

Sigma complexes, C-H activation and functionalisation

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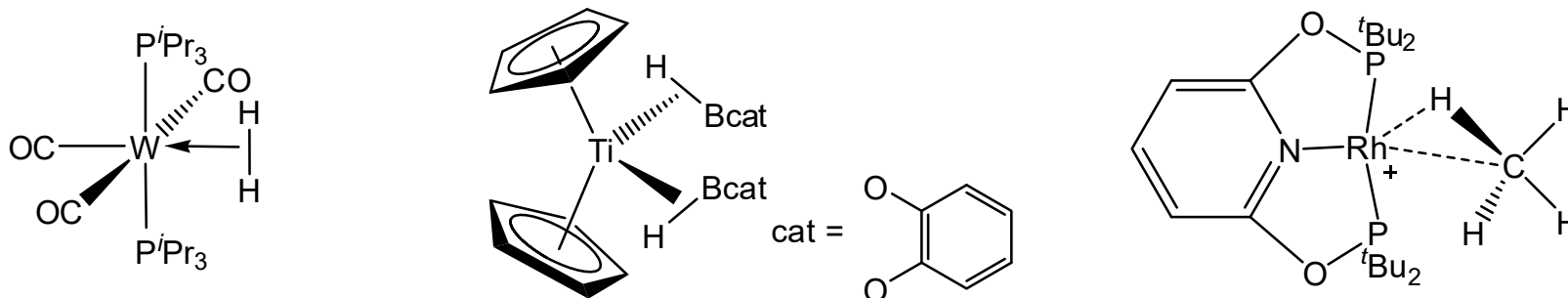
Transition metal sigma complexes: structure and bonding. Fundamental issues of electronic structure and bonding in sigma complexes featuring H-H, C-H, Si-H and B-H bonds, relevance to oxidative addition chemistry, spectroscopic probes of the nature of the interaction with the metal.

C-H activation: Fundamentals and catalysis. C-H...M bonds in organometallic chemistry, a brief survey. C-H activation processes and their mechanisms. Use of C-H activation in synthesis. A discussion of representative catalytic processes using C-H activation, concentrating on mechanism. C-H borylation chemistry.

Lecture 1

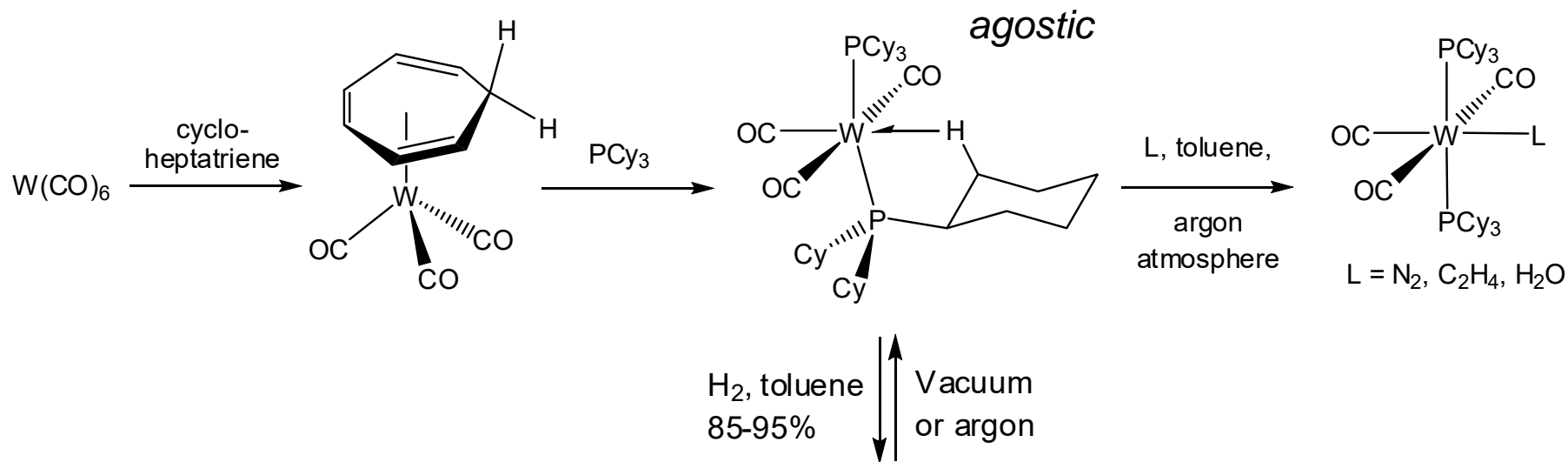
Sigma Complexes

1 Occurrence of transition metal sigma complexes

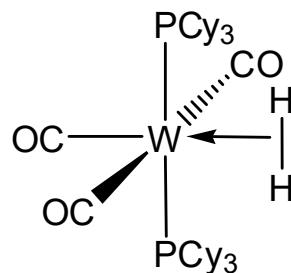


- Sigma complexes of dihydrogen, or featuring coordinated B–H, C–H or Si–H bonds, are a related series of complexes in which the E–H bonding pair of electrons is utilised as the donor towards a transition metal centre;
- Interactions of such ligands involve three-centre bonding and are typically characterised by weak binding and high degrees of fluxionality;
- Such systems can also be viewed as **arrested states** on the pathway to complete oxidative addition of the E–H bond;
- Knowledge of sigma complexes is of vital importance to understanding E–H bond activation processes, and in turn the wide range of catalytic processes in which such steps are implicated.

2 Beginnings: Kubas' η^2 dihydrogen complexes



Vibrational spectroscopy:
 $\nu(H-H) = 2690\text{ cm}^{-1}$
 (cf. 4300 cm^{-1} for free H_2)

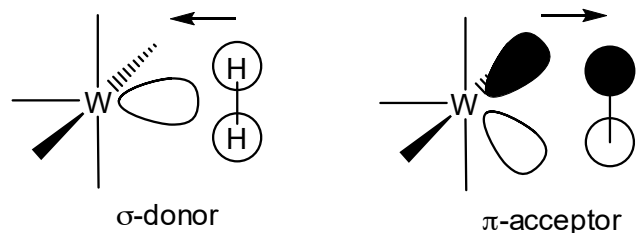


Yellow
 dihydrogen

1H NMR spectroscopy:
 $\delta_H = -4.20\text{ ppm}$
 (cf. $+4.5\text{ ppm}$ for free H_2)

$^1J_{HD} = 33.5\text{ Hz}$ for HD complex
 (cf. 43.2 Hz for free HD)

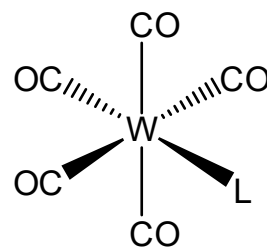
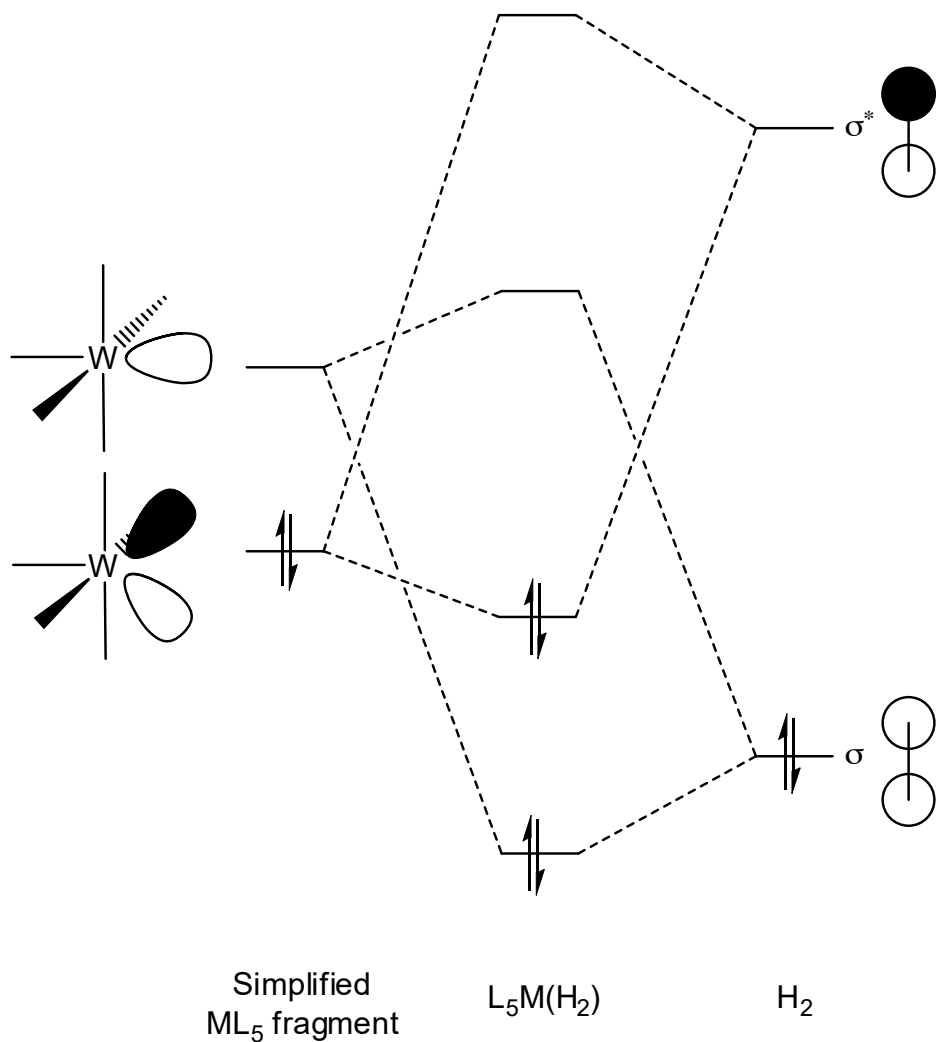
3 Bonding in dihydrogen complexes



Dihydrogen complexes are formally derived from **arrested oxidative addition** of the H₂ molecule;

Requires back-bonding from the metal into the H₂ σ* orbital, but not excessively so as to cleave the H-H bond.

Typically feature metals in low oxidation states, but are cationic, or feature ancillary π-acceptor ligands, such as CO or RNC.

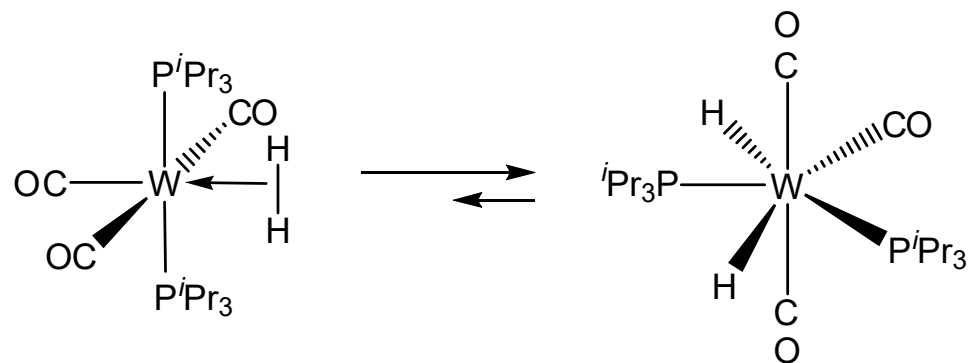


- L = H₂, $\nu = 1971 \text{ cm}^{-1}$
- L = C₂H₄, $\nu = 1973 \text{ cm}^{-1}$
- L = N₂, $\nu = 1961 \text{ cm}^{-1}$
- L = NEt₂H, $\nu = 1919 \text{ cm}^{-1}$

Stretching frequencies of the carbonyl ligand *trans* to L

4 Dihydrogen or bis(hydride) complex?

Kubas' initial dihydrogen complex was subsequently found to exist in solution as a 4:1 equilibrium mixture with the corresponding dihydride (minor component):



NMR for dihydrogen isomer:

$$\delta_H = -4.20 \text{ ppm}$$

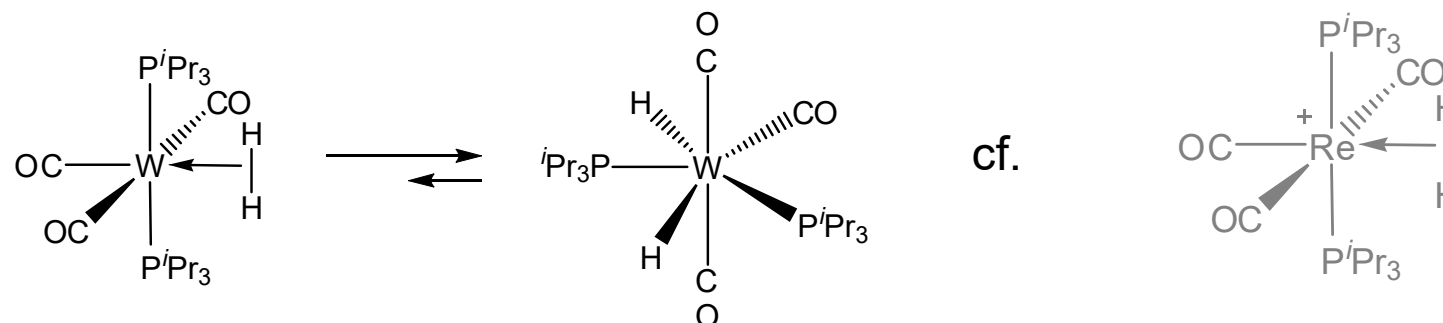
$$\delta_P = 33.5 \text{ ppm}$$

NMR for dihydride isomer:

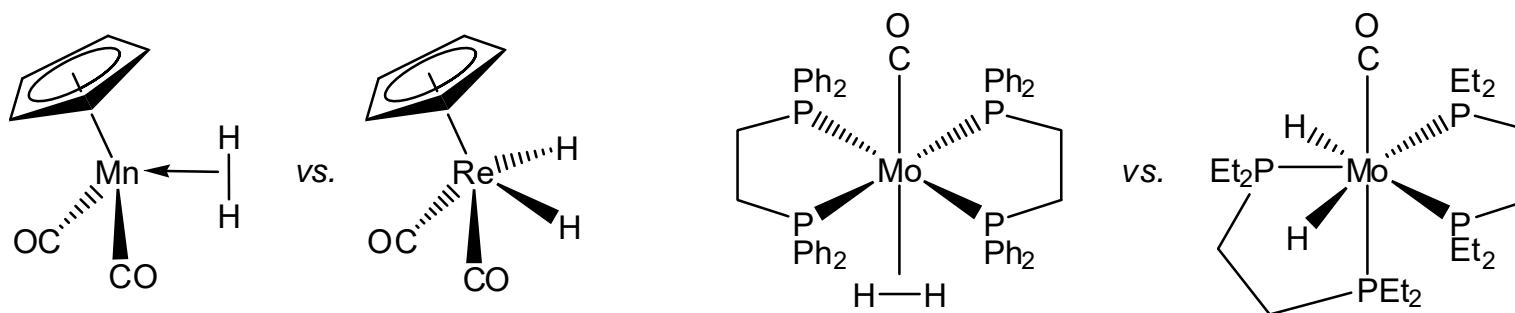
$$\delta_H = -2.15, -4.50 \text{ ppm}$$

$$\delta_P = 30.8, 39.5 \text{ ppm}$$

5 The role of charge and position in the periodic table (3d versus 5d)

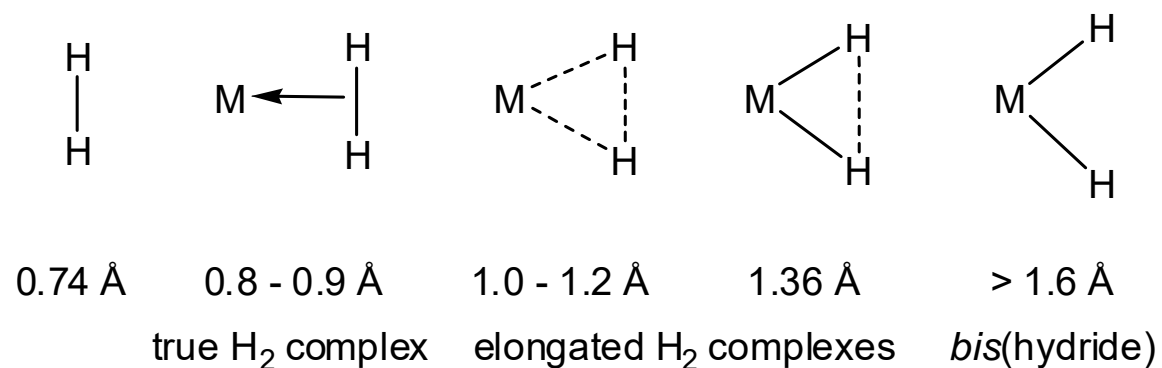


The iso-electronic rhenium cation is shown to exist solely as the dihydrogen isomer, due to **reduced** back-bonding in the cation (lower energy metal orbitals);



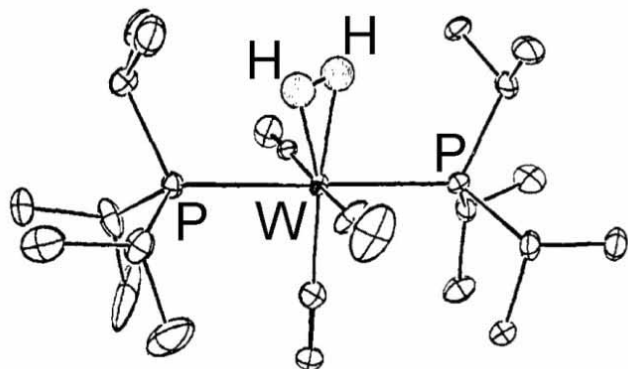
The extent of back-bonding from the metal centre plays a crucial role in determining the relative stabilities of isomeric pairs – thus 5d metal complexes and/or those featuring more electron releasing ligands show greater tendency to be bis(hydrides).

6 Characterisation of dihydrogen complexes: X-ray diffraction



X-ray crystallography is of very limited use in locating hydrogen atoms in the vicinity of heavy metal centres;

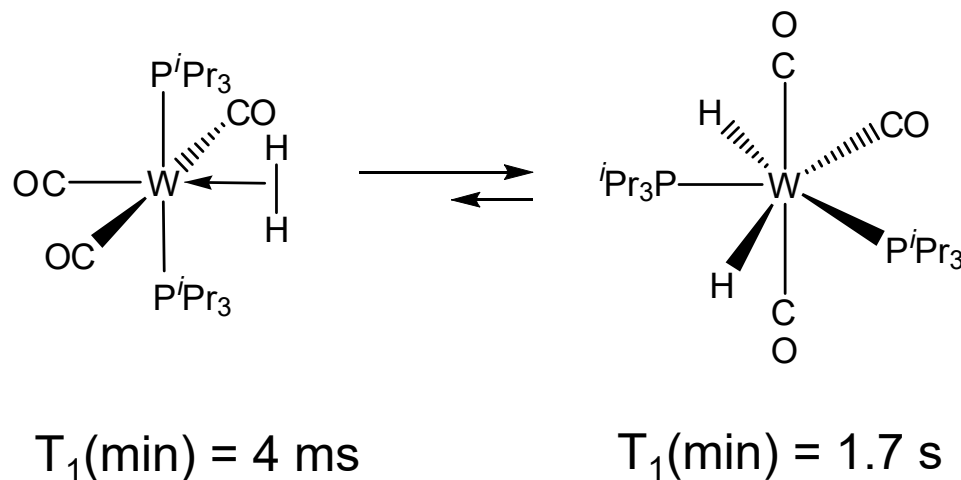
Neutron diffraction is better but needs very large crystals.



Molecular structure of related P/Pr₃ complex from X-ray and neutron diffraction studies.
 $d(\text{H-H}) = 0.84 \text{ \AA}$ (neutron diffraction)
cf. 0.74 \AA for uncoordinated dihydrogen

7 Characterisation of dihydrogen complexes: NMR Spectroscopy

A NMR-derived technique useful for characterizing H_2 complexes is *via* determination of the **spin-lattice relaxation time T_1** [strictly $T_1(\text{min})$];



Dipolar relaxation by interaction with a neighbouring hydrogen atom has an $1/r^6$ distance dependence.

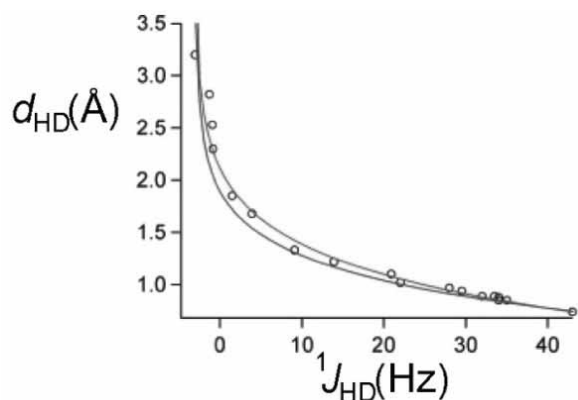
Longer relaxation times (>50 ms at 250 MHz) are therefore found for *bis*(hydride) systems than for dihydrogen complexes (typically <35 ms).

8 Characterisation of dihydrogen complexes: NMR Spectroscopy

In solution the $^1J_{\text{HD}}$ coupling constant obtained from the corresponding HD isomer has been shown to be correlated with the H–D separation.

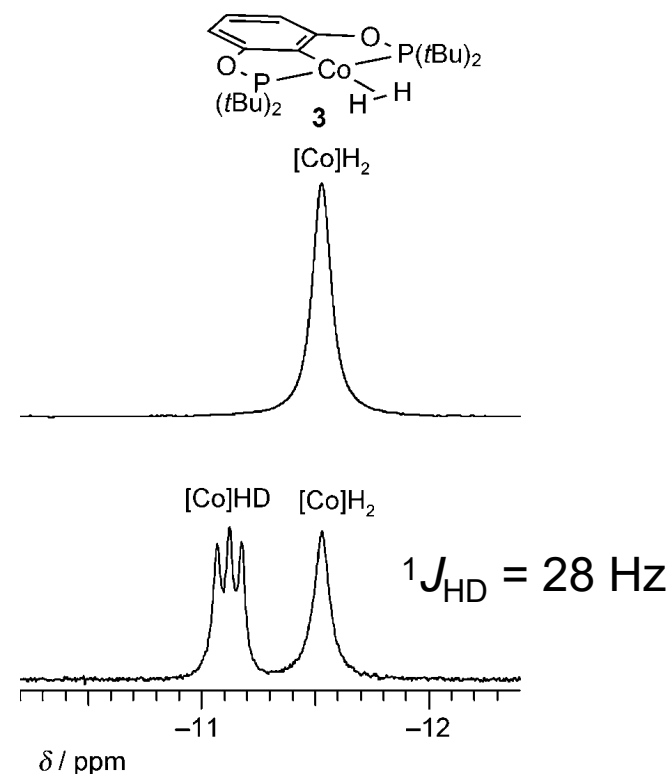
The value measured for Kubas' original system (33.5 Hz) is smaller than in free HD (43.2 Hz)

A reduction in $^1J_{\text{HD}}$ of 50 - 80% (*cf.* free HD) is observed for genuine H_2



Empirical correlation
of $^1J_{\text{HD}}$ and $d(\text{H-D})$

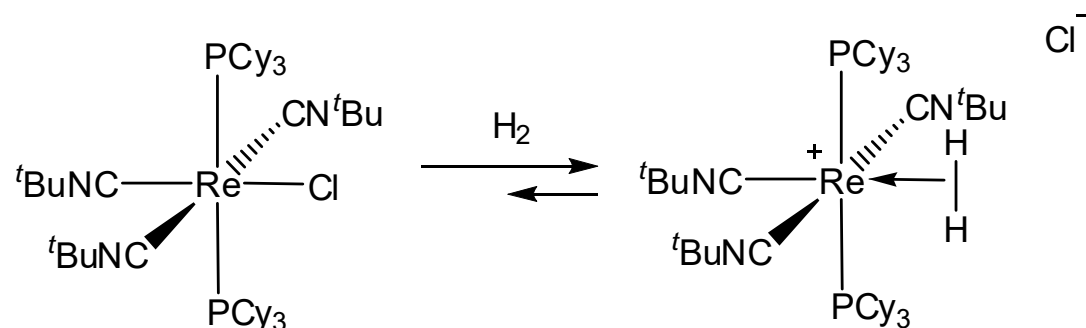
**Dihydrides isomers show no
(or very small) H–D coupling**



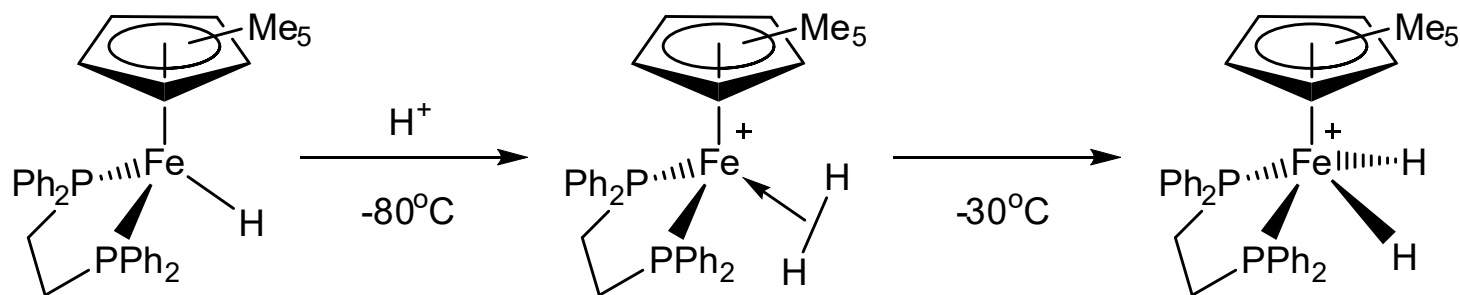
9 Synthetic approaches to dihydrogen complexes

Dissociation of a weakly bound ligand (i.e. agostic interaction): Kubas

In rare cases stronger bound ligands can be lost (i.e. chloride):



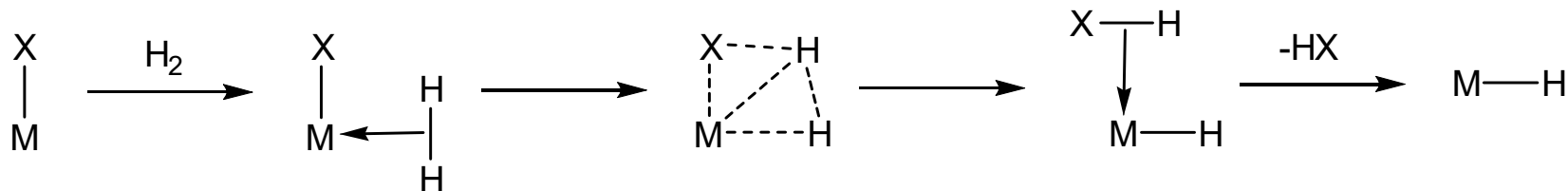
Protonation of a neutral hydride can lead to a dihydrogen complex. Need to use an acid with a weak conjugate base (i.e. HCl will not do).



Reference: *J. Am. Chem. Soc.*, 1996, **118**, 10792 (Heinekey *et al.*)

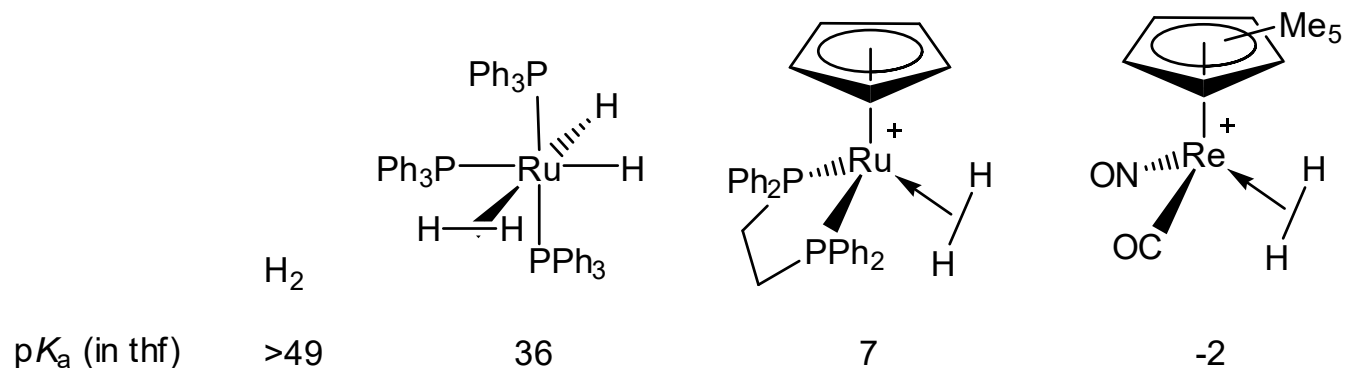
11 Reactivity of dihydrogen complexes

Exchange with *cis* ligands via σ -bond metathesis (where X = H, halide, alkyl *etc.*) or a σ -complex assisted metathesis (not shown, see lecture 2):



The four-centre transition state provides mechanism for exchange in d^0 systems, and a rationale for facile fluxional behaviour with *cis* hydrides (*i.e.* where X = H);

The hydrogen atoms of dihydrogen complexes also display markedly enhanced **Brønsted acidity** compared to free H_2 :



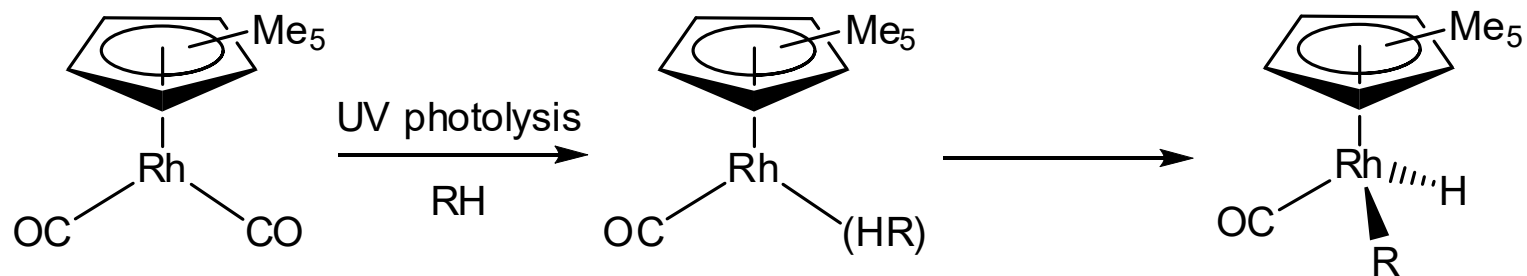
C–H sigma interactions

[see Appendix for B–H and Si–H sigma complexes]

12 Complexes containing coordinated C–H bonds

Complexes of alkanes with transition metals have been **implicated** through kinetic studies as intermediates in the oxidative addition of C–H bonds (see later).

Definitive structural characterisation of a metal alkane complex rare; spectroscopic data in solution has been obtained at low temperature:



alkane (short lived) complex
Kr–matrix

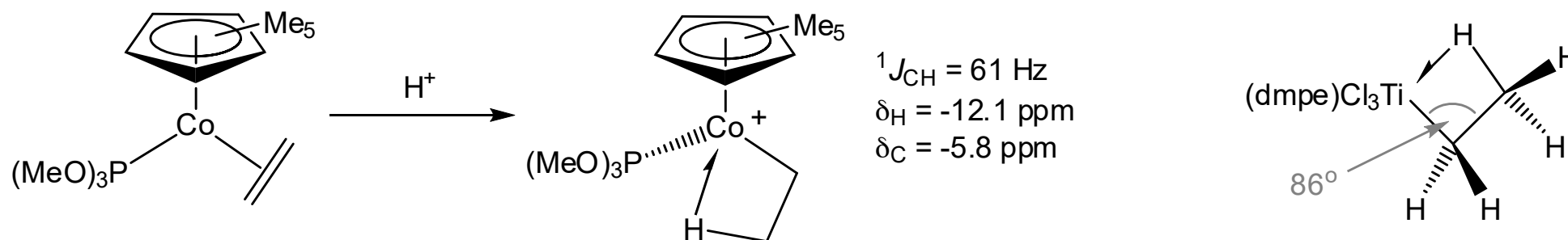
13 Agostic C–H bonds

Intramolecular coordination of alkyl CH bonds is less entropically disfavoured and consequently much more common.

Can be viewed as arrested CH oxidative addition or β hydride elimination processes.

Characterisation of agostic interactions: X-ray diffraction is unreliable for H atom positions, although can reveal distortion in the heavy atom skeleton.

More informative are reduced $\nu(\text{CH})$ stretching frequencies, upfield shifts in ^1H and ^{13}C resonances and reduced $^1J_{\text{CH}}$ coupling constants in NMR.

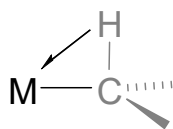


Reference: *J. Organomet. Chem.*, 1983, **250**, 395 (Green *et al.*)

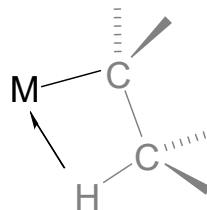
14 Aside: Agostic vs Sigma

A sigma interaction is closely related to an agostic interaction, but is an **intermolecular** interaction (3c-2e).

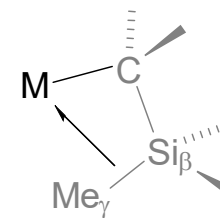
3c-2e
Intramolecular
agostic bonds



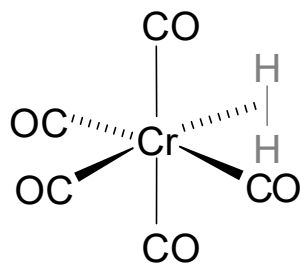
α -agostic



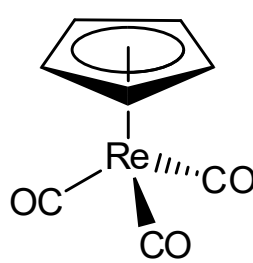
β -agostic



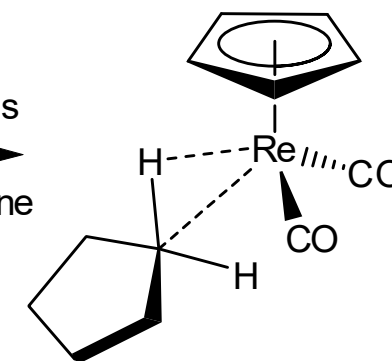
β -Si-C agostic



Dihydrogen sigma complex

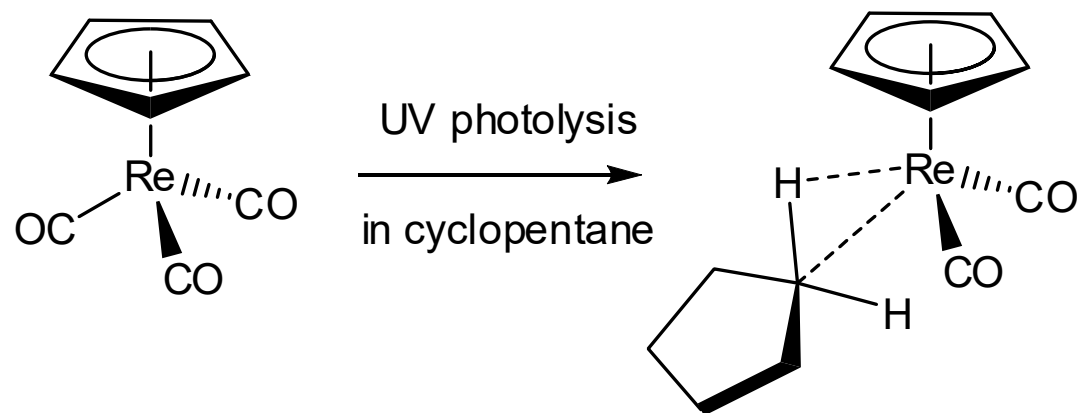


UV photolysis
in cyclopentane



Alkane sigma complex

15 Coordination of pentane and cyclopentane



Synthesis by photolysis in an alkane solvent in an NMR spectrometer probe at very low temperature (-80°C).

Not stable at room temperature

Binding of cyclopentane occurs in $\eta^2\text{-C,H}$ fashion, *i.e.* through a single CH bond: **one** isomer.

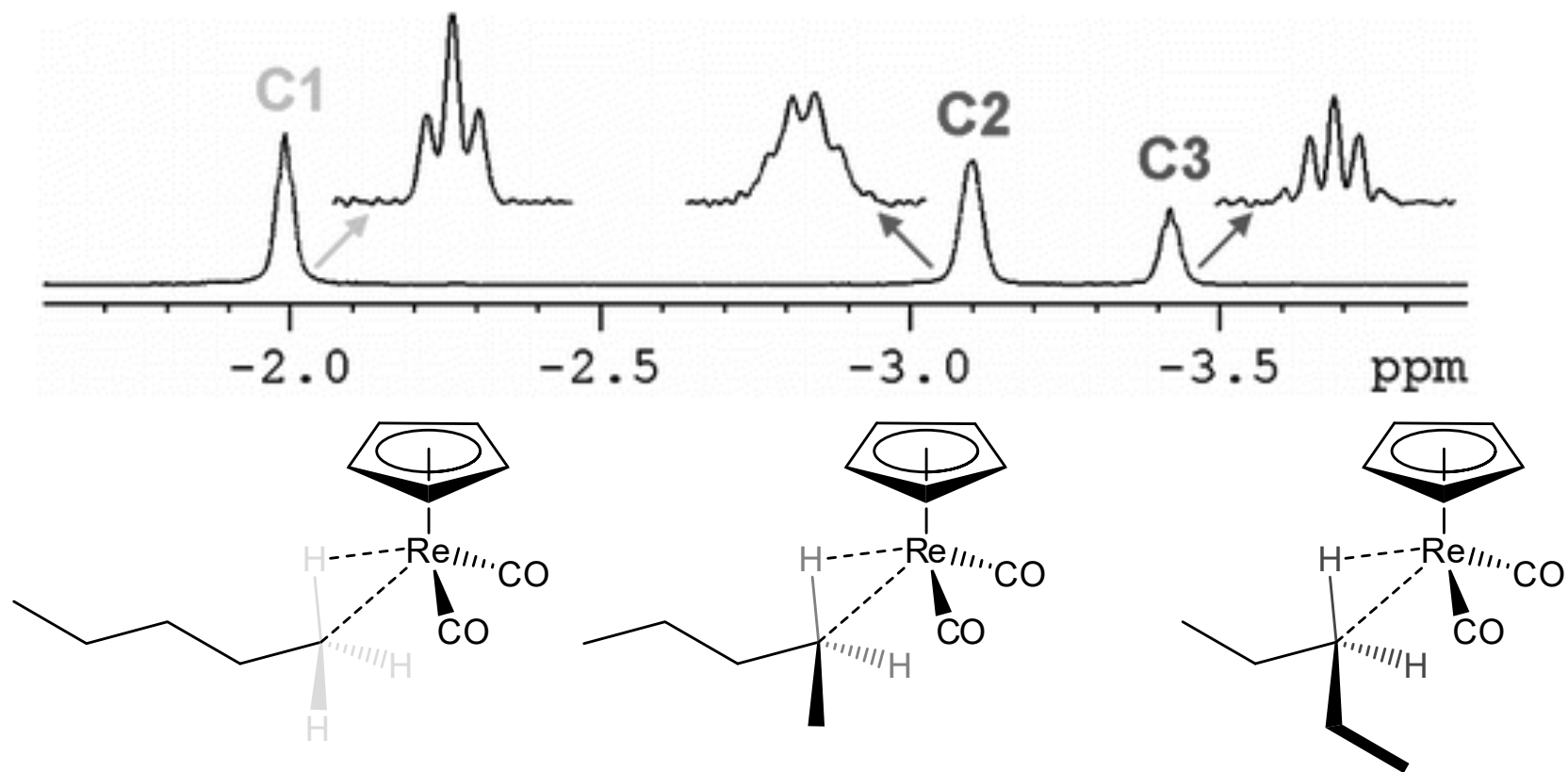
Downfield shifted ^1H NMR resonance for the coordinated pentane ($\delta_{\text{H}} = -2.32$ ppm).

Rapid fluxional exchange between CH bonds within the methylene (CH_2) group

16 Coordination of pentane and cyclopentane

Similar complexes are made with pentane (**three** isomers)

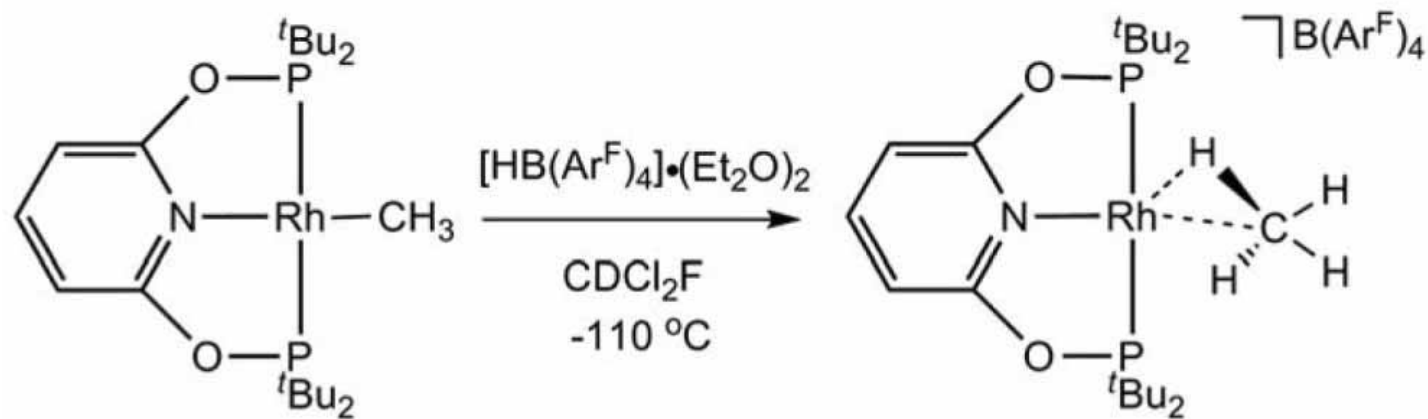
Preference for CH₂ vs. CH₃ coordination.



References: *J. Am. Chem. Soc.*, 2005, **127**, 4134 & 1998, **120**, 9953 (Ball *et al.*)

17 Coordination of methane

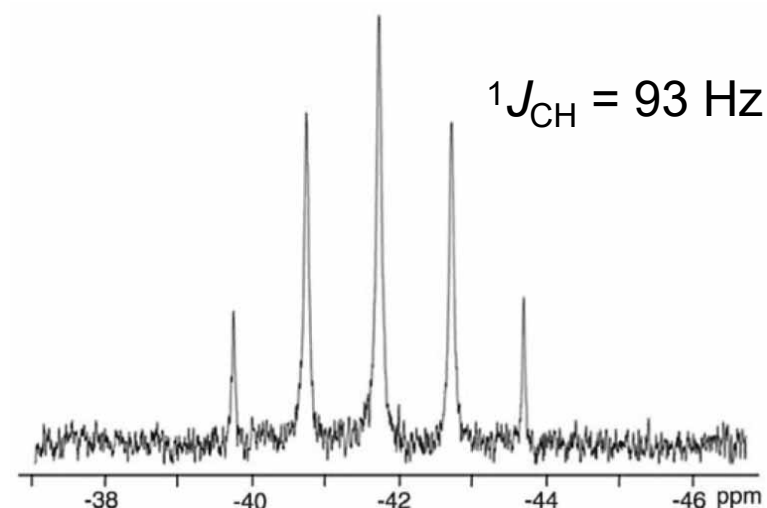
Synthesis: low temperature protonation of a Rh(I) methyl complex



Half-life at -87°C of 83 minutes

$\Delta G^\ddagger = 60.7 \text{ kJ mol}^{-1}$ for methane dissociation

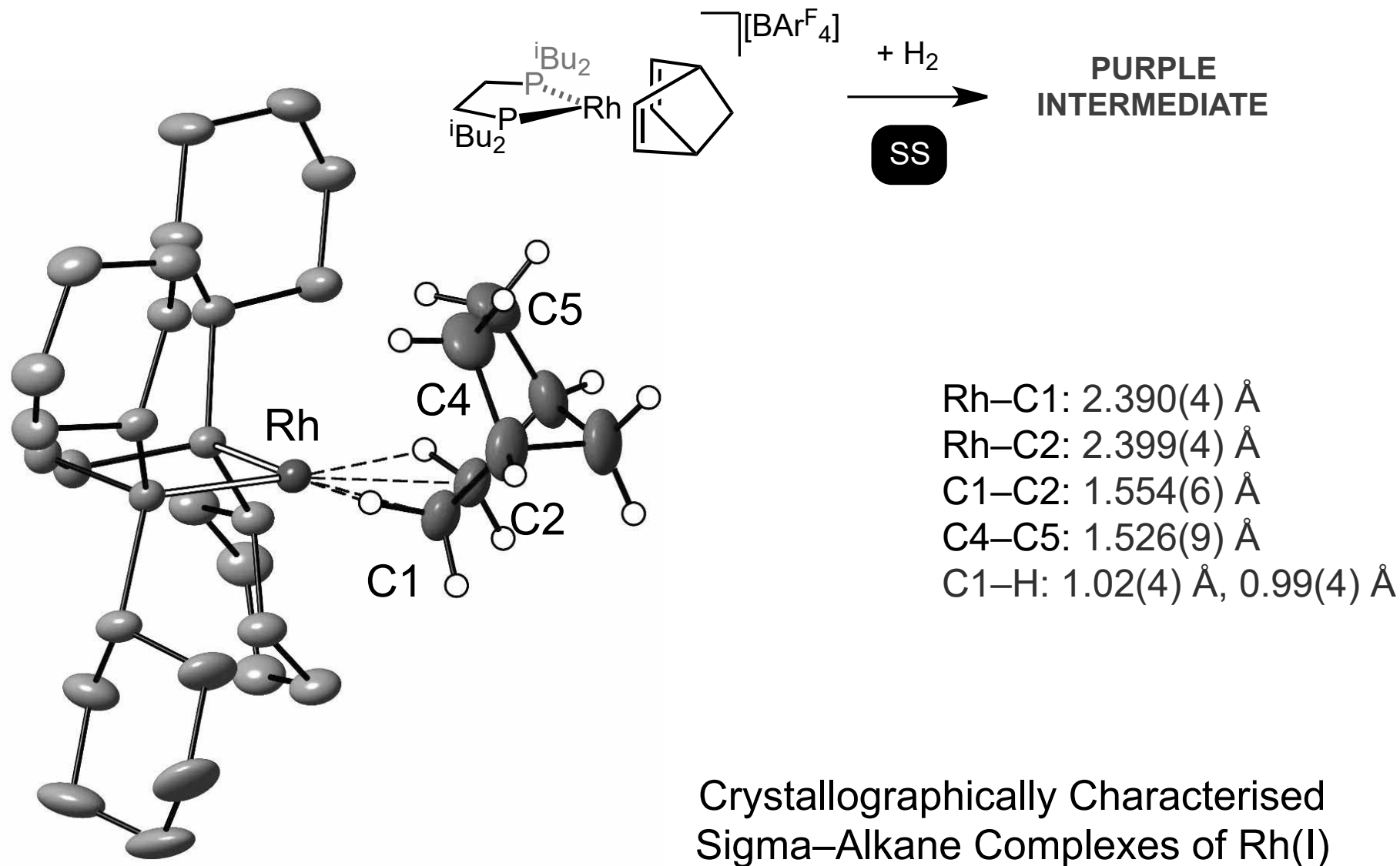
Rapidly fluxional CH_4 ligand even at -110°C



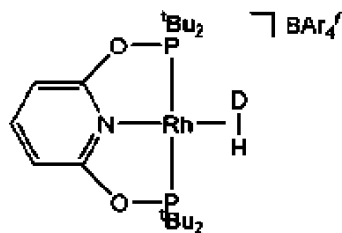
^{13}C NMR spectrum (^{13}C enriched) at -110°C
(free methane -4 ppm)

Reference: *Science*, 2009, **326**, 553; *JACS* 2013, **135**, 15933 (Brookhart *et al.*)

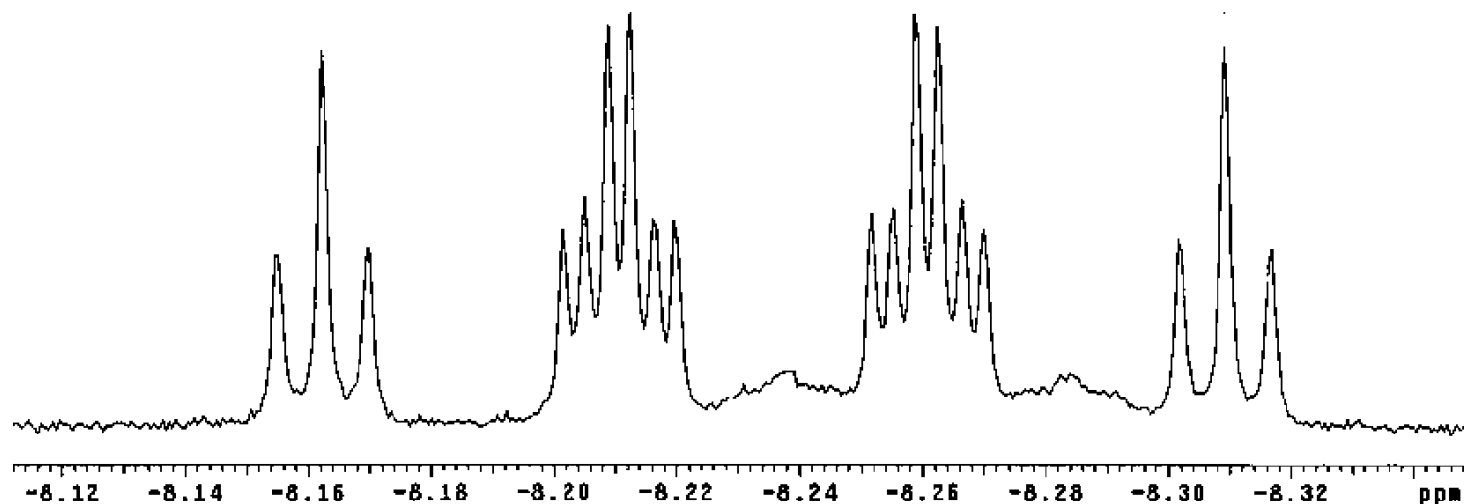
18 Characterisation in the Solid-State



Question



¹H NMR spectrum



$$J(\text{DH}) = 30 \text{ Hz}, J(\text{RhH}) = 27 \text{ Hz}, J(\text{PH}) = 4 \text{ Hz}$$

$$T_1(\text{min}) = 33 \text{ ms}$$

Reference: *Inorg. Chem.* **2012**, *51*, 4672 (Heinekey *et al.*)

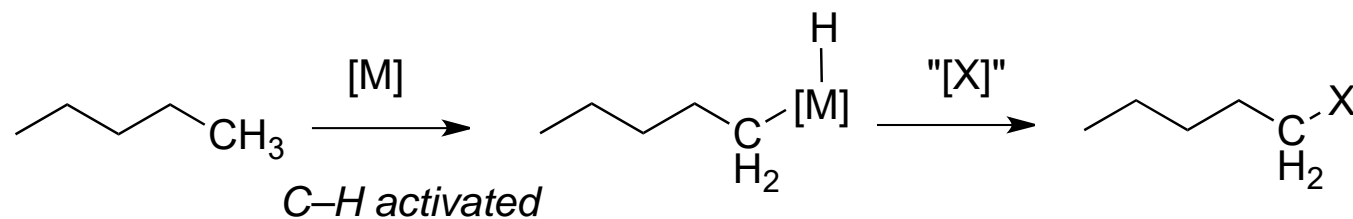
Lecture 2

C–H sigma interactions

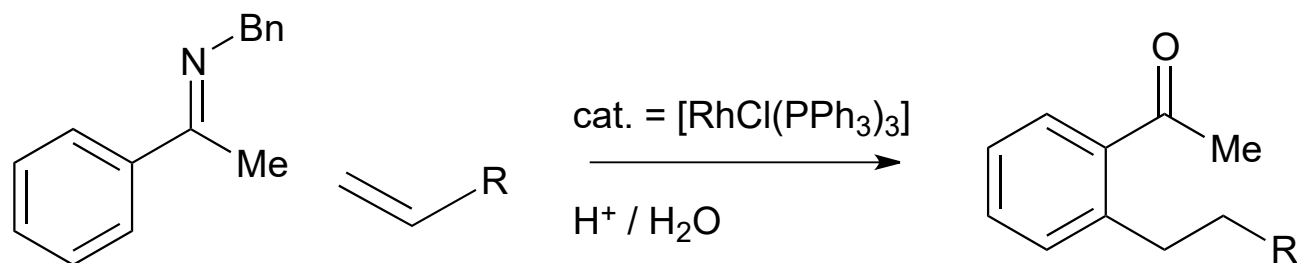
&

Catalysis involving C–H activation

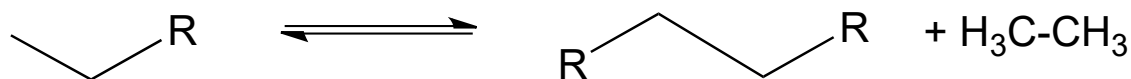
19 The Goal of C–H Activation and Functionalisation: Advantages



Activate a C–H bond *selectivity* (1°, 2° or 3°), *catalytically* to form a *product of value*.



Organic Synthesis



Hydrocarbon Upgrading

Lower weight alkanes to higher weight alkanes.

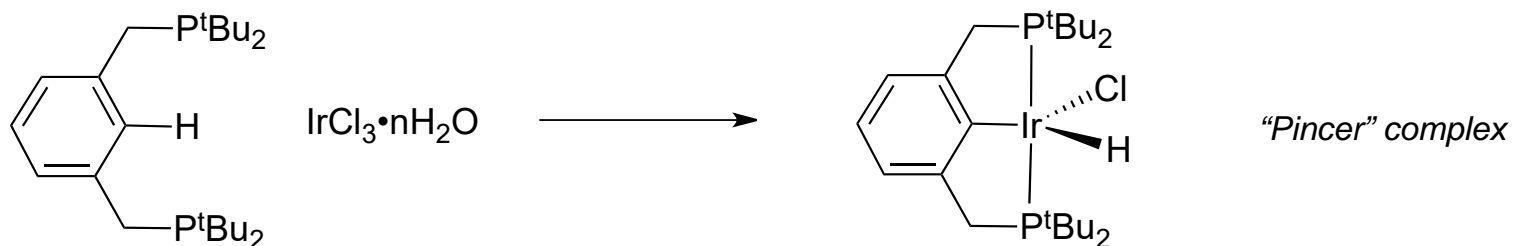
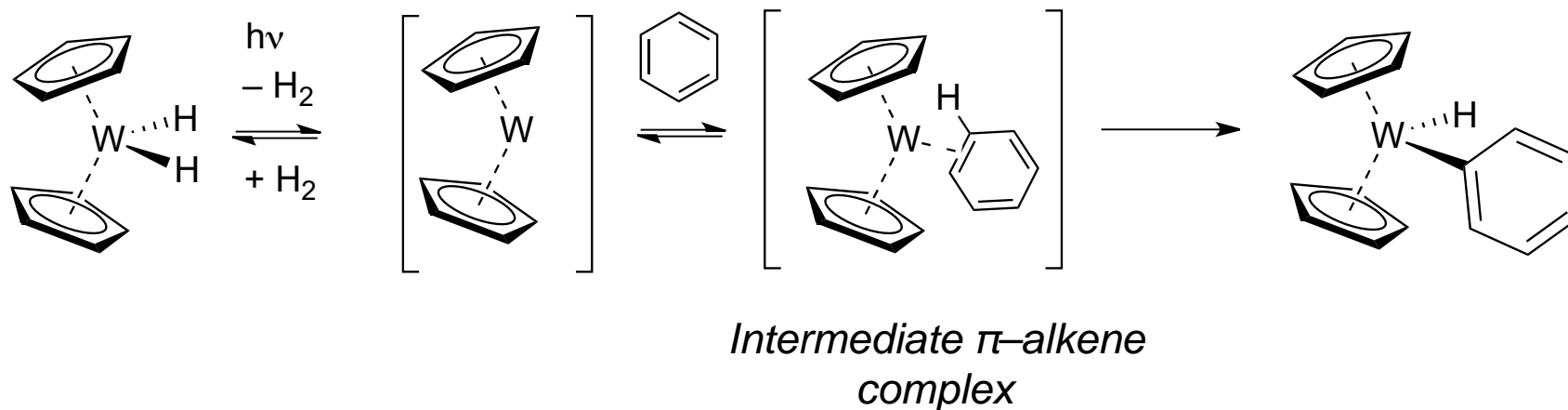
Important for efficient use of fossil-derived resources [Petrochemicals (C₆–C₁₂)]

Gas Flaring (more “economical” to burn methane)



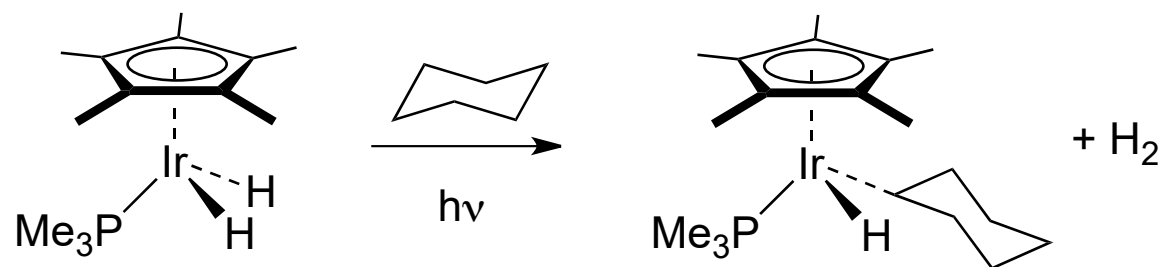
20 C–H Activation: A Historical Perspective

Prior to the 1980's C–H activations were considered difficult and only possible when assisted by π -complexation or intramolecular interactions. For example:

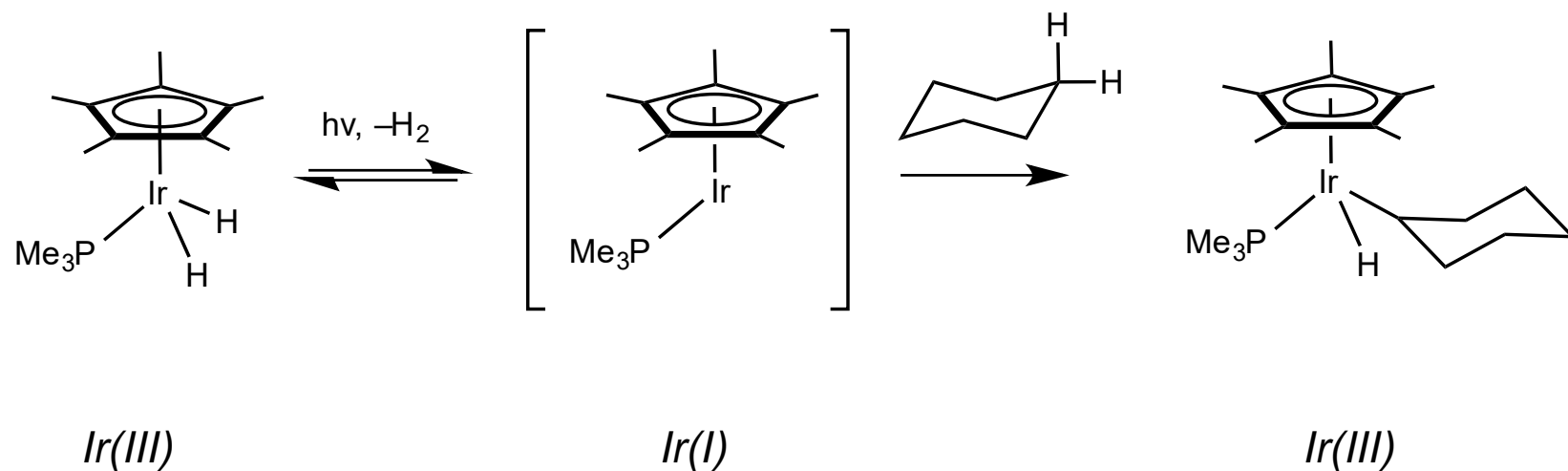


C–H bond brought in proximal to the metal centre

21 Breakthrough in C–H Activation (Oxidative Addition)

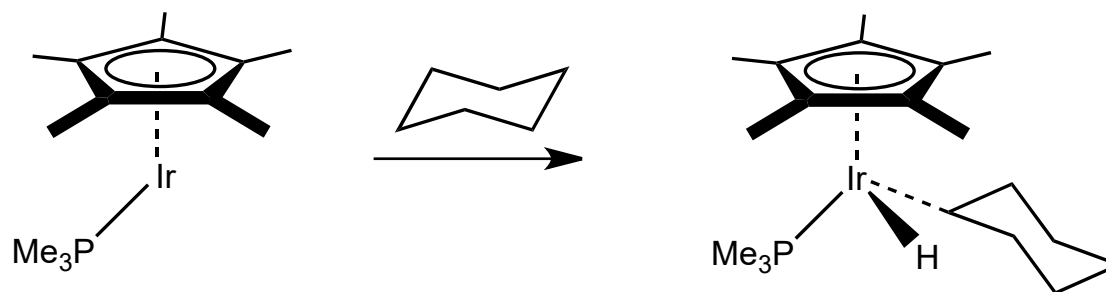


First example of intermolecular C–H activation to give stable metal alkyl hydrides. (Also promoted by high temperature).



22 Thermodynamics

A single strong C–H bond (380 – 450 kJmol⁻¹) is broken to form a weaker C–M (210 – 340 kJmol⁻¹) **but** also a M–H bond (300 kJmol⁻¹).



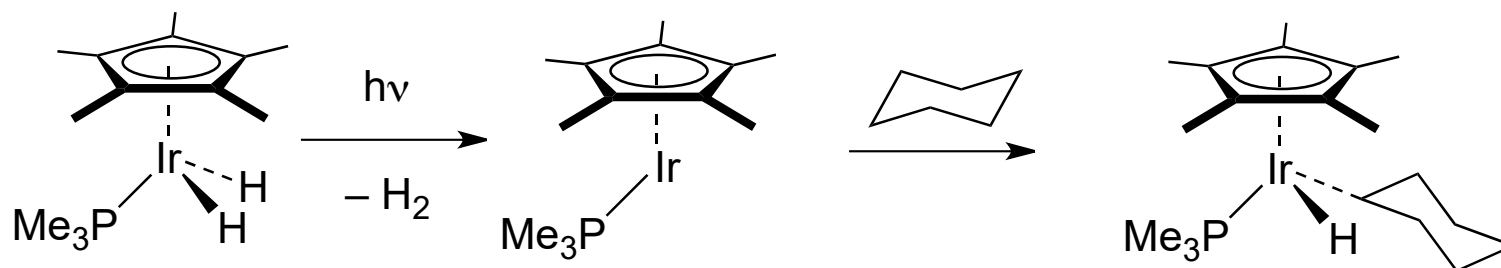
$$\Delta H = D(\text{C-H}) - D(\text{Ir-C}) - D(\text{Ir-H})$$

$$\Delta H = +401 - 213 - 310 = -122 \text{ kJmol}^{-1}$$

i.e. looks exothermic

23 Thermodynamics

Not the full story, need to consider all the bonds being made and broken:



$$\begin{aligned}\Delta H &= D(\text{C-H}) + \underline{D(\text{Ir-H})} - D(\text{Ir-C}) - \underline{D(\text{H-H})} \\ \Delta H &= +401 + 310 - 213 - 434 = \mathbf{+64 \text{ kJmol}^{-1}}\end{aligned}$$

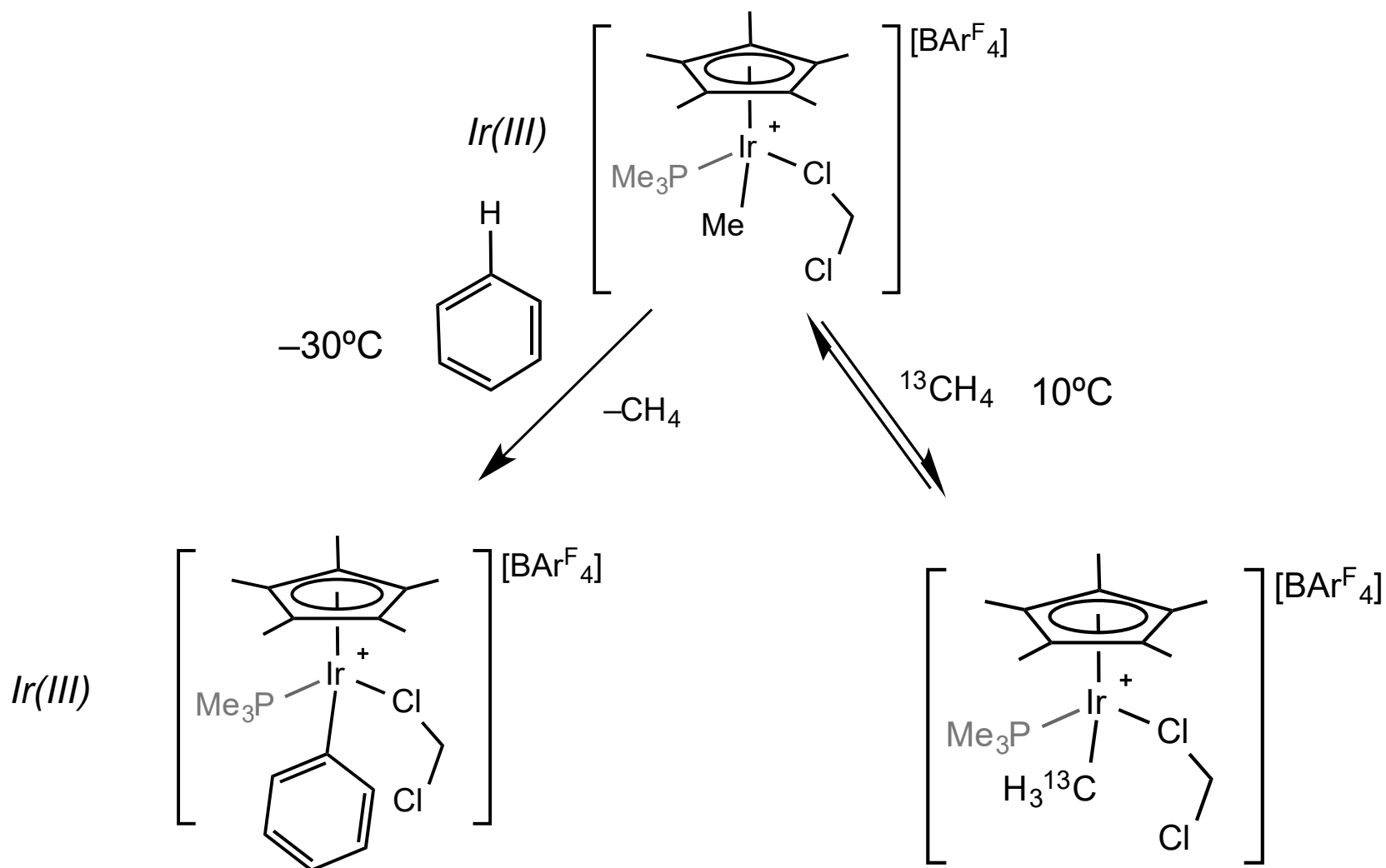
The addition of C-H bonds to transition metals is generally a **thermodynamically unfavourable process** when factoring in the energetic cost of dissociating a ligand to open up a coordination site.

Examples where C-H addition is thermodynamically favourable often involve effort and energy to generate highly reactive, coordinatively unsaturated, species (i.e. 16 or 14 electron).

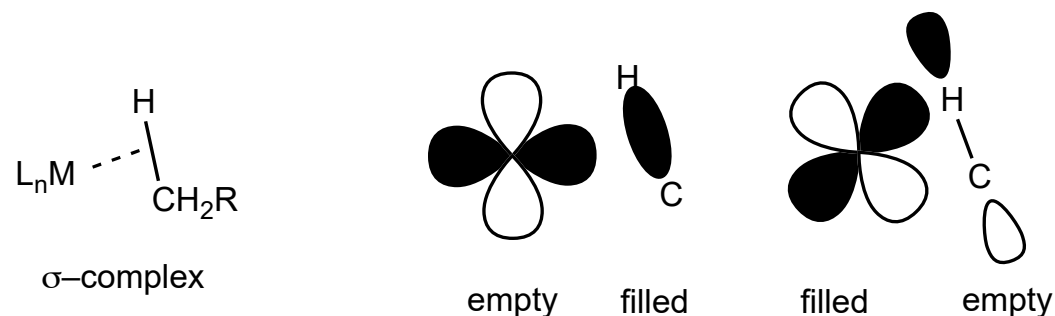
24 Pre-generation of a vacant site

When a vacant site is generated prior, C–H activation occurs very quickly

[Sigma Bond Metathesis Mechanism]

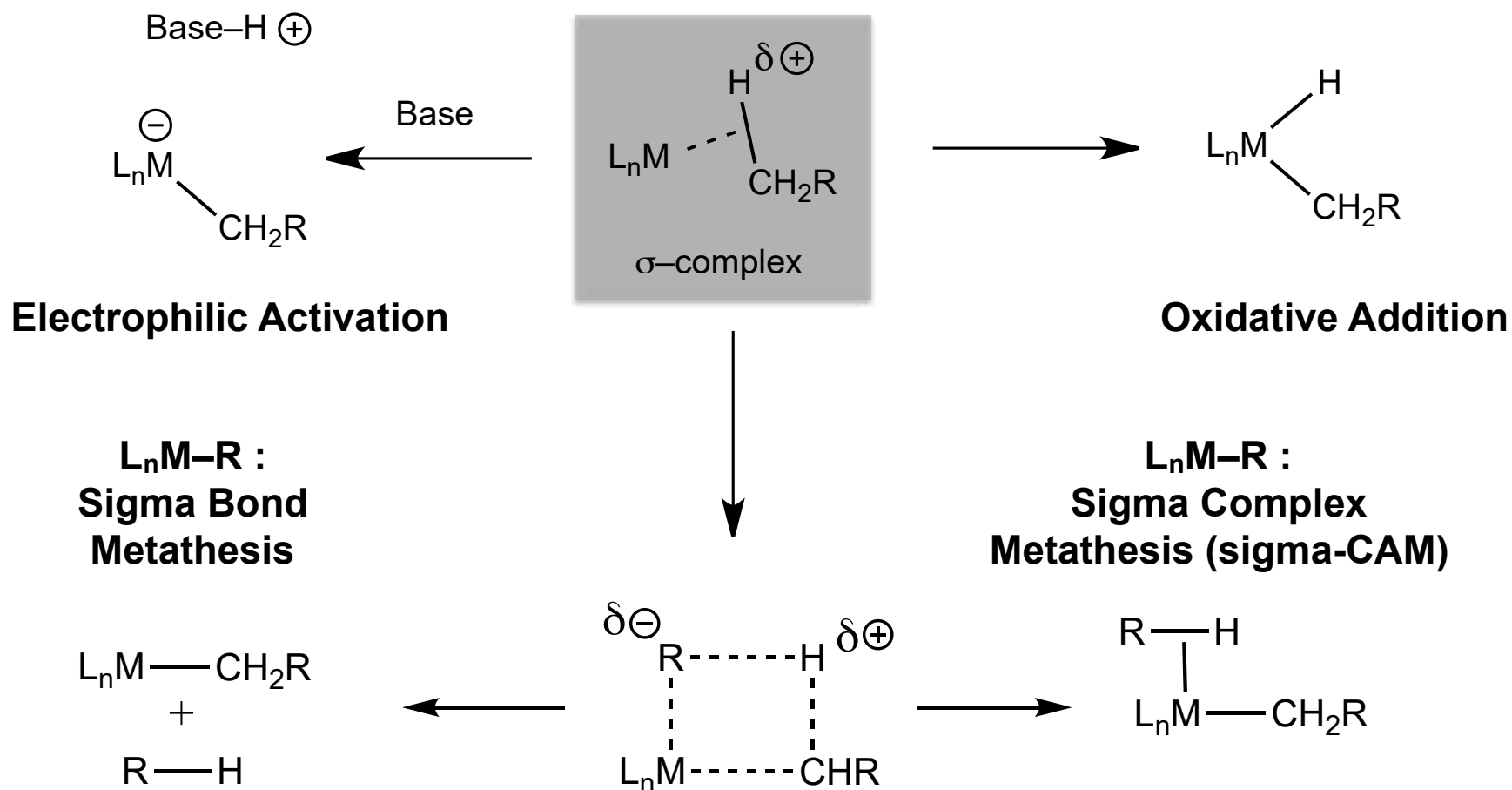


25 C–H Activation: Different overall pathways come from a common intermediate

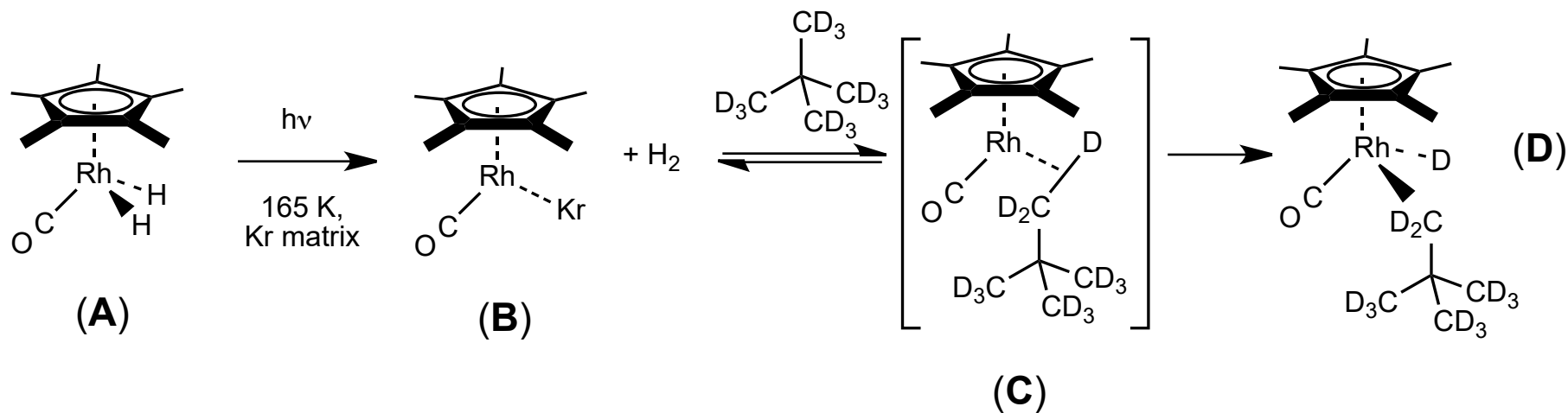


As for H_2 , depletion of electron density makes the C–H bond rather acidic.

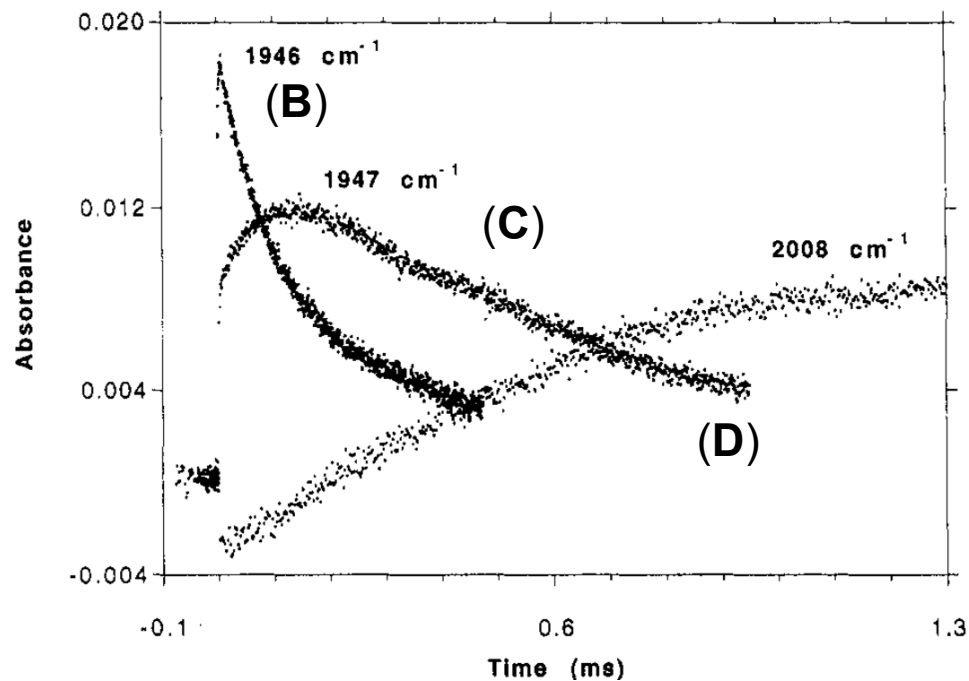
(inefficient σ^* back donation compared to C–H to M donation)



26 C–H Oxidative Addition - The generation of vacant sites and σ -intermediates



Intermediate σ -alkane complex (C)

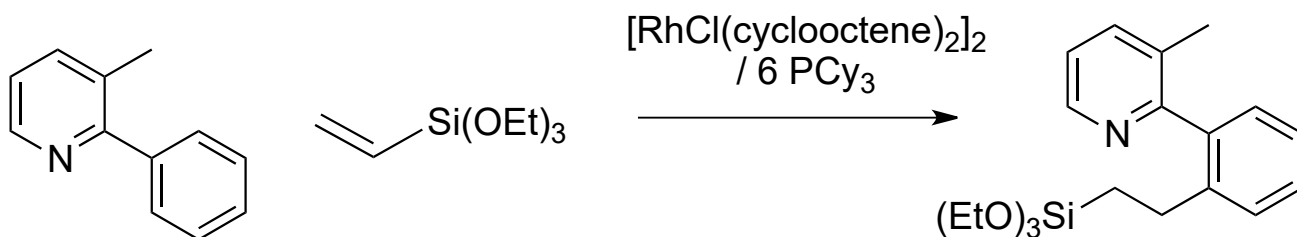
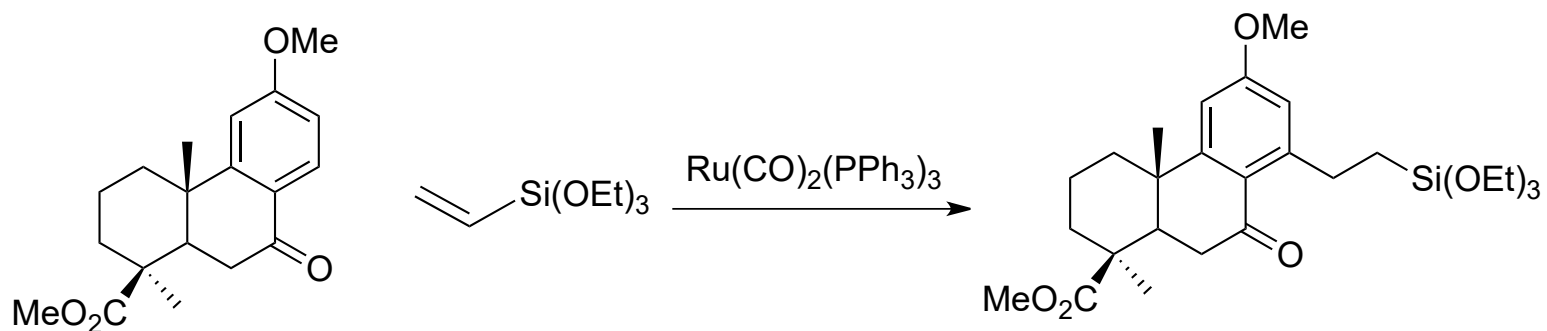
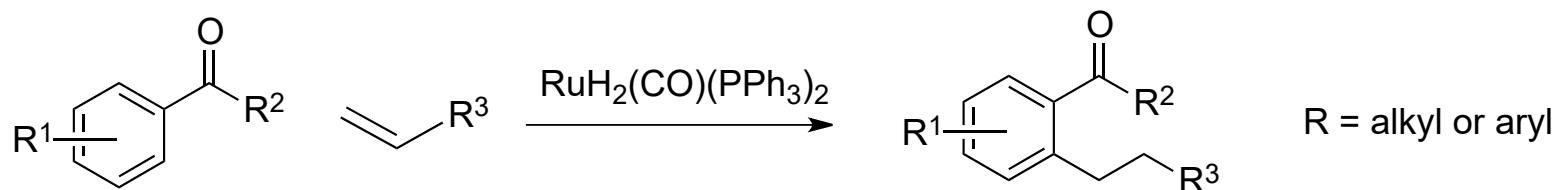


*Low-Temperature IR
flash kinetic study.
Note 1.5 ms timescale*

28 Oxidative Addition: Directed Intramolecular C–H Activation (Murai Reaction)

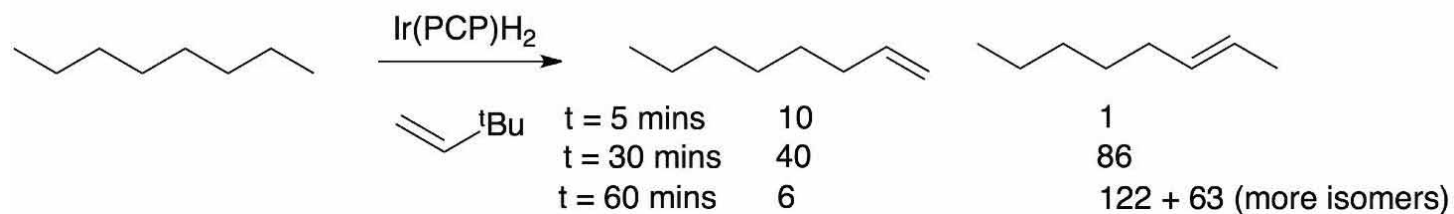
In 1993 Murai reported aryl ketones react with alkenes under mild conditions using $\text{RuH}_2(\text{CO})(\text{PPh}_3)_2$. This reaction has found use in synthesis.

Not limited to ketones or Ru-catalysts: Rh(I) catalysts also work.



29 Catalysis: Alkane Dehydrogenation

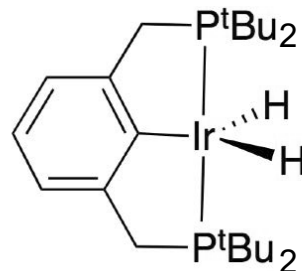
Alkane dehydrogenation turns a low value product (alkane) into a higher value product with a useful functional groups



kinetic product

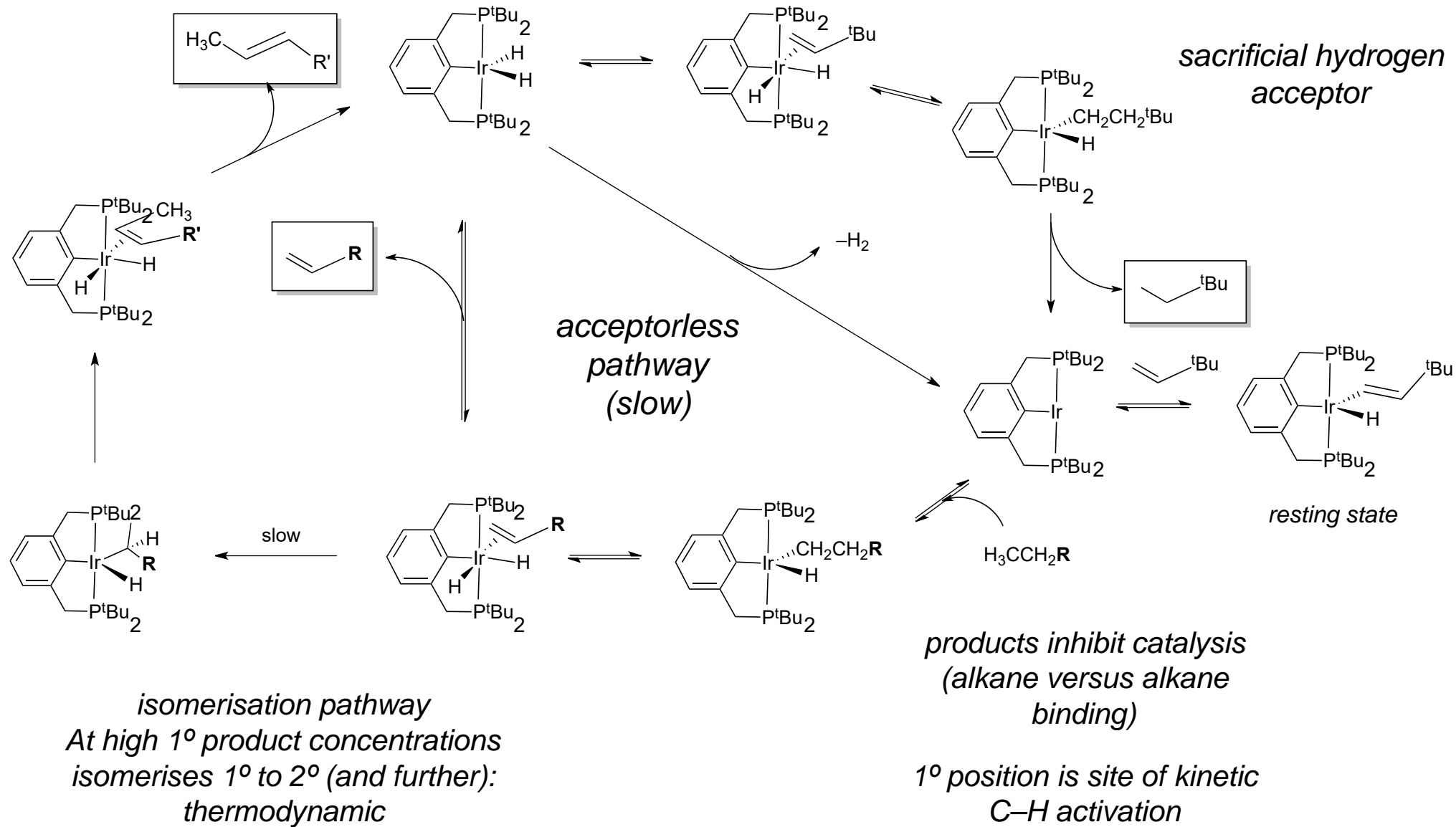
thermodynamic product

cat. =



$\text{Ir}(\text{PCP})\text{H}_2$

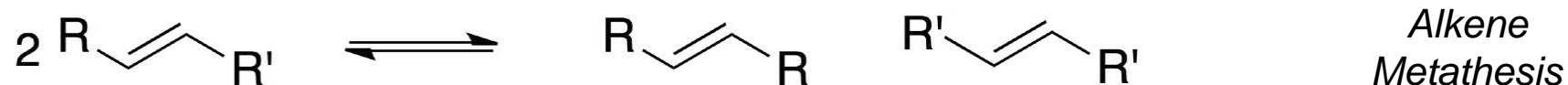
30 Catalysis: Alkane Dehydrogenation, Mechanism



31 Catalysis: Alkane Metathesis

Alkane metathesis is the formal cleavage of a C–C bond and reformation of bonds to make different alkenes (cf. alkene metathesis).

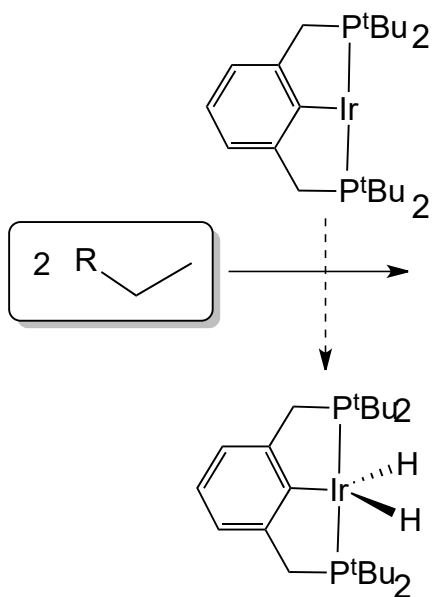
Could be used in synthesis or petroleum refining.



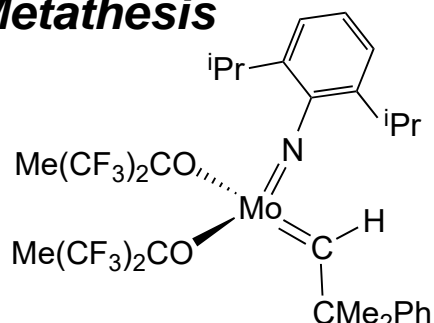
By combining alkane dehydrogenation, alkene metathesis and hydrogenation this difficult process can be achieved:

32 Catalysis: Alkane Metathesis, Mechanism

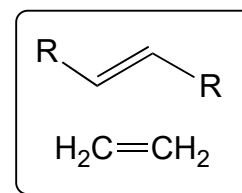
Dehydrogenation



Metathesis

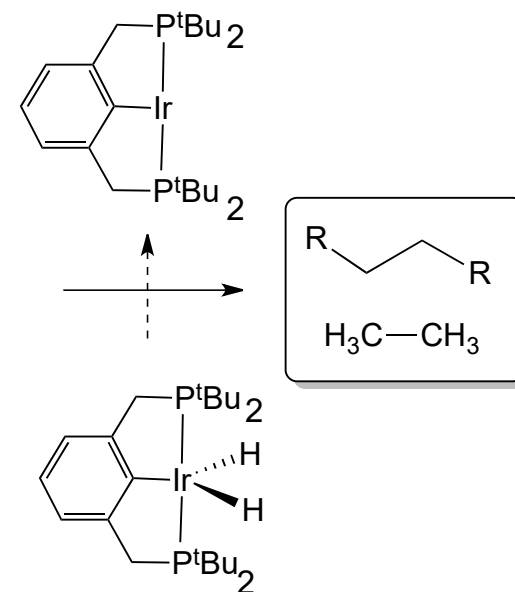


Schrock's catalyst

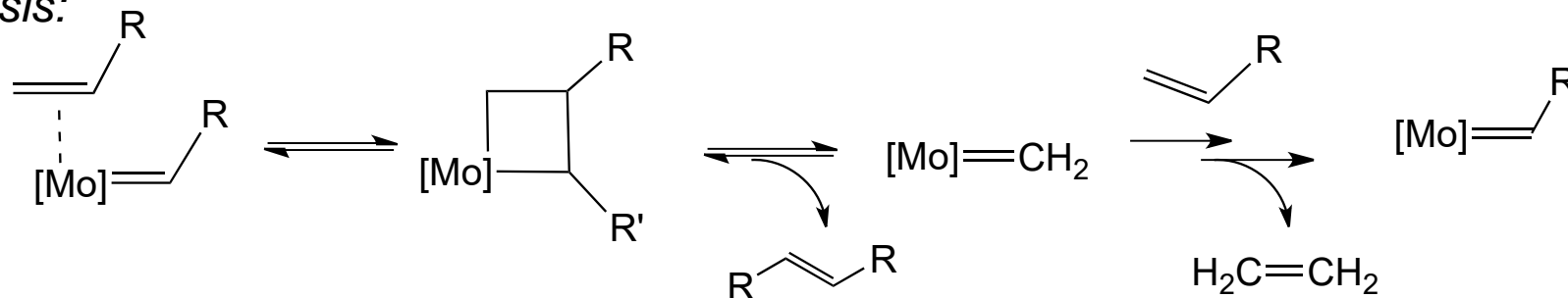


(other alkanes also produced due to isomerisation and cross metathesis)

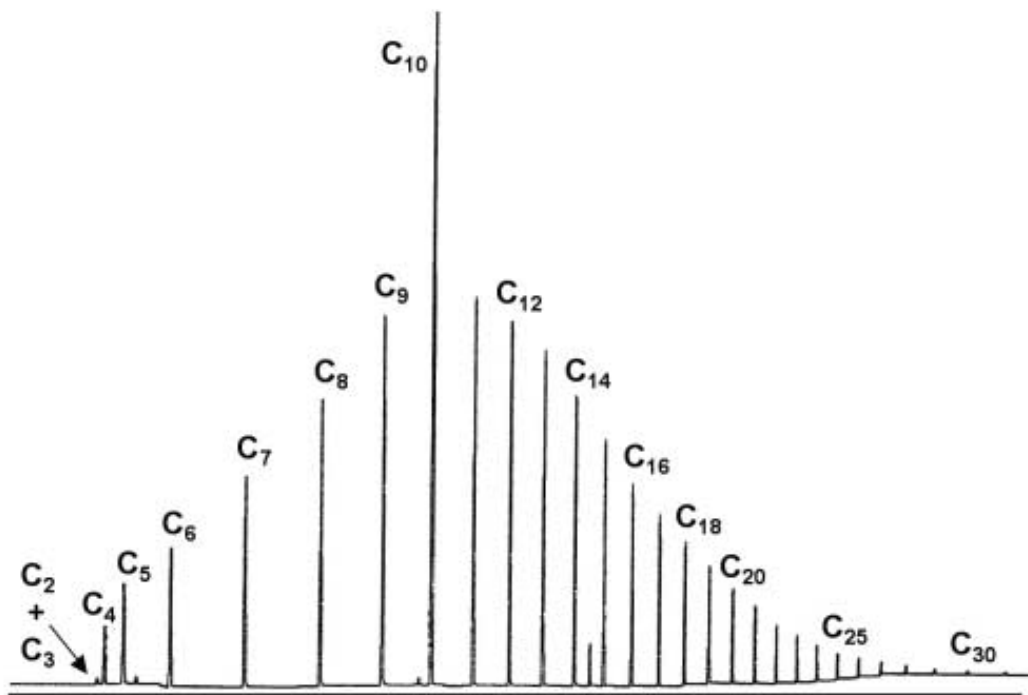
Hydrogenation



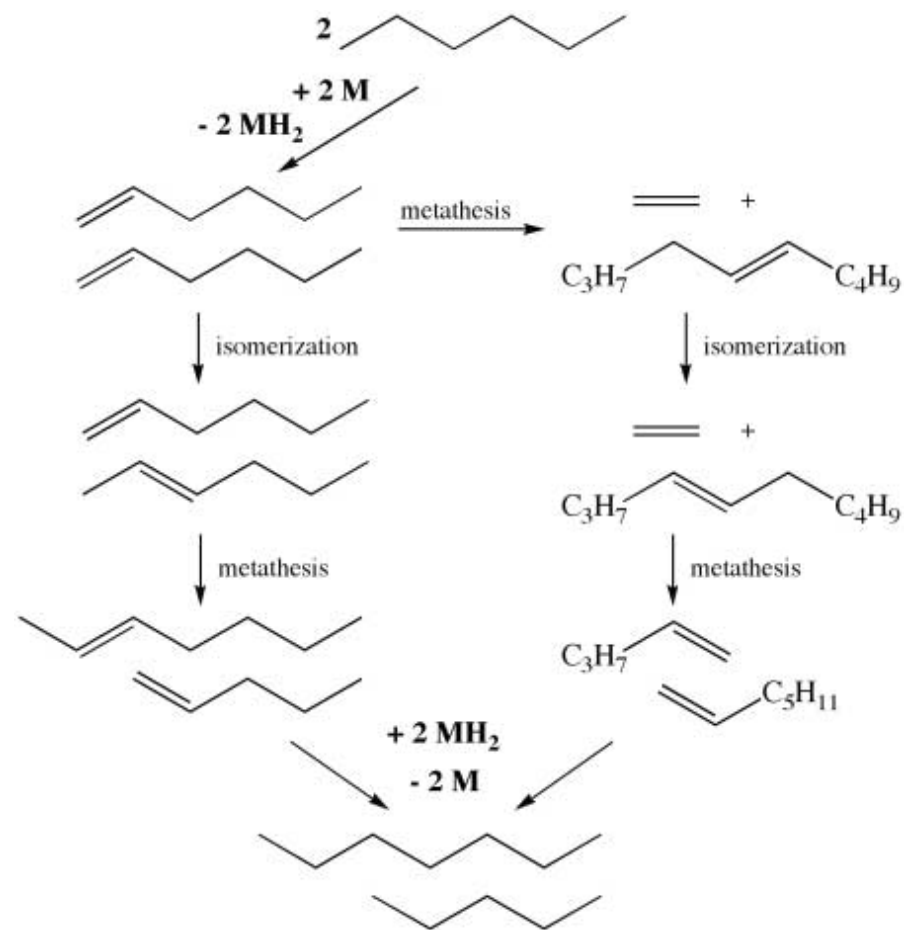
Metathesis:



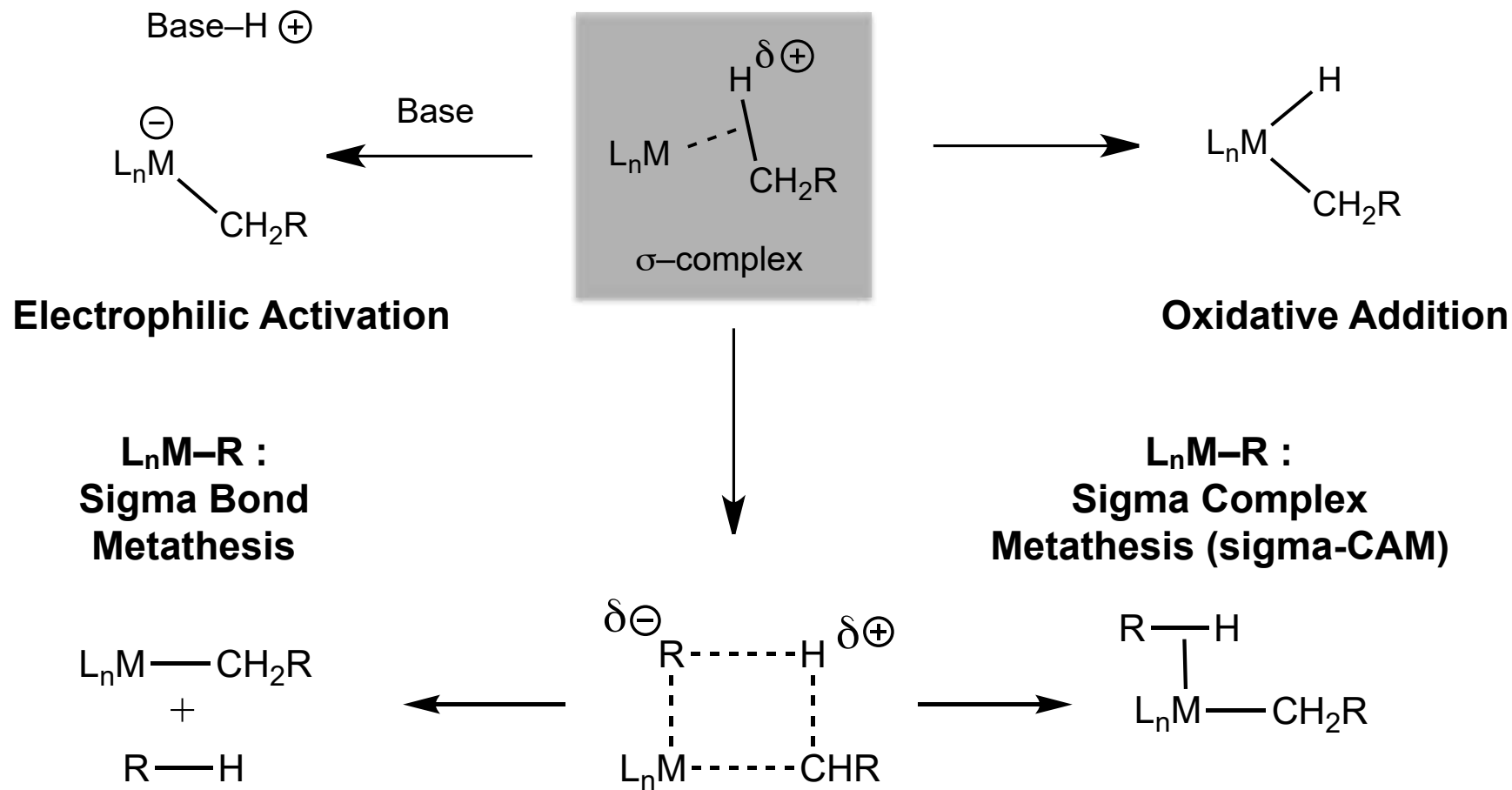
33 Catalysis: n-decane alkane metathesis



Distribution of alkanes

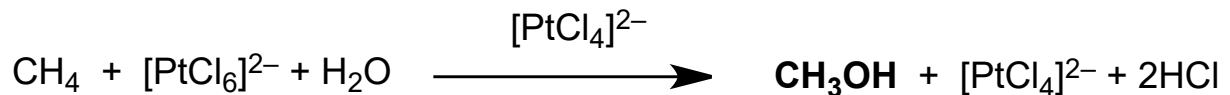


Possible routes to alkane disproportionation (lower and higher alkanes formed)



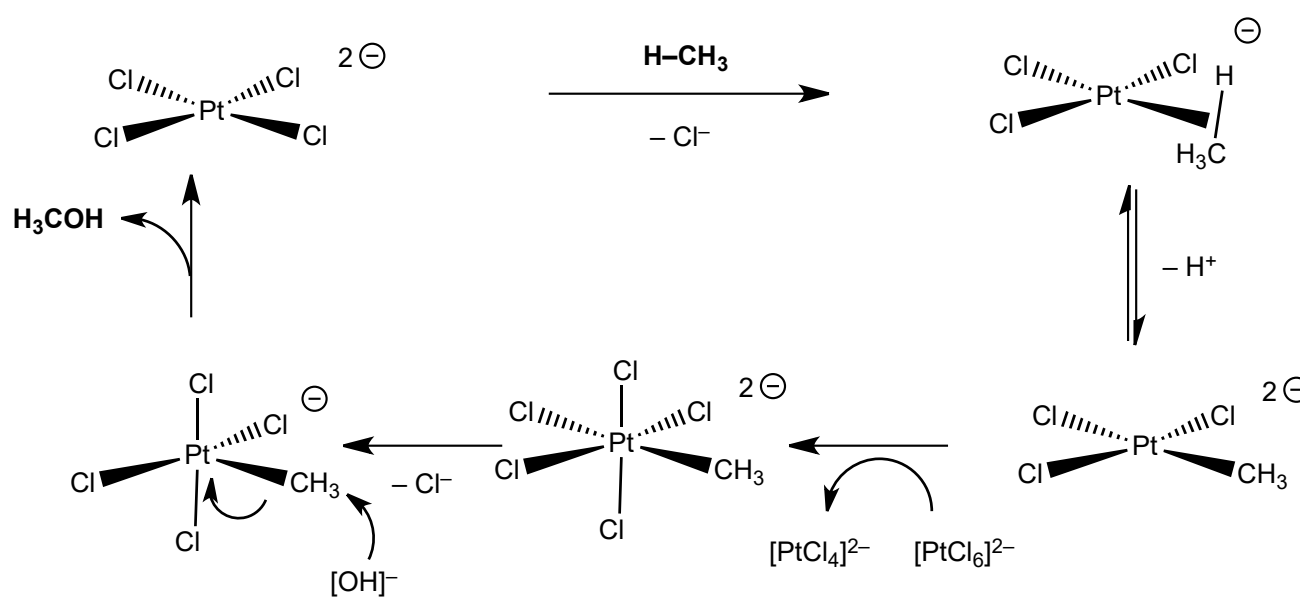
34 Electrophilic C–H Activation

Shilov in early 1970's reported methane to methanol oxidation that is stoichiometric in Pt(IV).



Shilov *Chem. Rev.* **1997**, *97*, 2879.

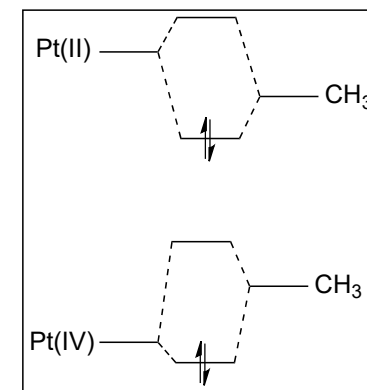
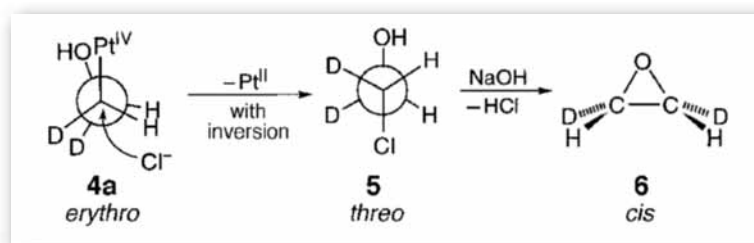
Mechanism accepted to proceed via electrophilic C–H activation



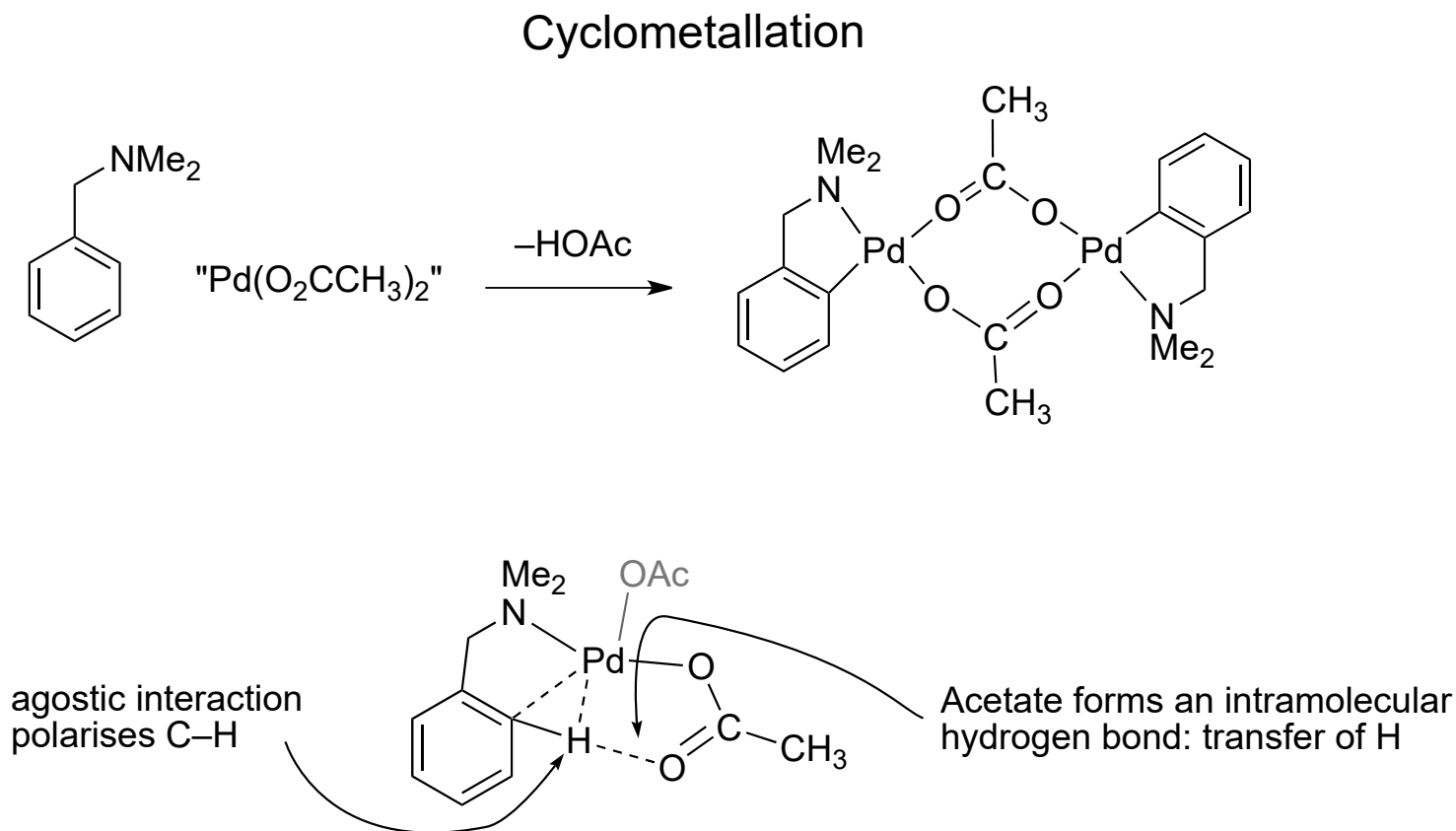
Alternatively, OA to give a Pt(IV) alkyl hydride that then can be deprotonated.

Stereochemical inversion at carbon suggests nucleophilic attack by hydroxide: S_N2

Stoichiometric in [PtCl₆]²⁻

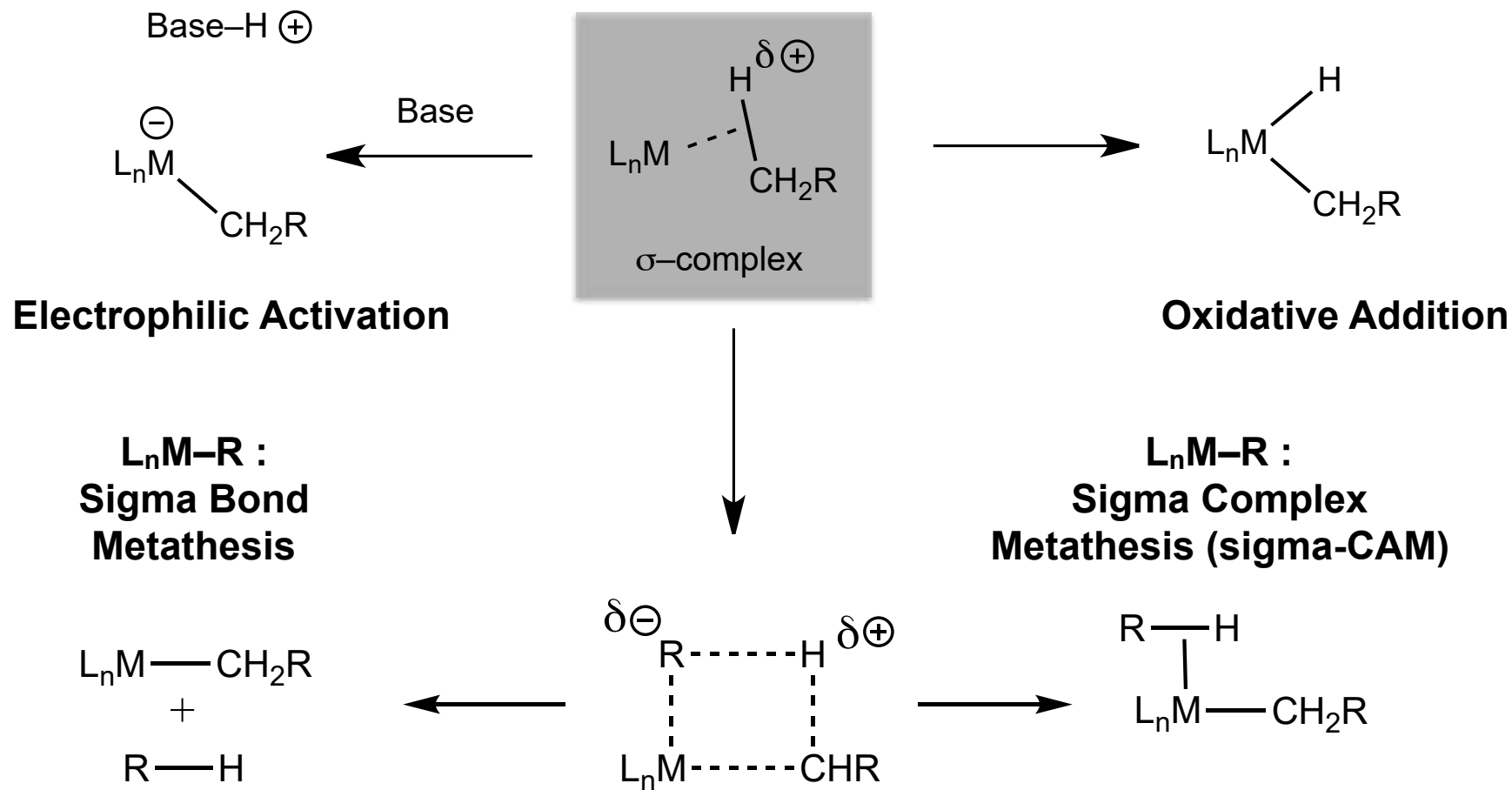


35 Base-Assisted Electrophilic C–H activation Concerted Metallation Deprotonation "CMD"



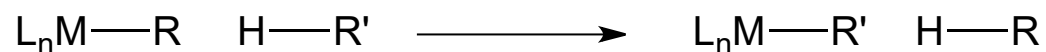
Kinetic studies (in particular volume of activation ΔV^\ddagger) indicate a **highly ordered transition state**

Electrophilic metal centre and nucleophilic base: "ambiphilic"

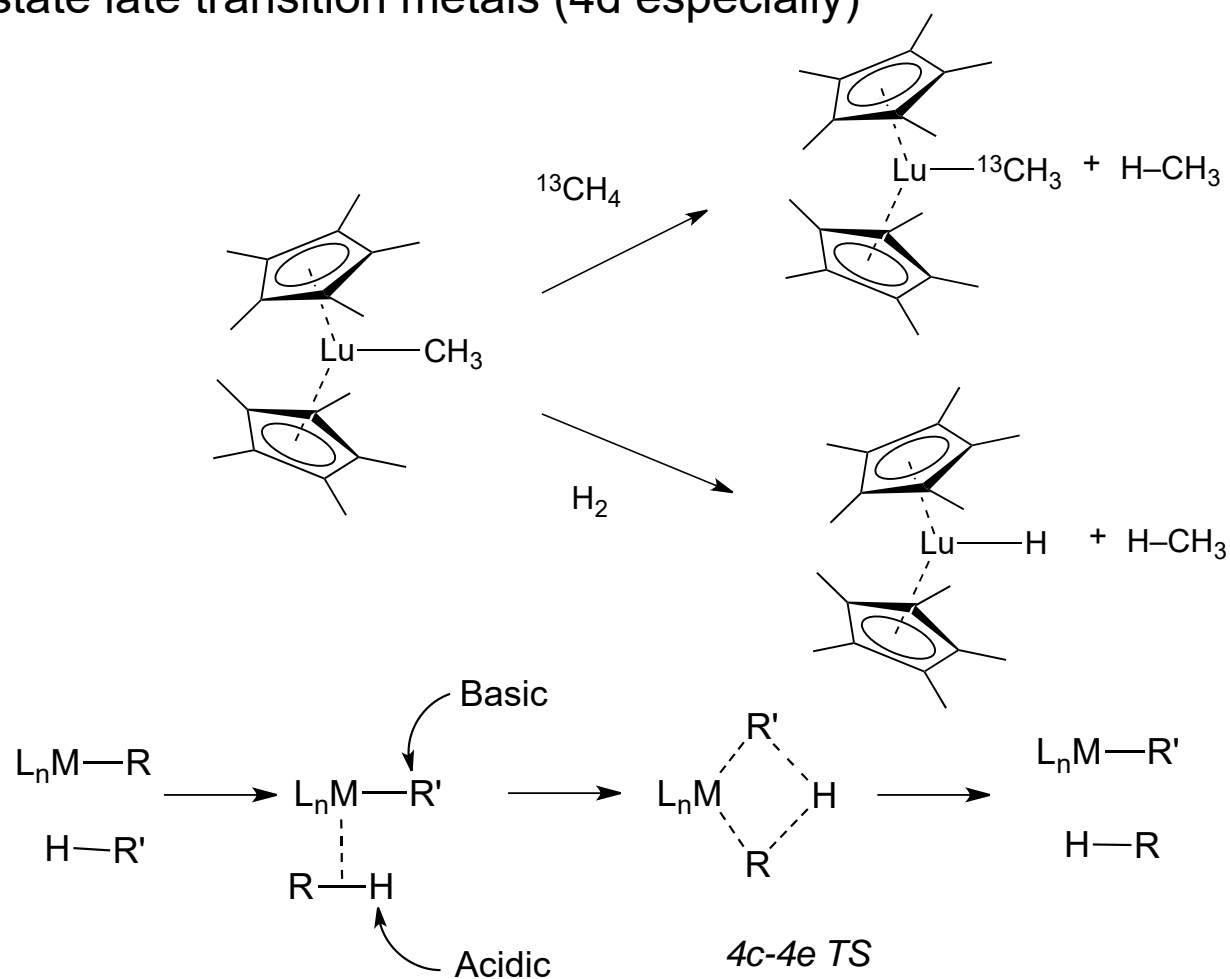


36 Sigma-Bond Metathesis

An example of sigma bond metathesis is the exchange of an alkyl group between a TM-alkyl and an alkane

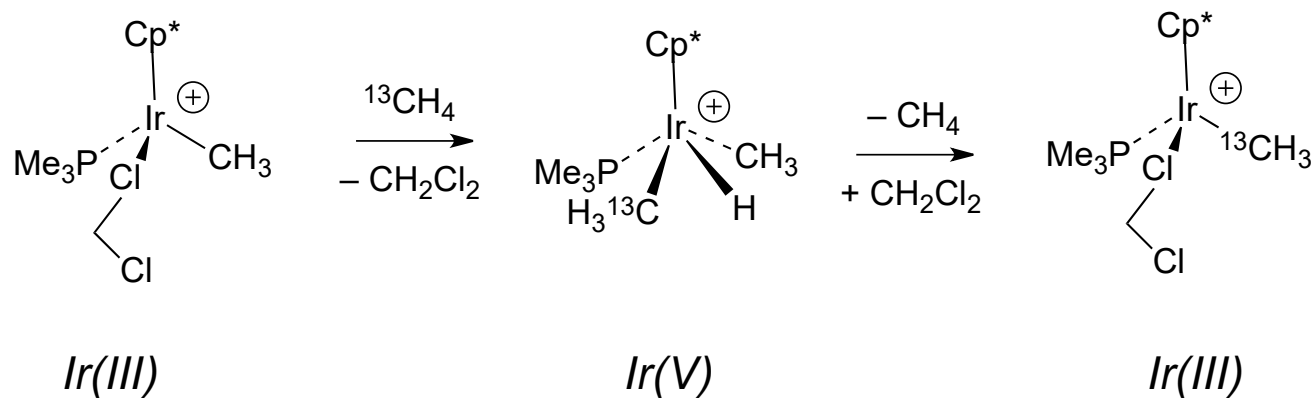
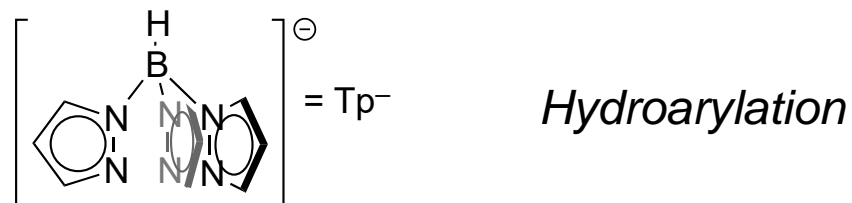
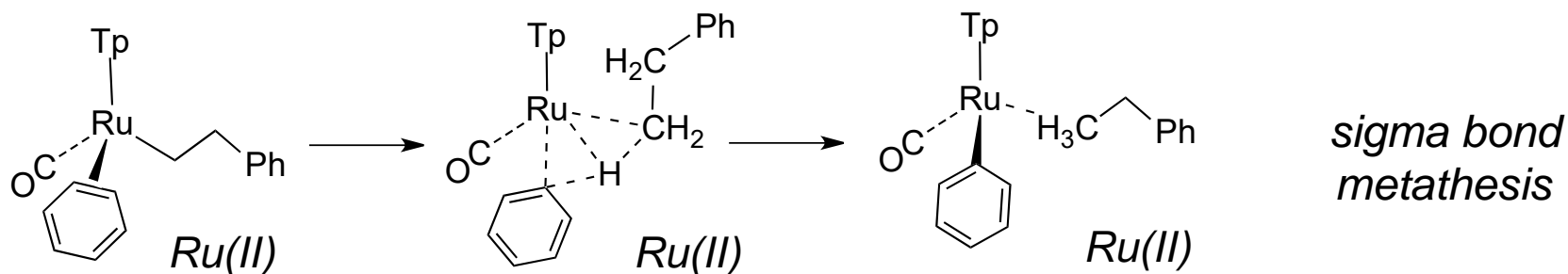


Suggested to occur when Oxidative Addition is not possible: d^0 , lanthanide (f orbitals core-like), higher oxidation state late transition metals (4d especially)



37 Sigma-Bond Metathesis: d⁶ Complexes

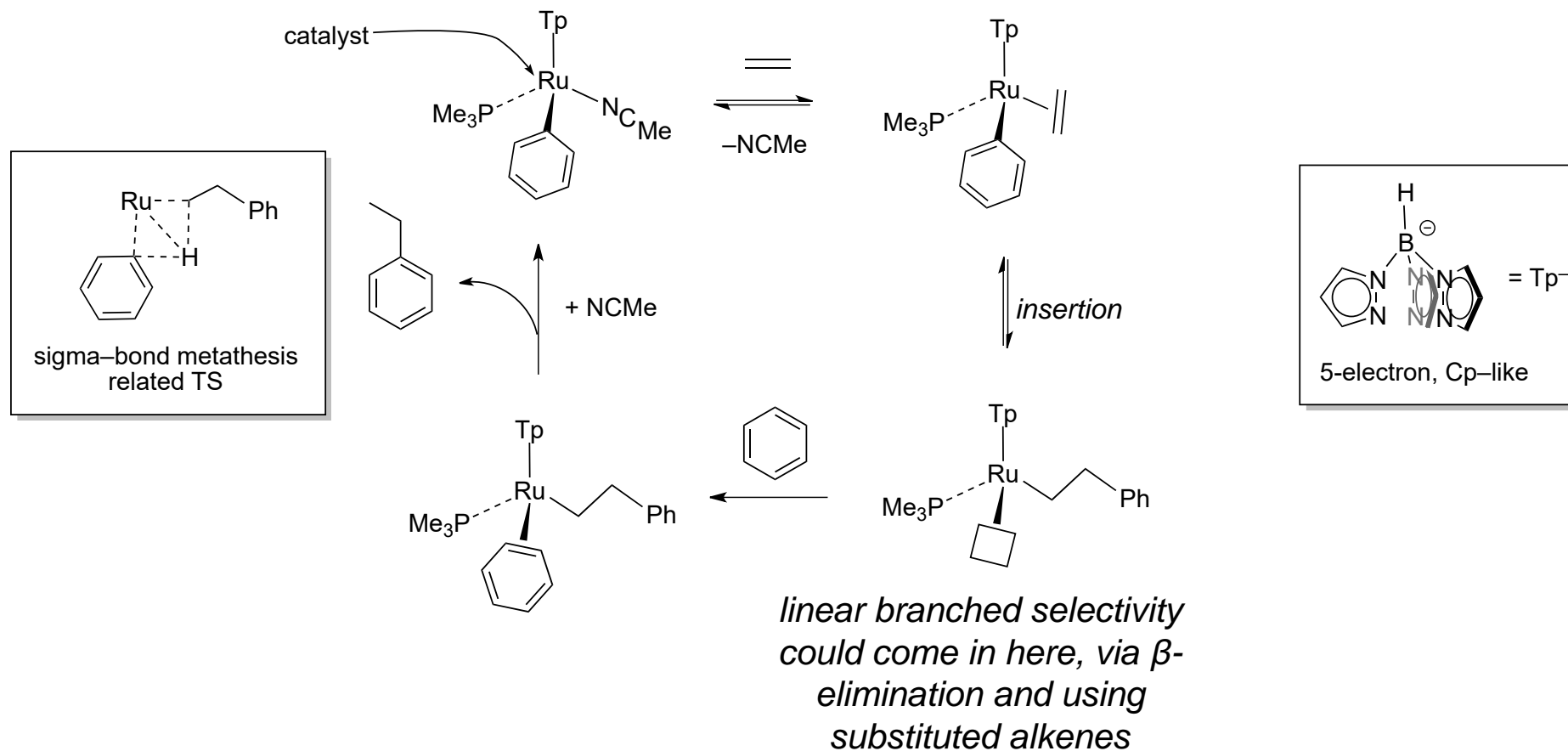
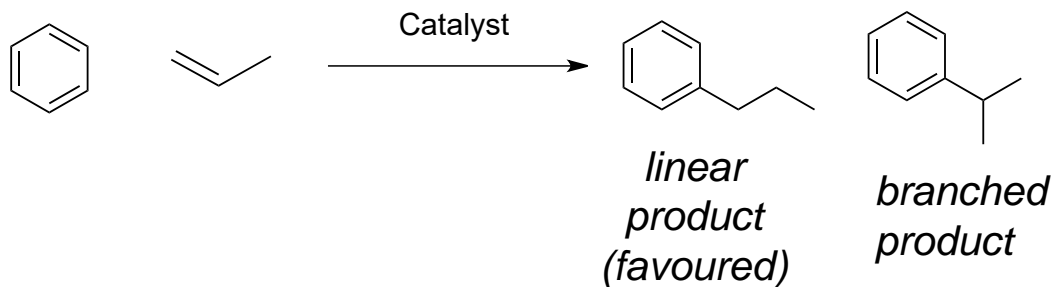
Very difficult to distinguish between the two mechanistic extremes of oxidative addition and sigma-bond metathesis. The isolation of intermediates or calculations can help:



*Oxidative Addition/
Reductive Elimination*

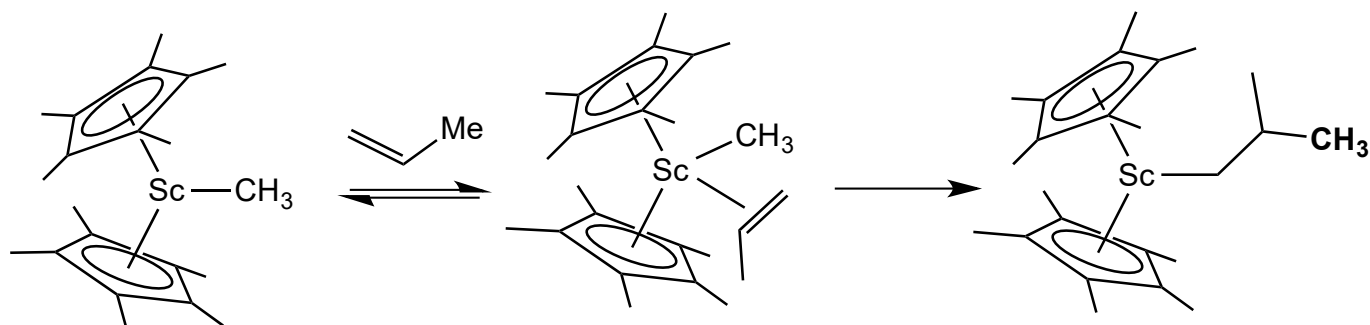
38 Catalysis: Intermolecular C–H Activation (Alkene Hydroarylation)

Hydroarylation offers a concise and atom efficient route (cf. Friedel–Crafts) to build functionality into feedstock chemicals

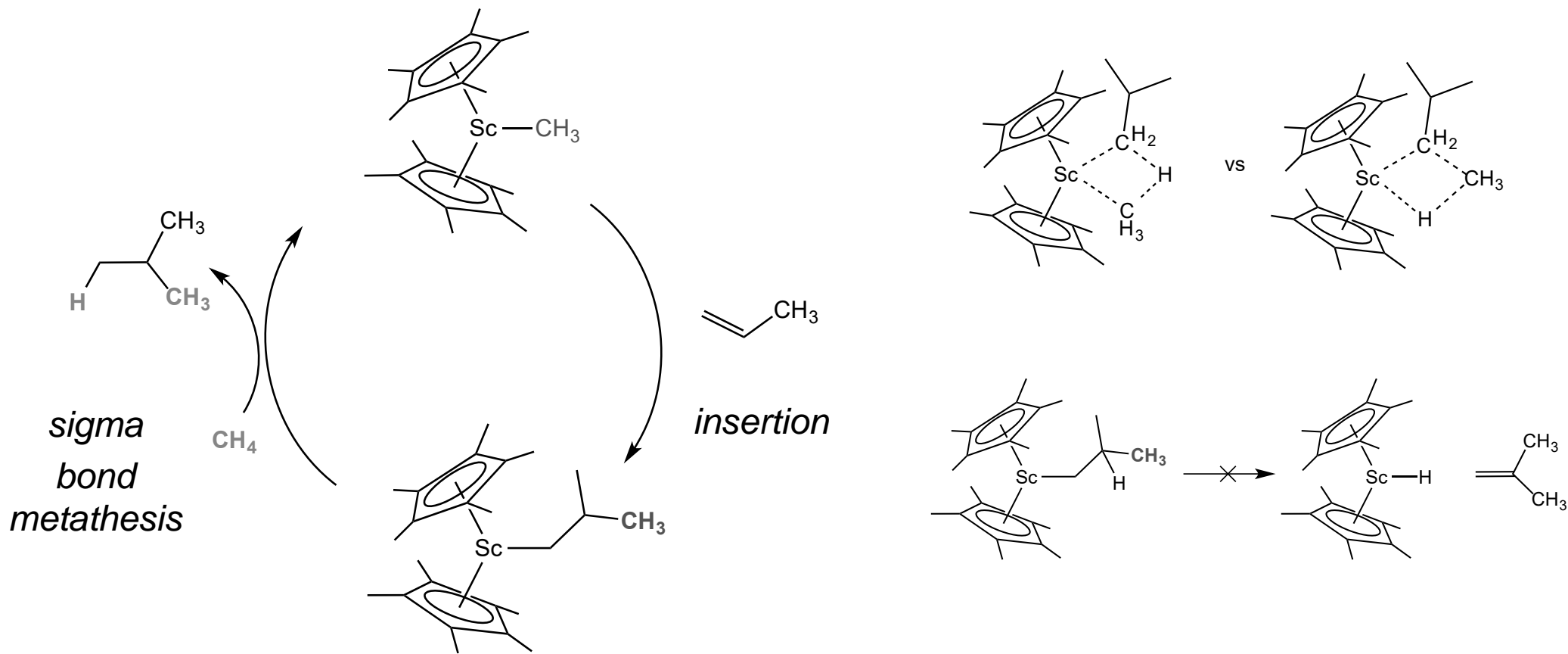


39 Catalysis: Methane Functionalisation, Hydromethylation of Olefins

Cp^*_2ScMe is known to insert propene



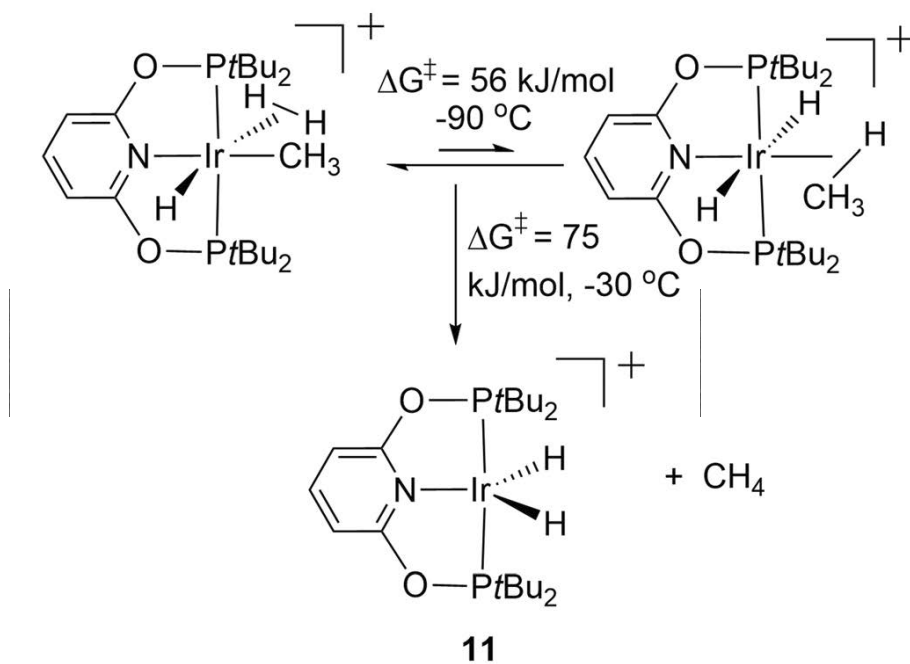
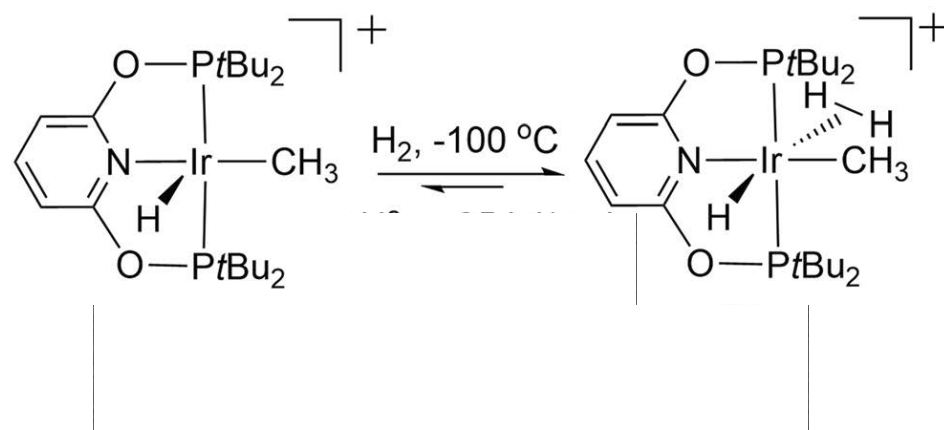
Combine into a catalytic cycle with methane functionalisation



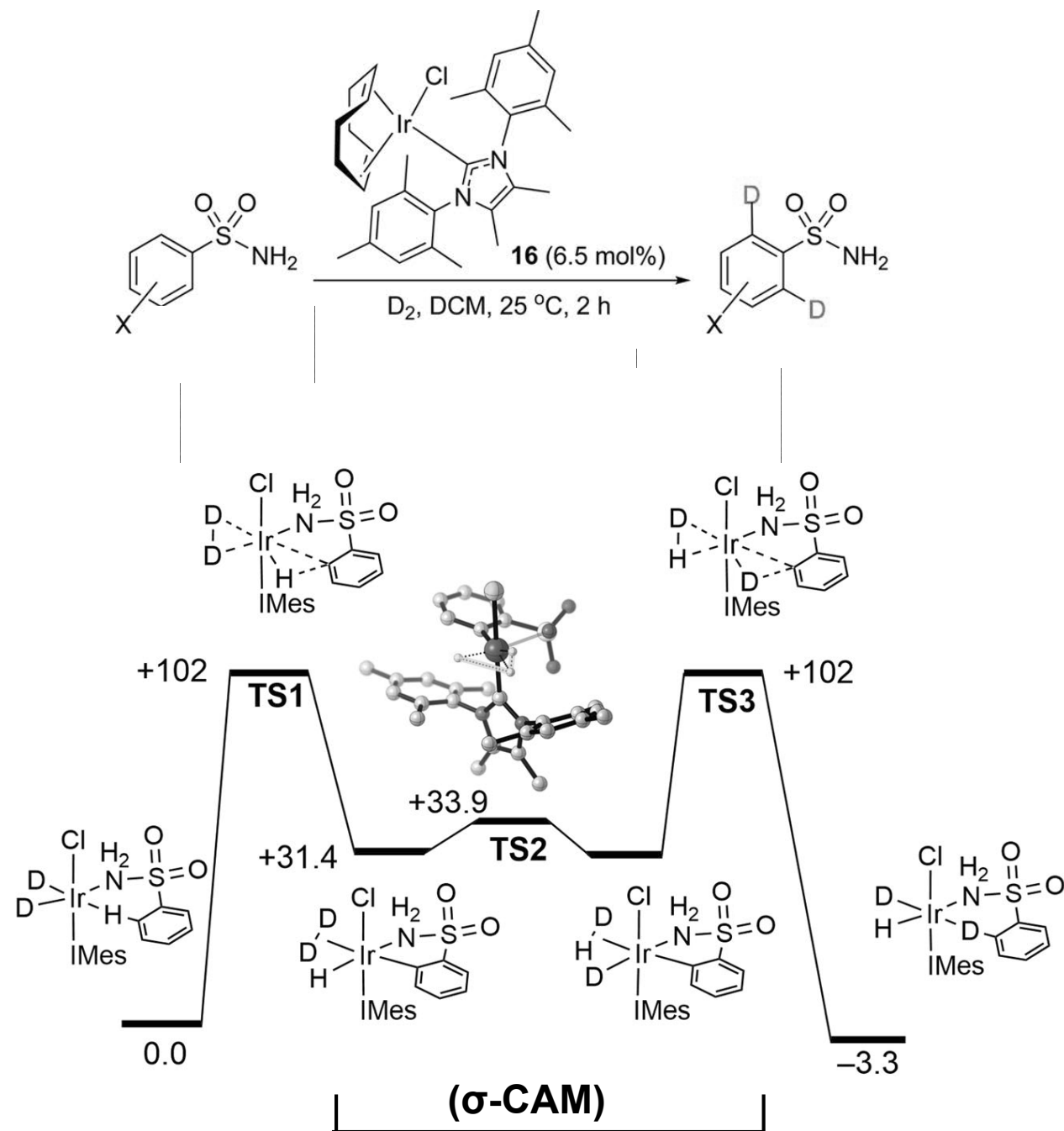
4 turnovers in 2 weeks!

JACS 2003, **125**, 7995 (Tilley)

40 Sigma Complex Metathesis (σ -CAM)

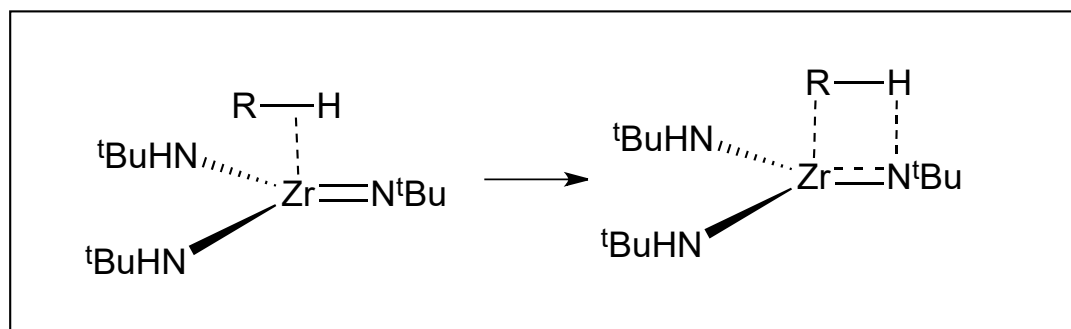
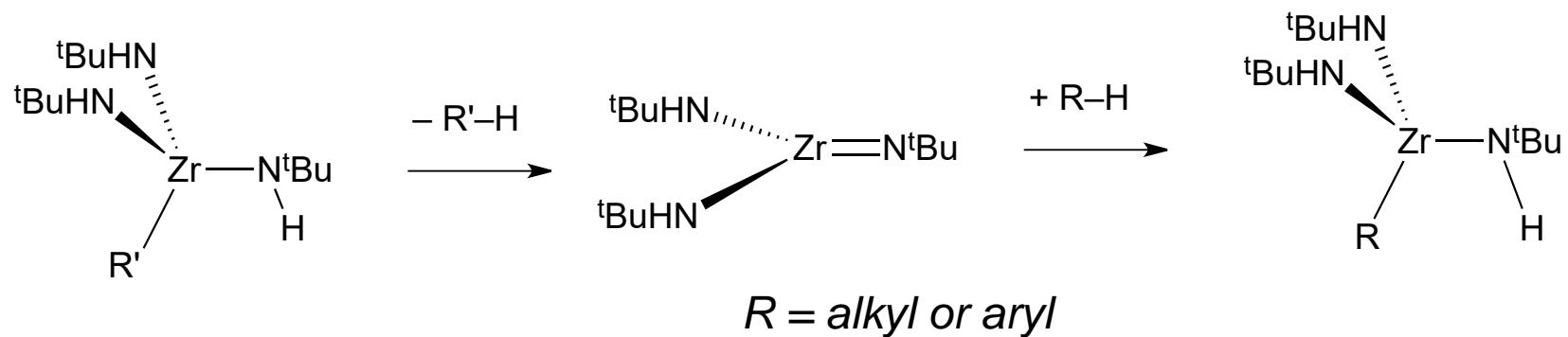


41 Sigma Complex Metathesis in Catalysis (σ -CAM)



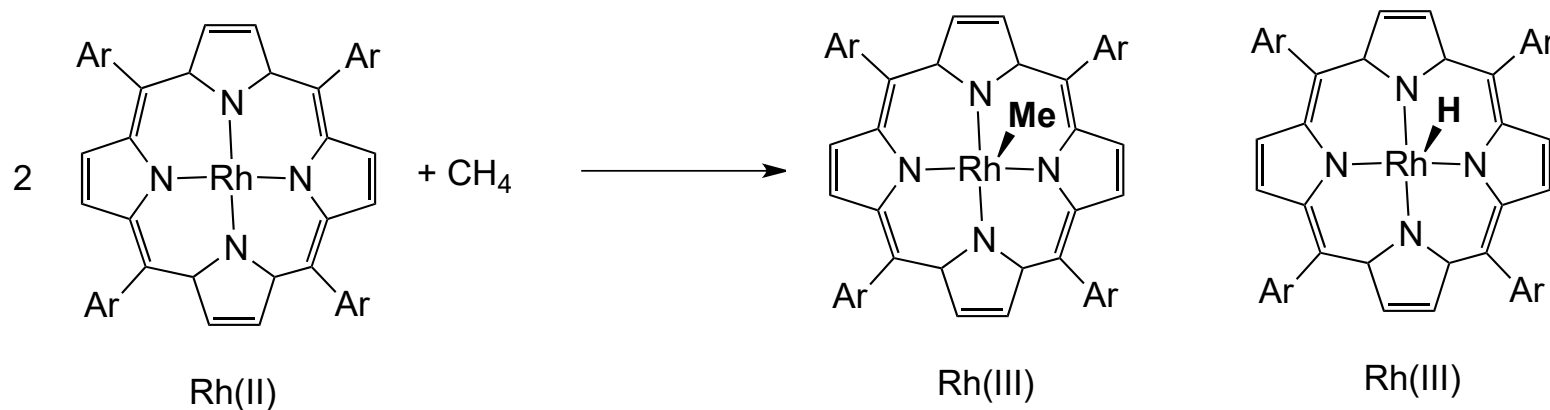
42 1,2-Addition

Zr(IV) amido alkyl complexes can undergo 1,2-elimination of alkane to generate a transient imido that then reacts with alkanes



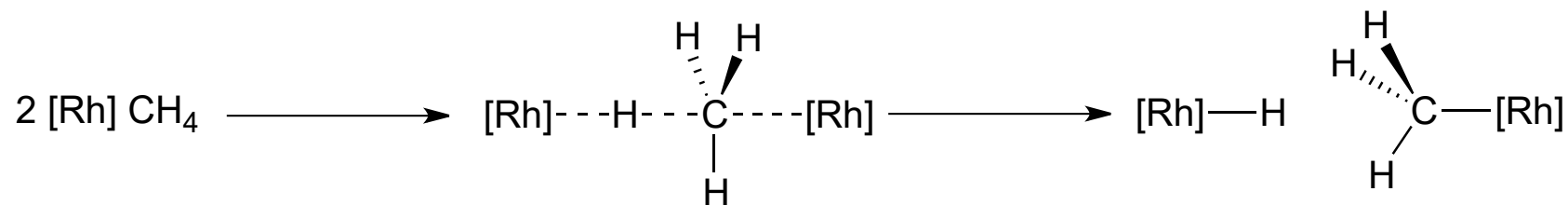
43 Metalloradical

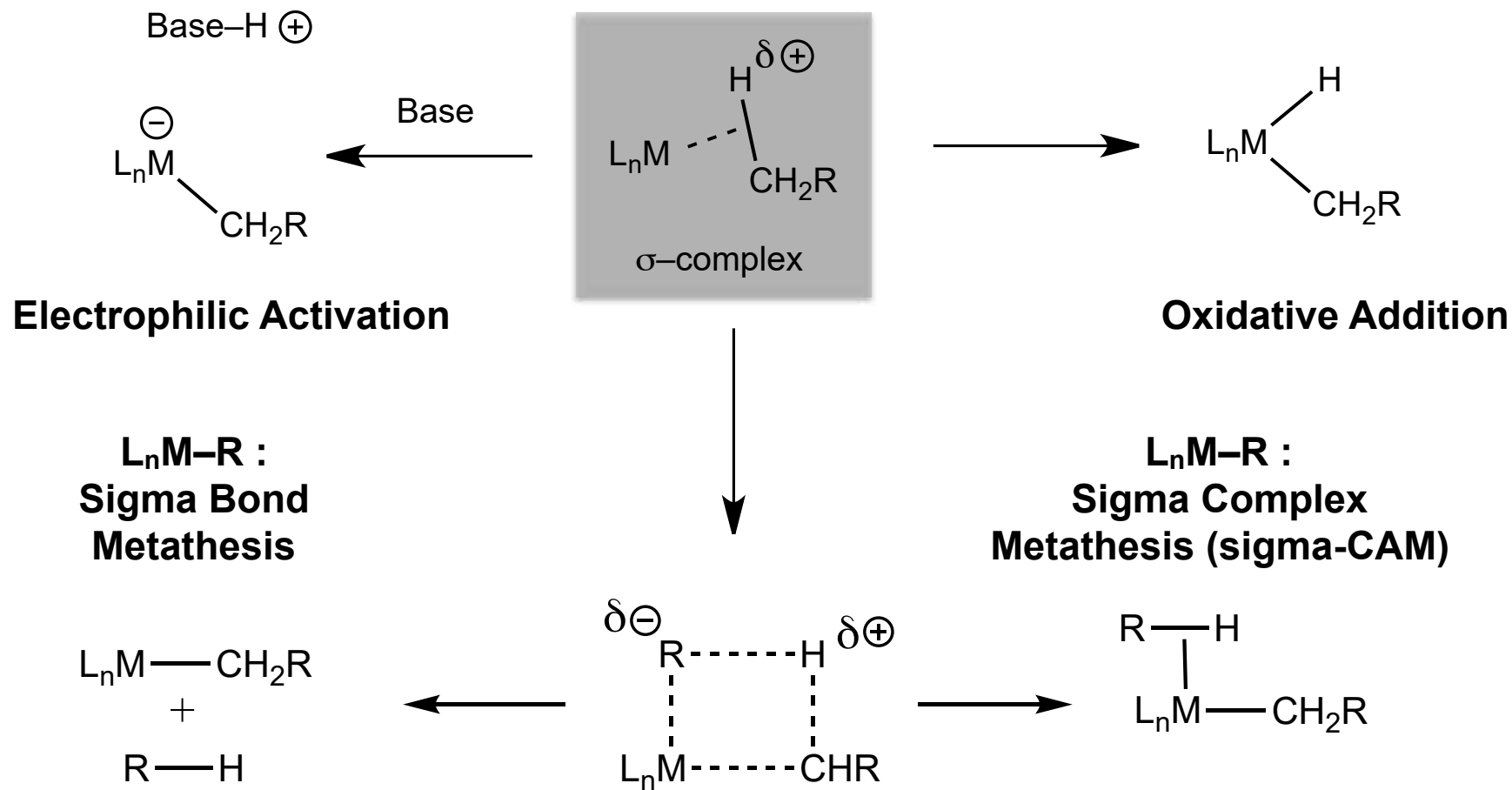
Examples of C–H activation at two metal centres are rare. Metalloporphyrins can do it.



Ter-molecular transition state

(entropically disfavoured kinetically $\Delta S^\ddagger = -170 \text{ JK}^{-1} \text{ mol}^{-1}$: three body problem)





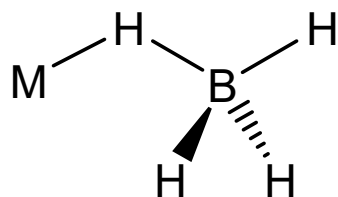
Appendix

Sigma complexes containing coordinated B–H bonds

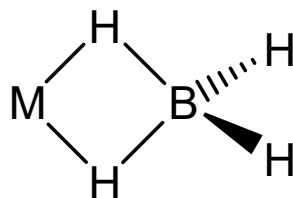
Borohydride (tetrahydroborate) complexes have been studied as models for the coordination of the **iso-electronic methane molecule**.

Massively enhanced stability attributed to the additional electrostatic contribution to the metal-ligand interaction with $[\text{BH}_4]^-$

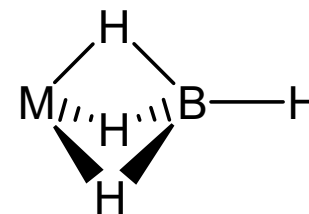
Typically highly fluxional.



'monodentate' $\eta^1\text{-H}$
e.g. $(\text{RPh}_2\text{P})_3\text{Cu}(\text{BH}_4)$



'bidentate' $\eta^2\text{-H,H}$
e.g. $(\text{RPh}_2\text{P})_2\text{Cu}(\text{BH}_4)$

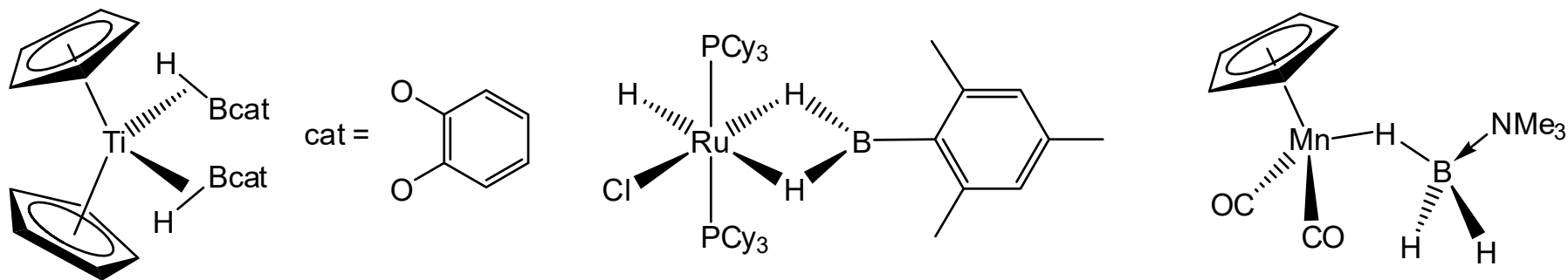


'tridentate' $\eta^3\text{-H,H,H}$
e.g. $\text{U}(\text{BH}_4)_4$ gas-phase

Sigma complexes containing coordinated B–H bonds

Complexes of neutral boranes are a more recent development (1996) and have relevance to BH oxidative addition and derived catalytic processes (i.e. hydroboration and C–H/C–B bond exchange) – see later.

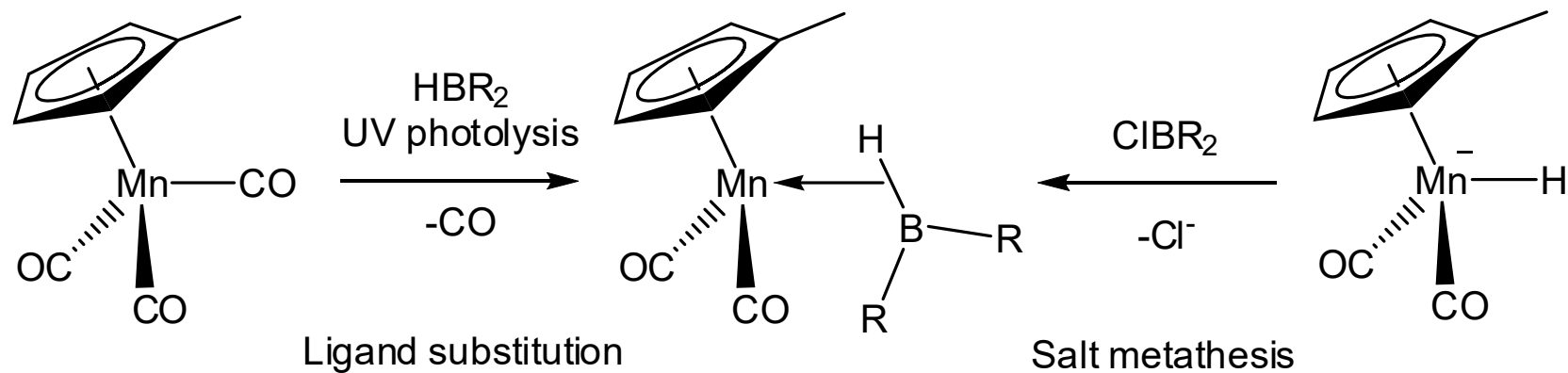
More stable than alkane complexes: B–H polarisation and B– $\rho\pi$ contribution when the B is sp^2 -hybridised



References: *J. Am. Chem. Soc.*, 1996, **118**, 10936; *J. Am. Chem. Soc.*, 1999, **121**, 11704

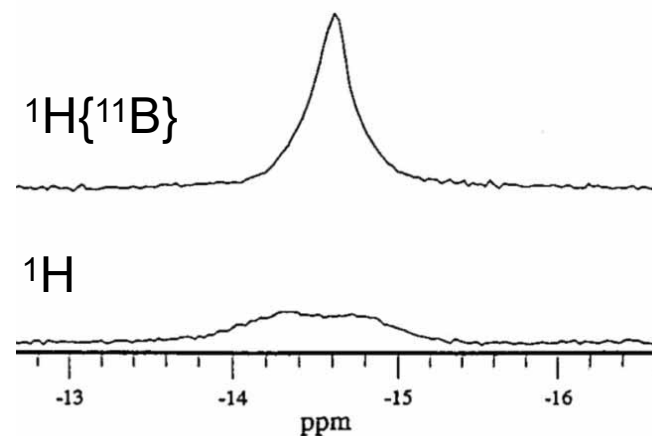
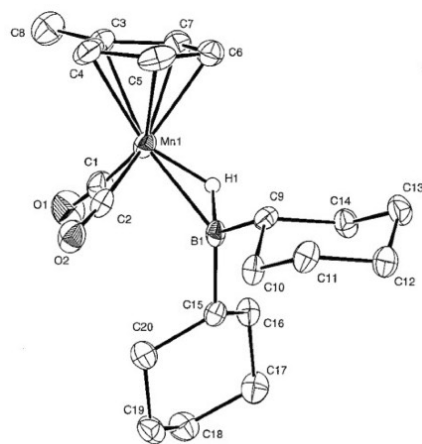
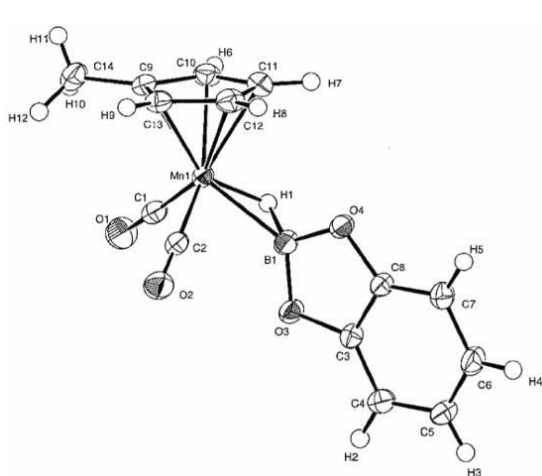
Half-sandwich manganese sigma borane complexes

Sigma borane complexes of manganese can be accessed by two synthetic routes involving either ligand substitution or salt metathesis



Half-sandwich manganese sigma borane complexes

Spectroscopic and crystallographic data imply that the BH bond remains intact, but is weakened on coordination [$J(\text{BH})$ is reduced by about 20 – 40%].



X-ray crystal structures of catecholate and dicyclohexyl derivatives

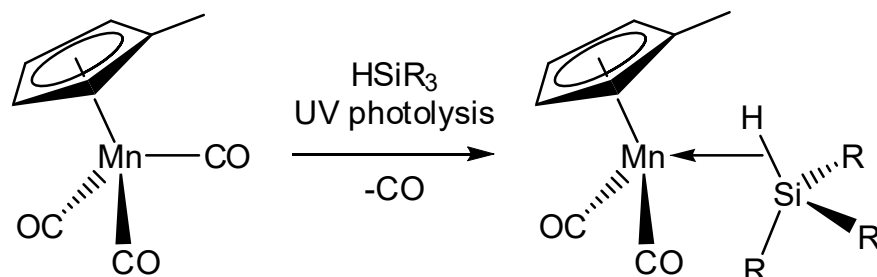
^1H NMR spectrum of catecholate derivative in the hydride region

Reference: *J. Am. Chem. Soc.*, 2000, **122**, 9435 (Hartwig *et al.*)

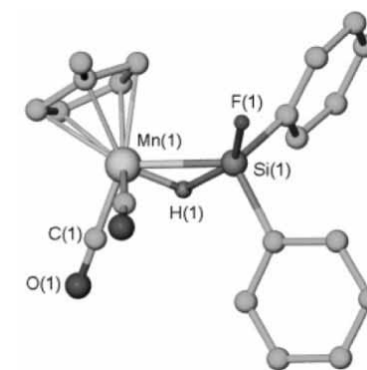
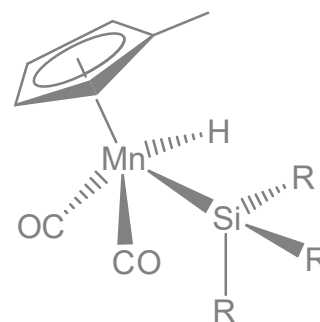
Silane complexes: $M \cdots H-Si$

Coordinated silanes are much more common than alkane analogues.

More polar, more basic nature of the Si-H bond makes silanes better σ -donors, and the lower lying nature of the SiH σ^* orbital makes them better π -acceptors.



Synthesis by photolytic substitution of CO by a silane

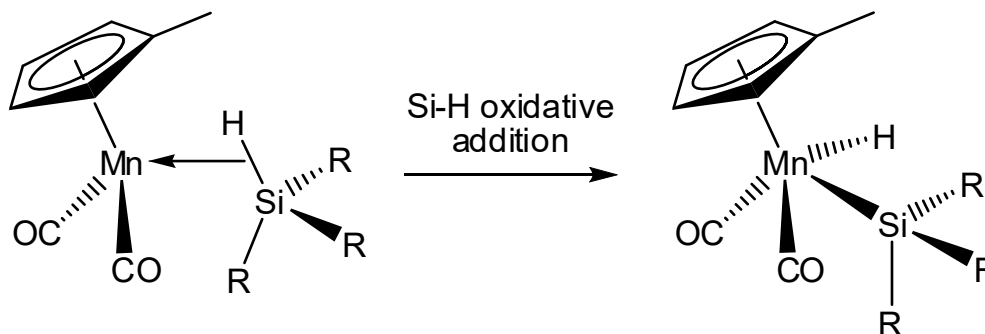


Neutron diffraction structure

The neutron structure of $(\eta^5-C_5H_4Me)Mn(CO)_2(HSiFPh_2)$ shows a Si-H distance (1.80 Å) which is *ca.* 20 % longer than in the uncoordinated silane.

Silane complexes

NMR data (notably the magnitude of the $^1J_{\text{SiH}}$ coupling constant) are an important structural probe.



| Compound | $ J_{\text{Si-H}} $ / Hz | $d(\text{Si-H})$ / Å | $d(\text{Mn-H})$ / Å | $d(\text{Mn-Si})$ / Å |
|--|--------------------------|----------------------|----------------------|-----------------------|
| HSiCl_3 | 338 | 1.478 | - | - |
| $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2(\text{HSiCl}_3)$ | 38 | 1.823 | 1.578 | 2.320 |
| $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})(\text{PMe}_3)(\text{HSiCl}_3)$ | 22 | 1.833 | 1.580 | 2.288 |
| | | - | - | - |

More electron rich metal centres promote greater oxidative addition and a reduced magnitude of $^1J_{\text{SiH}}$ and a shorter Mn-Si distance.

Similar structural trends observed by introducing EWGs at the silane (e.g. F).