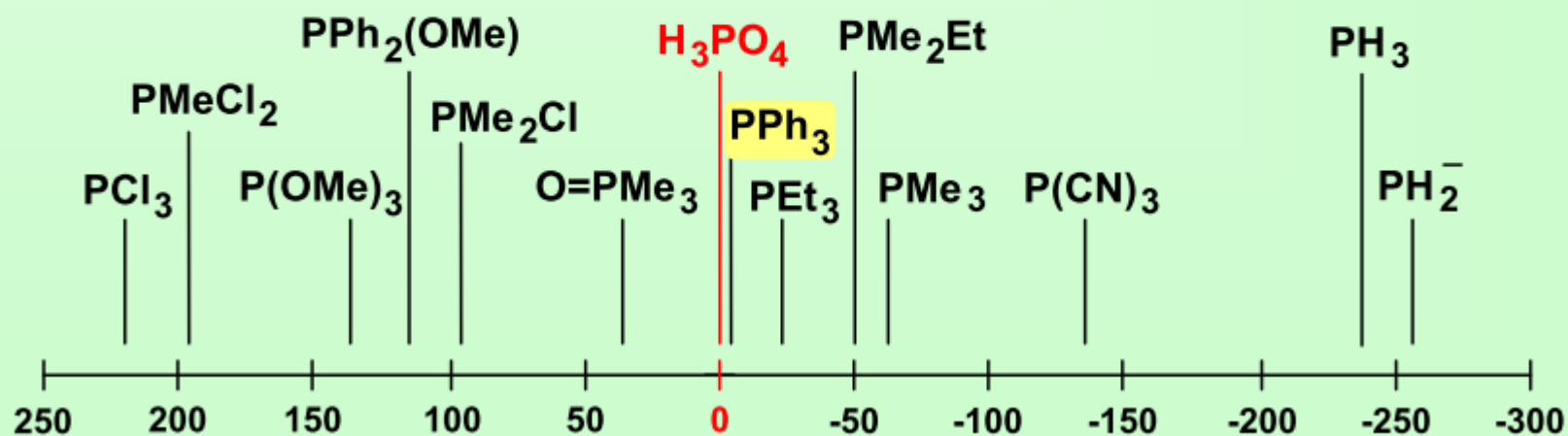
$^{31}\text{P}$  NMR very useful for diamagnetic complexes

## NMR – $^{31}\text{P}$ characteristics of phosphine complexes

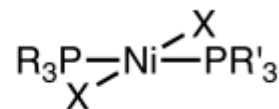
$^{31}\text{P}$  NMR shifts: + 245...-163 ppm

Downfield Region

Upfield Region

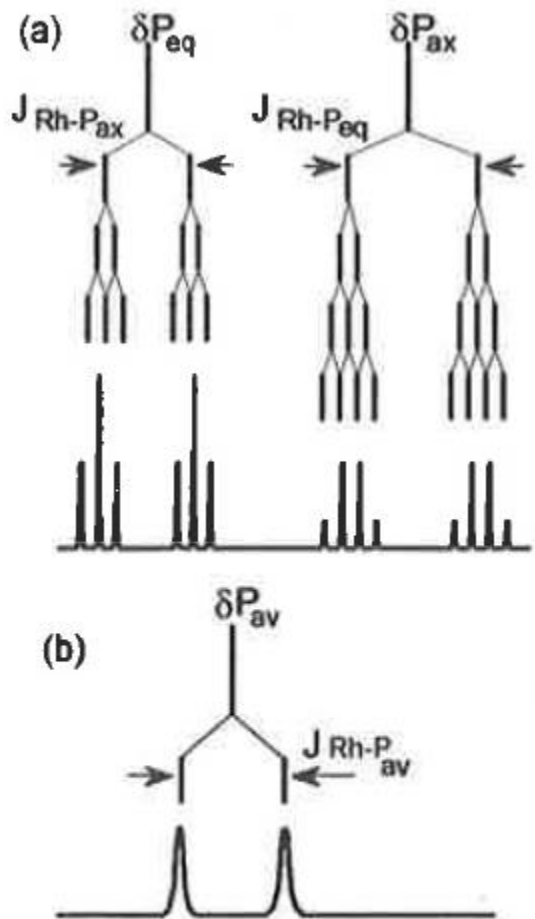


cis  $J_{\text{P-P}}$  65 Hz

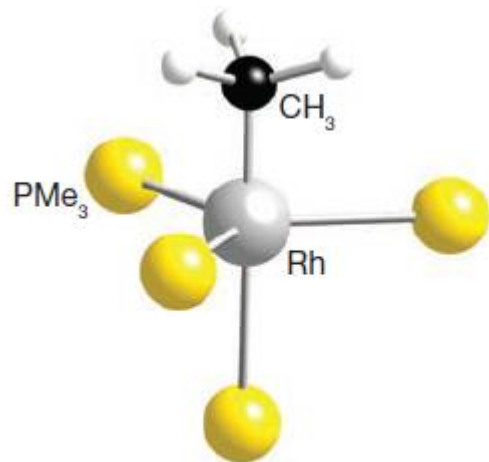


trans  $J_{\text{P-P}}$  300 Hz





**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.



3  $[\text{RhMe}(\text{PMe}_3)_4]$

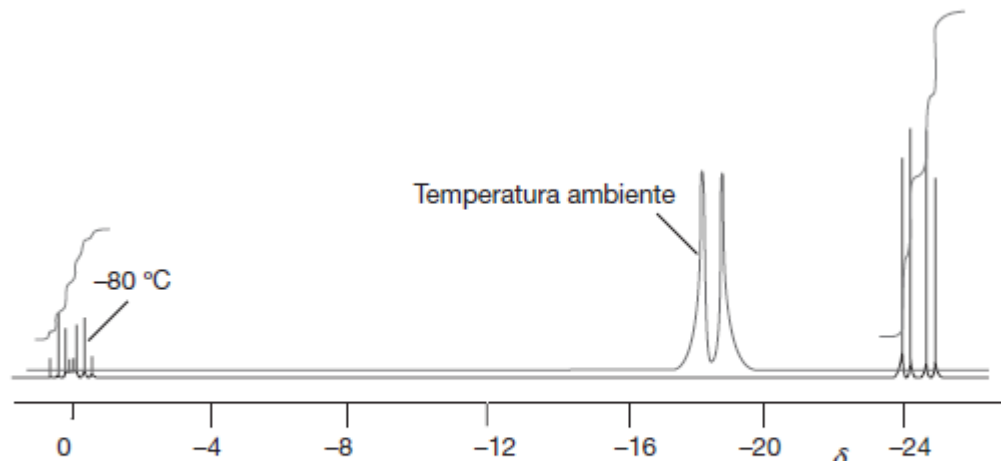


FIGURA 8.27 Gli spettri  $^{31}\text{P}$ -NMR di  $[\text{RhMe}(\text{PMe}_3)_4]$  (3) a temperatura ambiente e a  $-80\text{ }^\circ\text{C}$ .

Dato che la temperatura a cui gli spettri NMR vengono registrati può essere cambiata facilmente, spesso i campioni possono venire raffreddati a una temperatura a cui la velocità di interconversione diventa abbastanza lenta da permettere di osservare risonanze separate. Per esempio, la Figura 8.27 mostra gli spettri  $^{31}\text{P}$ -NMR idealizzati di  $[\text{RhMe}(\text{PMe}_3)_4]$  (3) a temperatura ambiente e a  $-80\text{ }^\circ\text{C}$ . A basse temperature lo spettro consiste di un doppietto di doppietti di intensità relativa 3 a circa  $\delta = -24$ , che deriva dagli atomi di P equatoriali (accoppiati con  $^{103}\text{Rh}$  e con il singolo  $^{31}\text{P}$  assiale), e un quartetto di doppietti di intensità 1, derivante dall'atomo di P assiale (accoppiato con  $^{103}\text{Rh}$  e con i tre atomi  $^{31}\text{P}$  equatoriali).

A temperatura ambiente lo scambio tra i gruppi  $\text{PMe}_3$  li rende tutti equivalenti e si osserva un doppietto (dall'accoppiamento con  $^{103}\text{Rh}$ ).

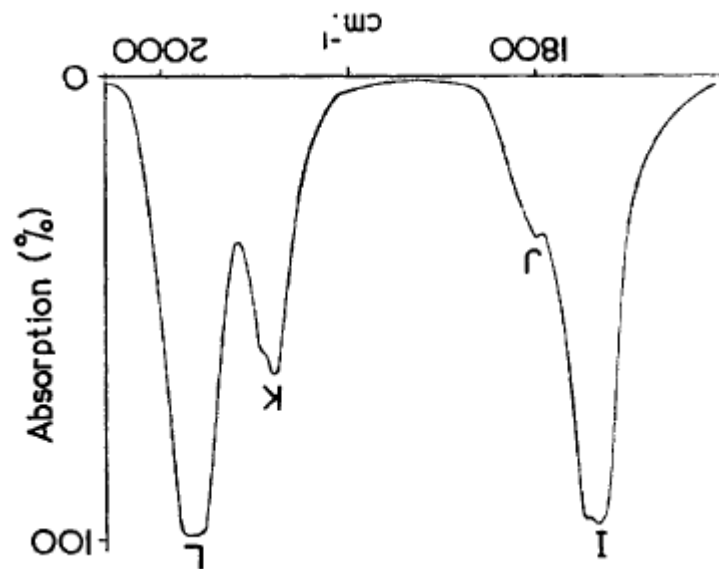
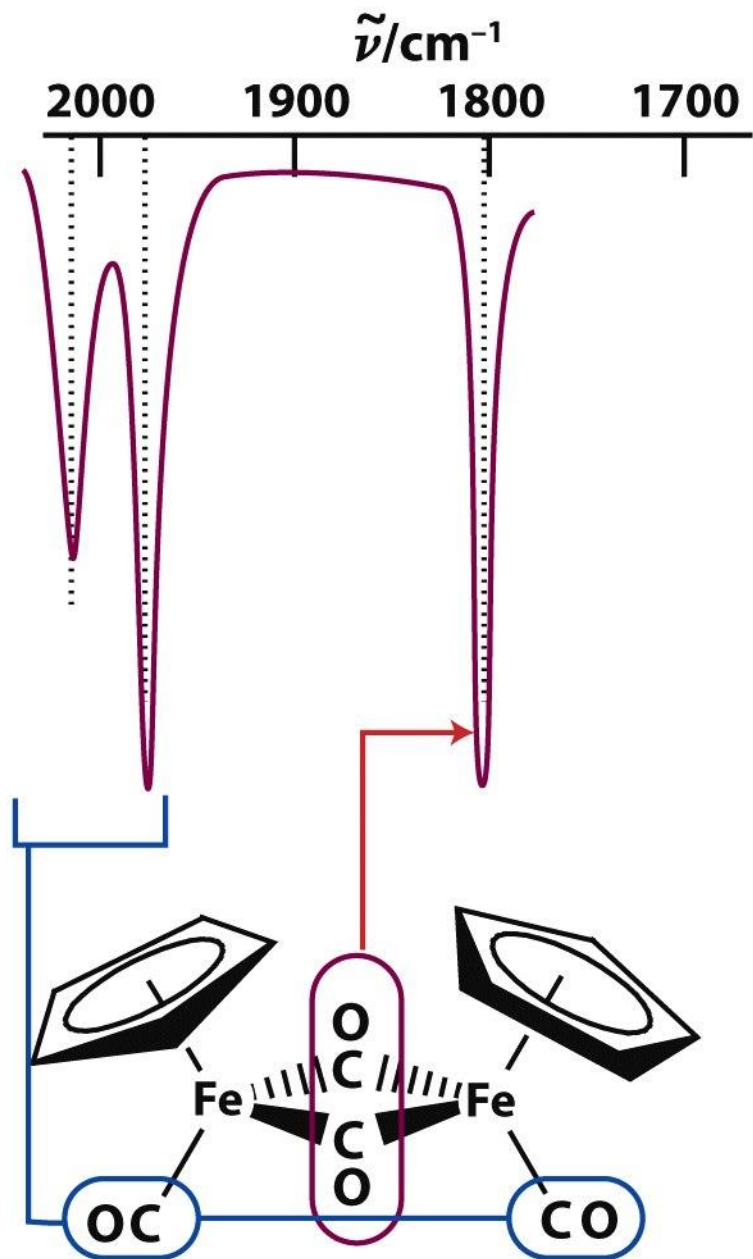
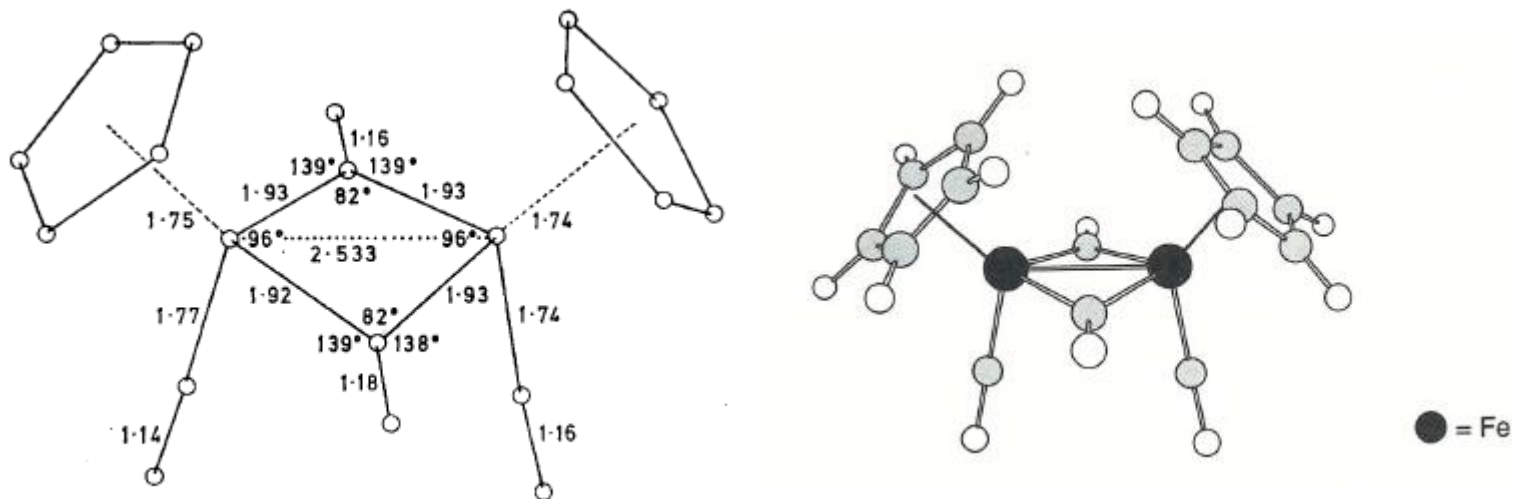


FIGURE 4 The infrared spectrum of  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  in dimethyl sulphoxide solution (1700—2100  $\text{cm}^{-1}$  region)

## The *cis*-Isomer of Bis-( $\pi$ -cyclopentadienyldicarbonyliron)

By R. F. BRYAN\* and P. T. GREENE



FIGURE

*Acta Cryst.* (1958), **11**, 620

## Studies of some Carbon Compounds of the Transition Metals. I. The Crystal Structure of Dicyclopentadienyldi-iron Tetracarbonyl

By O. S. MILLS\*

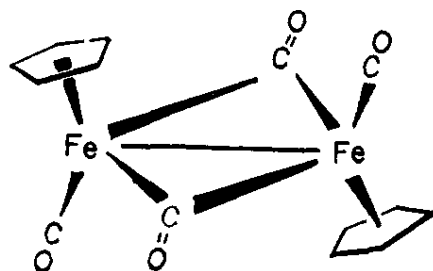


# A Definitive Identification of the Structures of Dicyclopentadienyldiiron Tetracarbonyl in Solution

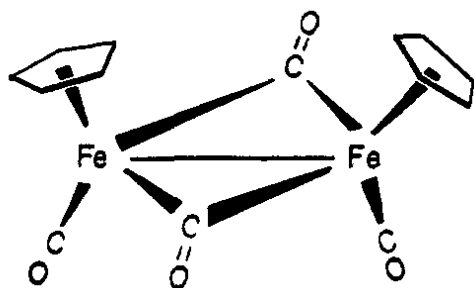
J. G. Bullitt,<sup>11</sup> F. A. Cotton, T. J. Marks<sup>12</sup>

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

*Received January 10, 1970*

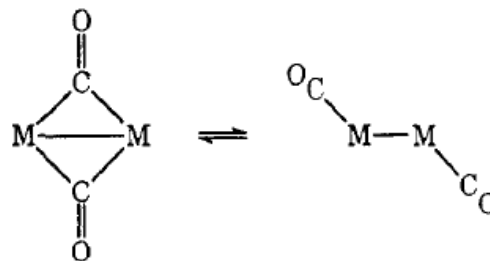


I ( $C_{2h}$ )



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.<sup>10</sup>

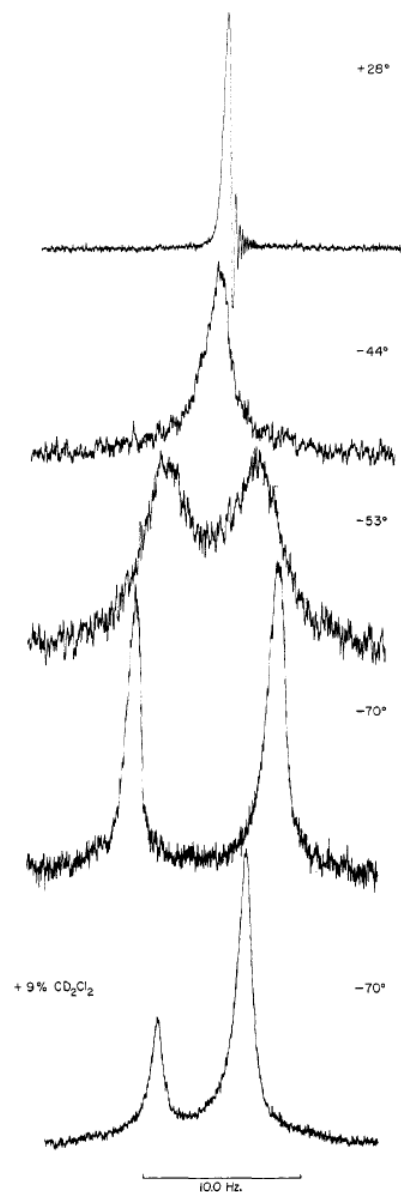
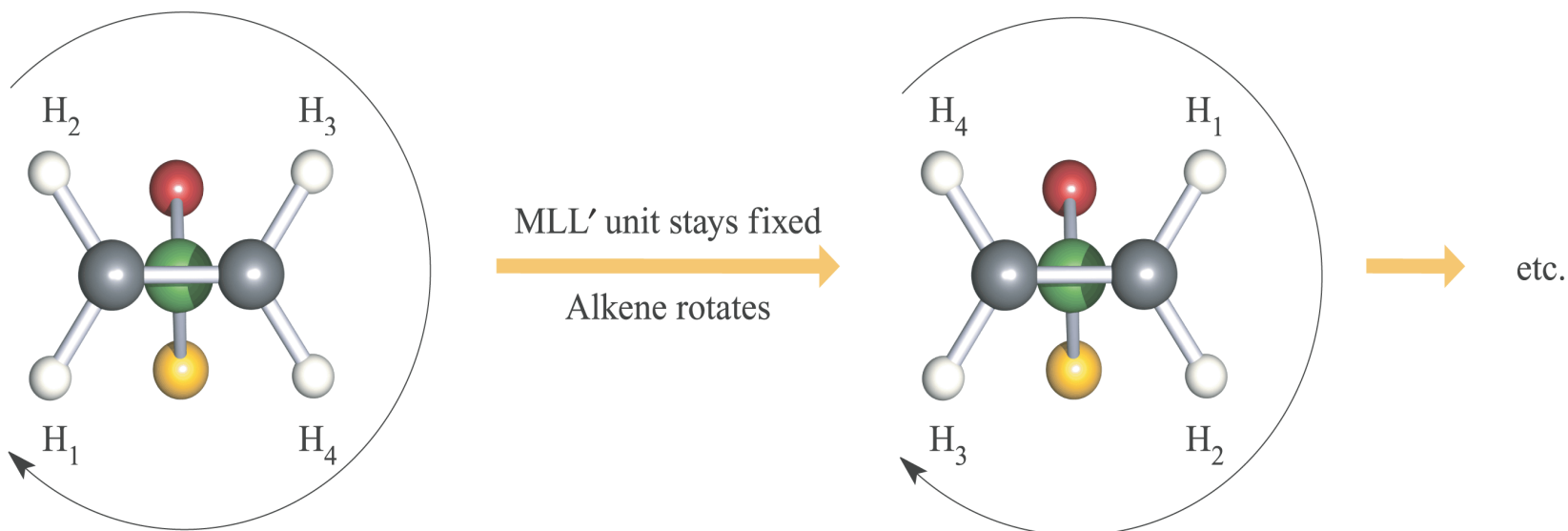


Figure 1. Pmr spectra (100 MHz) for  $(C_5H_5)_2Fe(CO)_4$  at various temperatures. Upper four traces made using  $C_6D_6CDCl_3$ - $CS_2$  (1/3, v/v). Lower trace made using same solvent to which ~9% volume of  $CD_2Cl_2$  was added.

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

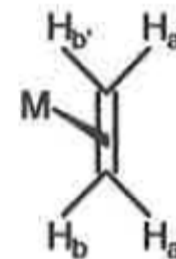
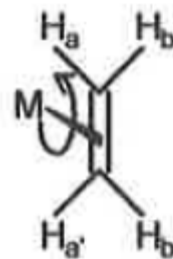
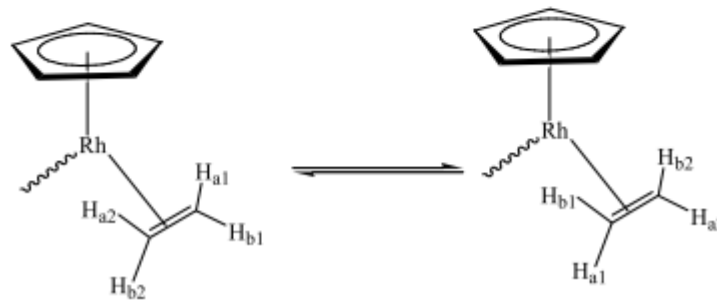
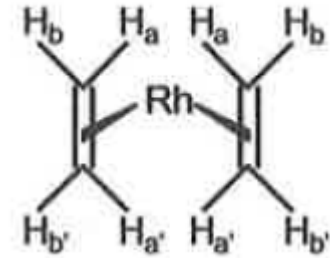
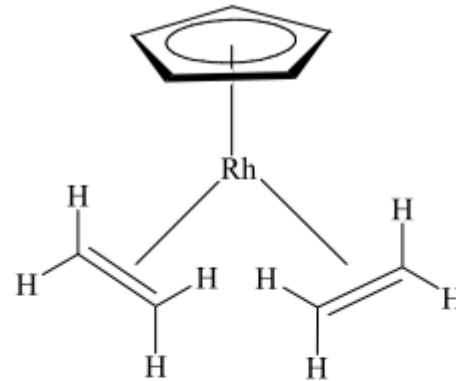
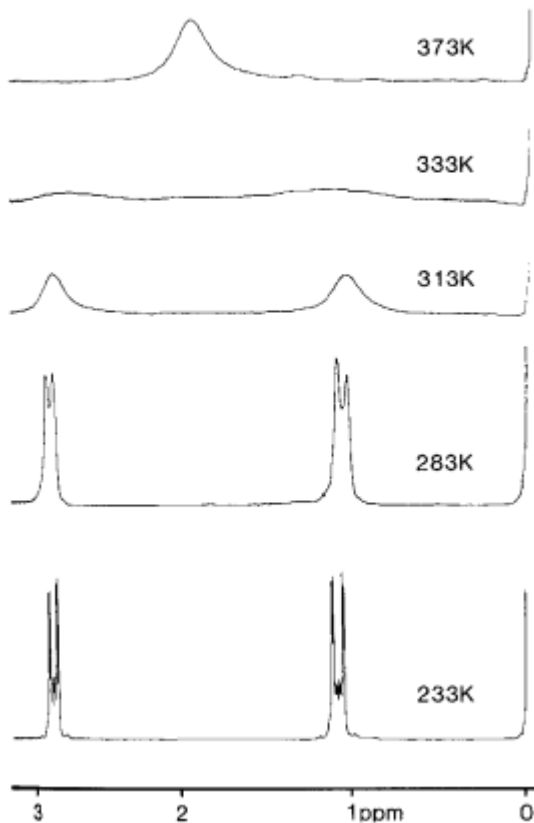
The structures of both the *cis*- and *trans*-isomers of  $(\eta^5-Cp)_2Fe_2(CO)_4$  have been confirmed by X-ray crystallography. In solution, both isomers are present, and the terminal and bridging CO ligands undergo intramolecular exchange. Above 308 K, interconversion of the *cis*- and *trans*-forms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

# Flussionalità del legame $\eta^2$ -alchene



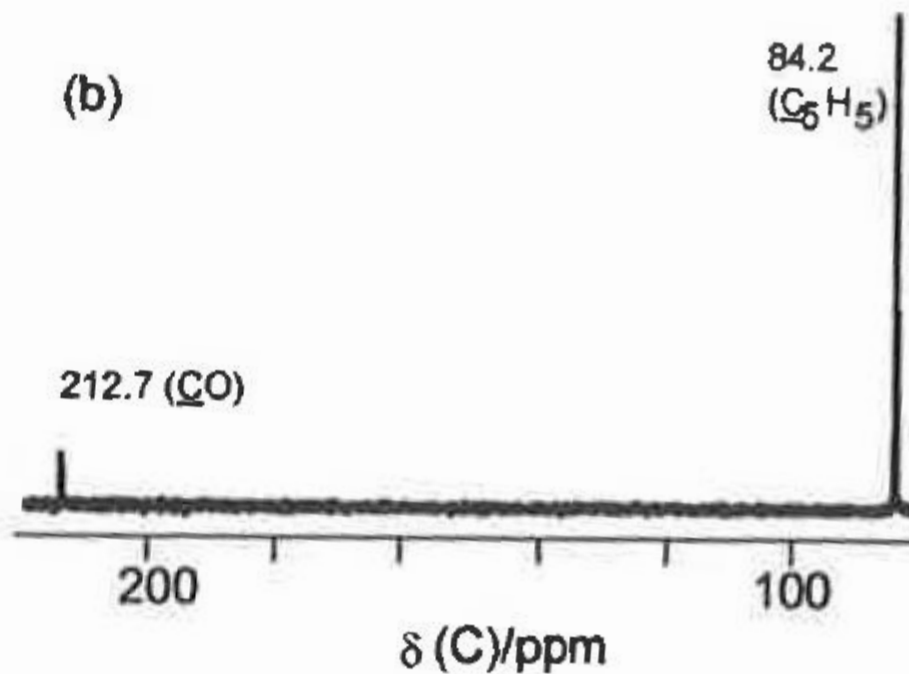
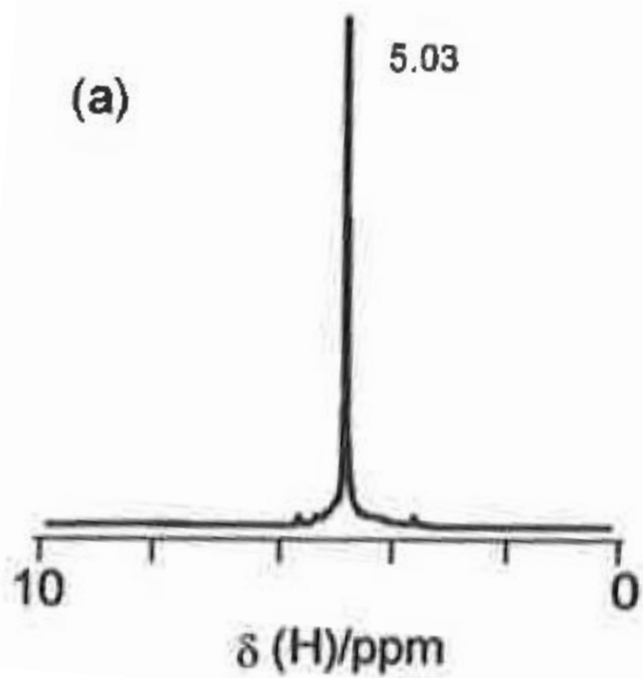
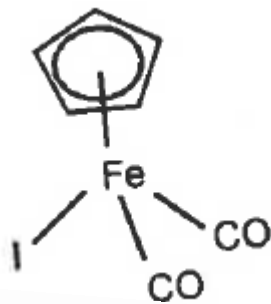
# FluSSIONALITÀ del legame $\eta^2$ -alchene

## Dynamics in alkene complexes

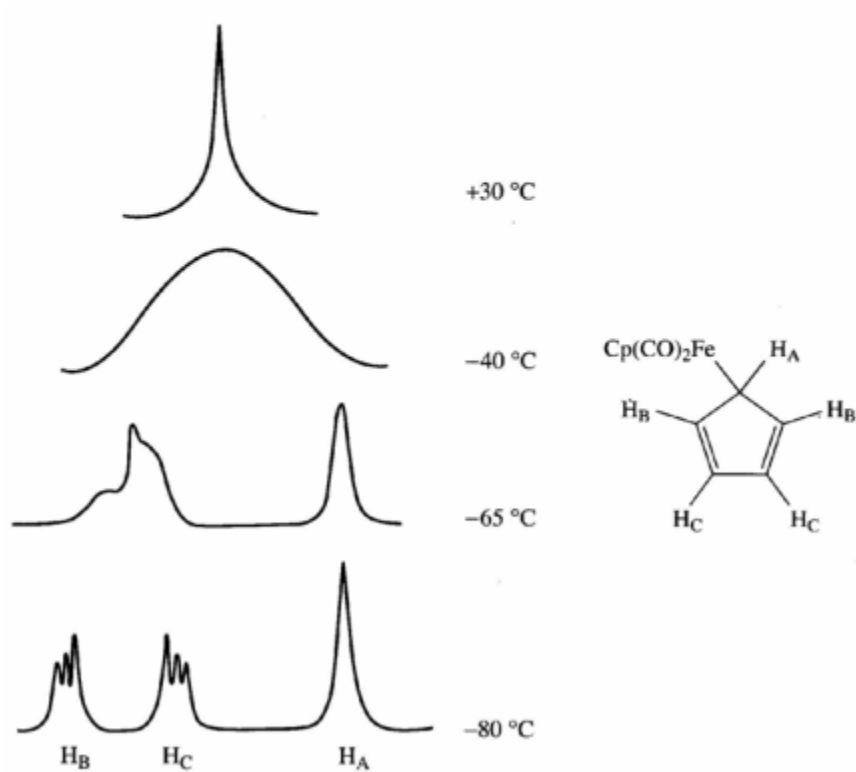
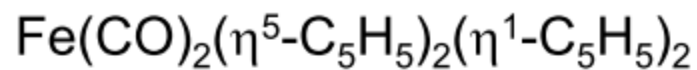




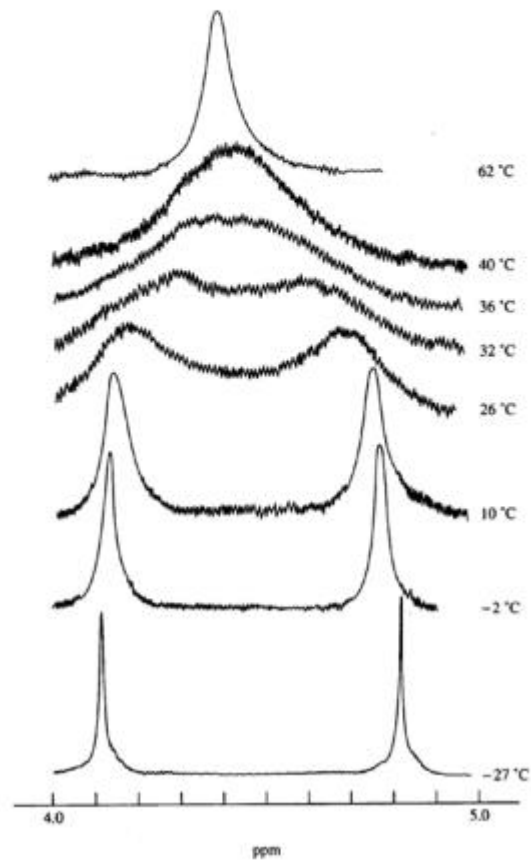
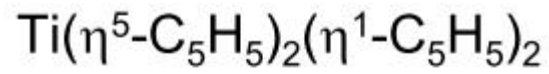
# Flussionalità del legame $\eta^5$ -ciclopentadienile

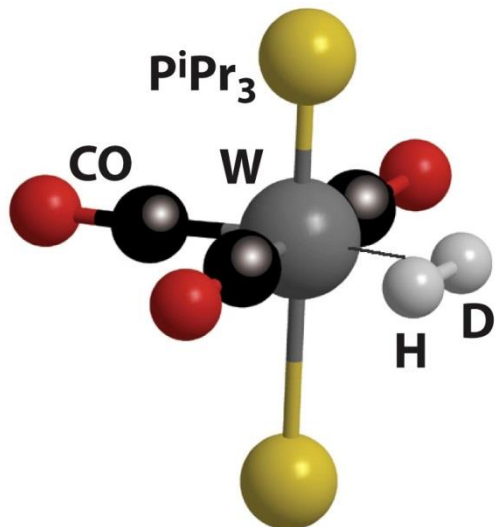


# $\eta^1$ -Ciclopentadienile - Ring-Whizzing

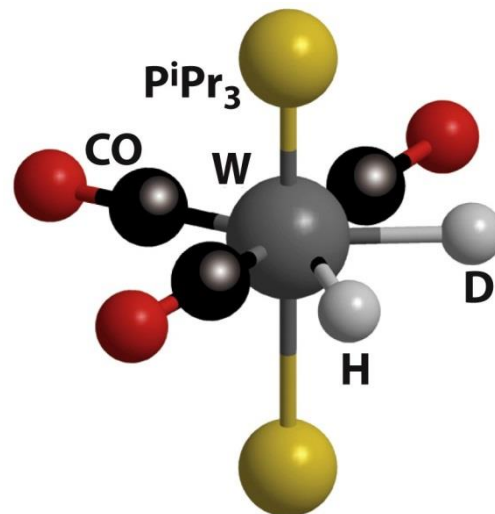


# Flussionalità del ciclopentadienile





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

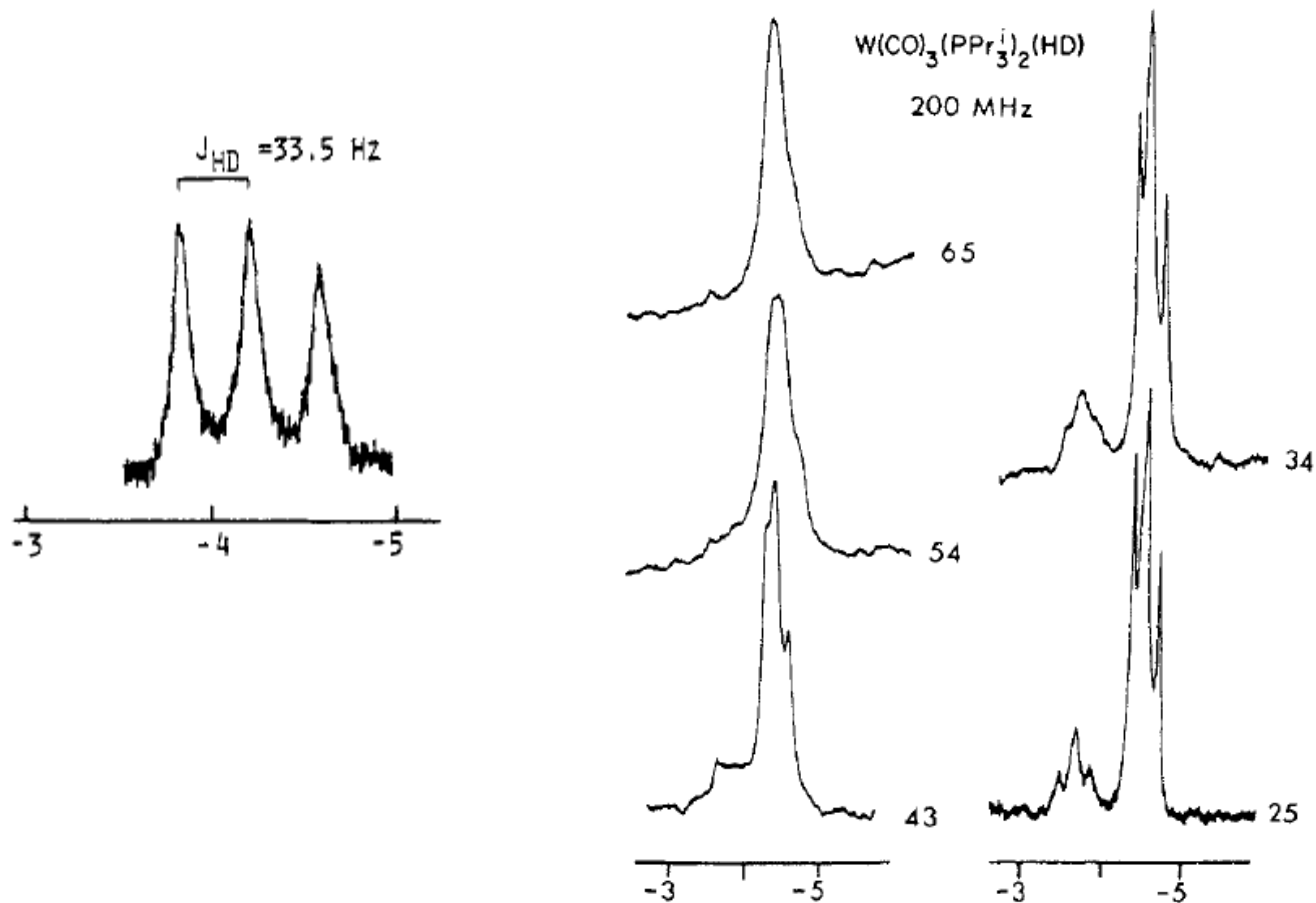


NMR:  $J_{\text{HD}} < 2 \text{ Hz}$

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

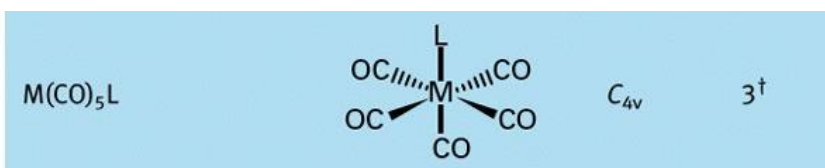
The  $^1\text{H}$  NMR spectrum of the monodeuterated complex  $\text{W}(\text{CO})_3(\text{P-}i\text{-Pr}_3)_2(\text{HD})$  provides unequivocal evidence for direct H-H bonding in the  $\eta^2\text{-H}_2$  ligand. The signal at  $-4.2$  ppm is split by spin 1 deuterium into a 1:1:1 triplet with  $J(\text{HD}) = 33.5$  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.<sup>21</sup> 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.



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

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

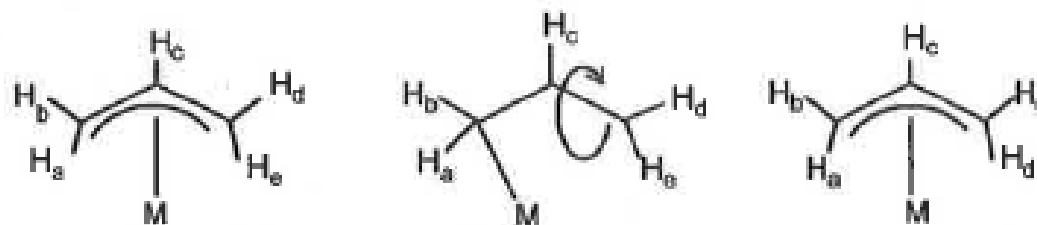
**Hooke's Law:** 
$$\bar{\nu} = \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}} ; \mu = \frac{m_x m_y}{m_x + m_y}$$



**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) <sup>b</sup>	1991 (1949)	
$CH_3CO$	2115	2011	(1970) <sup>b</sup>	2003 (1963)	1664 (1625)

For example, frequently the four protons attached to the terminal carbon atoms in the  $\pi$ -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  $\pi$ -bound to  $\sigma$ -coordinated followed by a rotation of one end of the ligand around the central C–C bond before the  $\pi$ -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  $\sigma$ -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.