

# **Cleaving carbon-carbon bonds by inserting tungsten into unstrained aromatic rings**

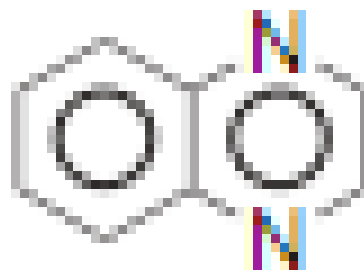
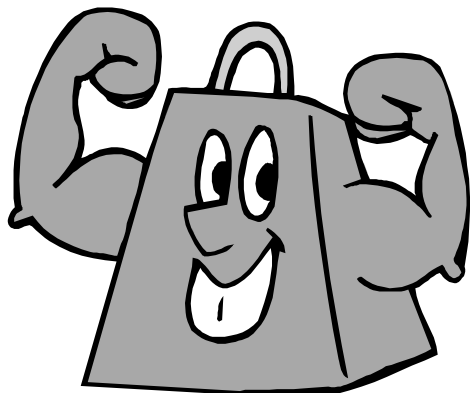
Aaron Sattler & Gerard Parkin  
Nature, Vol 463, 28. January 2010

Ben Williams and Michele Seiler

# Why this is impressive...

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Attempting to cleave a strong C-C bond that is part of an unstrained aromatic ring



quinoxaline

# Let's talk about cleavage...

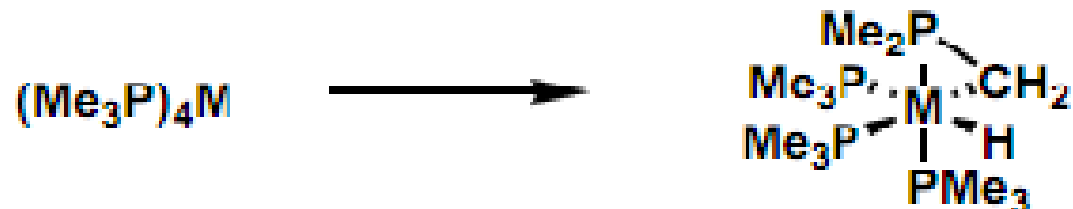
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Two main types of bond cleavage: C-H and C-C

## C-H Bond Cleavage

More common

Uses oxidative addition mechanism



# More cleavage...

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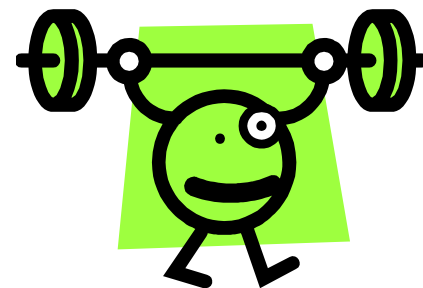
## C-C Bond Cleavage

More rare, more difficult

Thermodynamic and Kinetic Factors

## Kinetic Factors

Greater steric hindrance



## Thermodynamic Factors

M-C bonds weaker than M-H bonds

# Working around it...

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## Kinetic Factors

Using a metal that would hold the C-C bond closer

## Thermodynamic Factors

Use organic substrates where cleavage of C-C bond results in relief of ring strain or formation of aromatic system.

# Bring on the chemistry...

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Interested in hydrodenitrogenation...

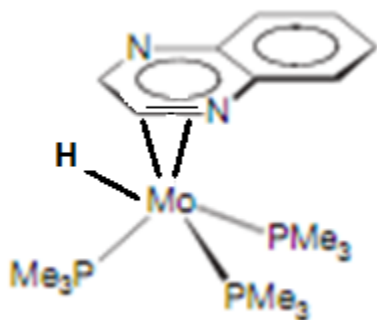
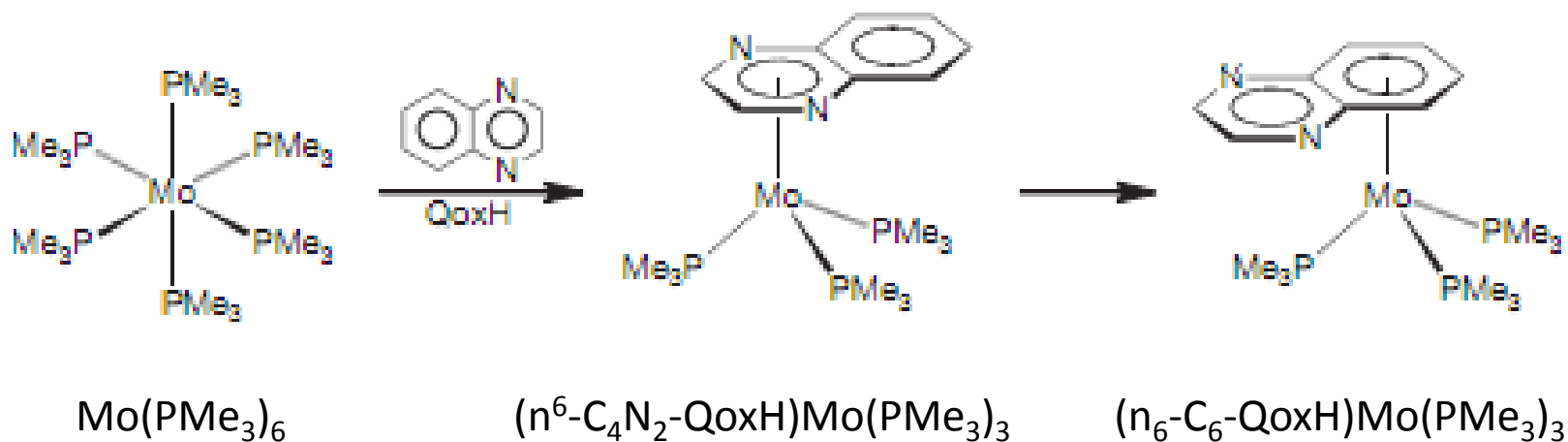
Process by which nitrogen is removed from a petroleum stream...



Success would mean a way to attach heterocyclic nitrogen compounds to surface of hydrodenitrogenation catalysts!!!!

Started with Mo chemistry and then extended to W chemistry...

# Molybdenum...



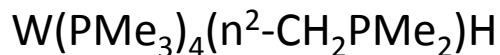
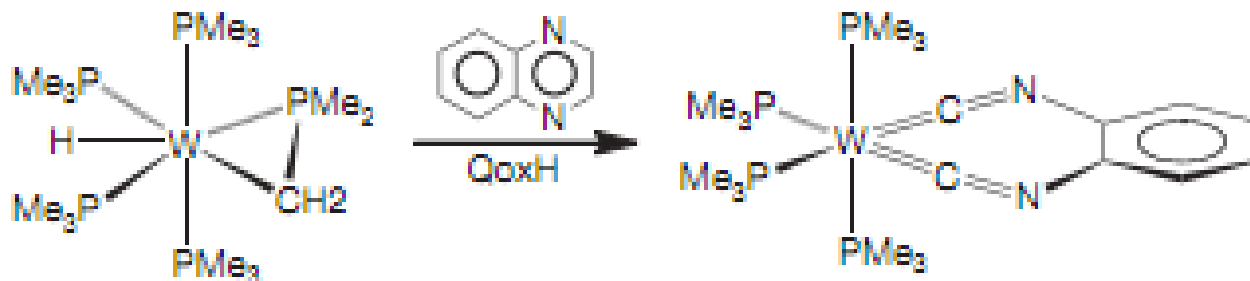
intermediate  
 $(n^2\text{-N,C-Qox})\text{Mo}(\text{PMe}_3)_4\text{H}$

# Moving on down...

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## First W Reaction...

C-C bond cleavage and dehydrogenation



Red crystals

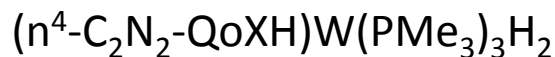
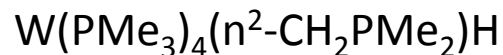
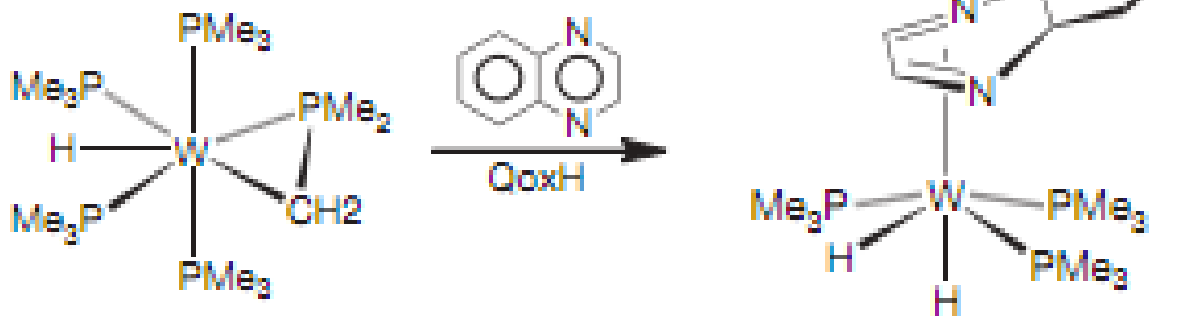
Yield = 15%

# Moving on down...

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## Secondary W Reaction...

No cleavage seen...



Dark yellow crystals

Yield = 24%

# Reaction Extensions...

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Used 2 other reactants to more generally characterize reaction...

6-methylquinoxaline ( $\text{Qox}^{\text{MeH}}$ )

Formed  $[\kappa_2\text{-C}_2\text{-C}_6\text{H}_3\text{Me}(\text{NC})_2]\text{W}(\text{PMe}_3)_4$  in 15% yield

Dark Green crystals

6,7-dimethylquinoxaline ( $\text{Qox}^{\text{Me}_2\text{H}}$ )

Formed  $[\kappa_2\text{-C}_2\text{-C}_6\text{H}_2\text{Me}_2(\text{NC})_2]\text{W}(\text{PMe}_3)_4$  in 18% yield

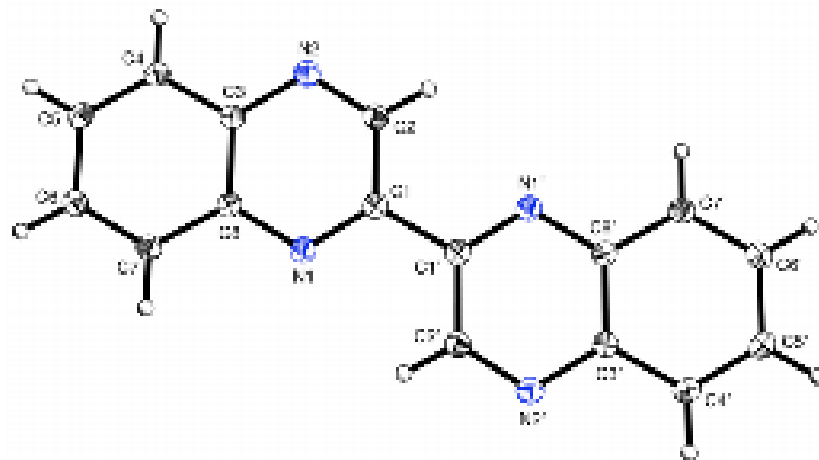
Red crystals

# So where did the hydrogen come from???

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Obvious thought might be from the  $H_2$  liberated during formation of  $[\kappa_2-C_2-C_6H_4(NC)_2]W(PMe_3)_4$

Also might see during the conversion of QoxH to 2,2' – biquinoxaline  $(2,2'-Qox)_2$



# Hydrogen fun...

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Ran each experiment in H<sub>2</sub> atmosphere...

Saw considerable increase in yield for each case:

(n<sup>4</sup>-C<sub>2</sub>N<sub>2</sub>-QoXH)W(PMe<sub>3</sub>)<sub>3</sub>H<sub>2</sub>-- 86% yield

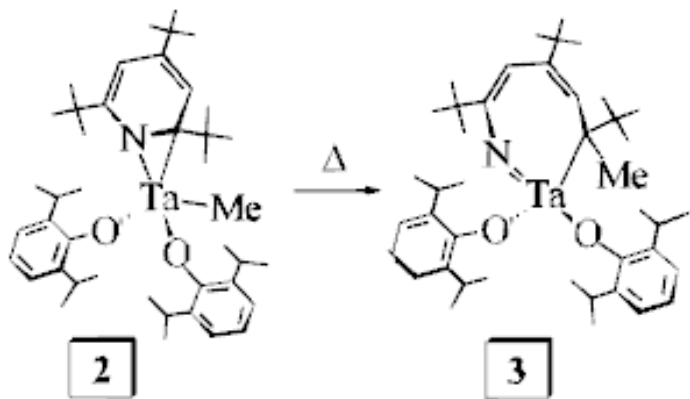
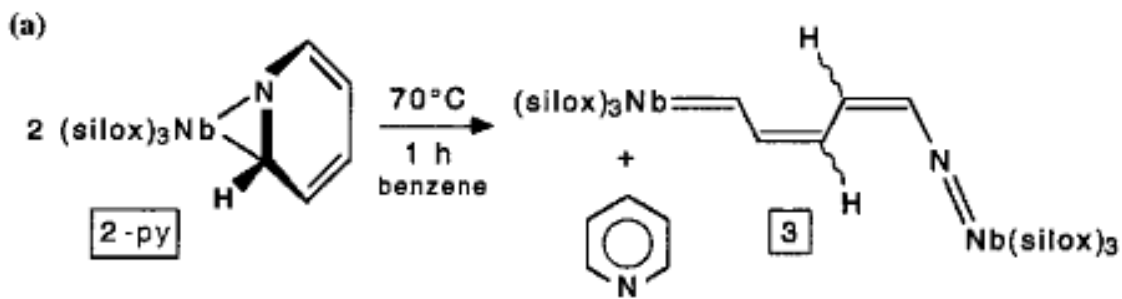
(n<sup>4</sup>-C<sub>2</sub>N<sub>2</sub>-Qox<sup>Me</sup>H)W(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub> -- 49% yield

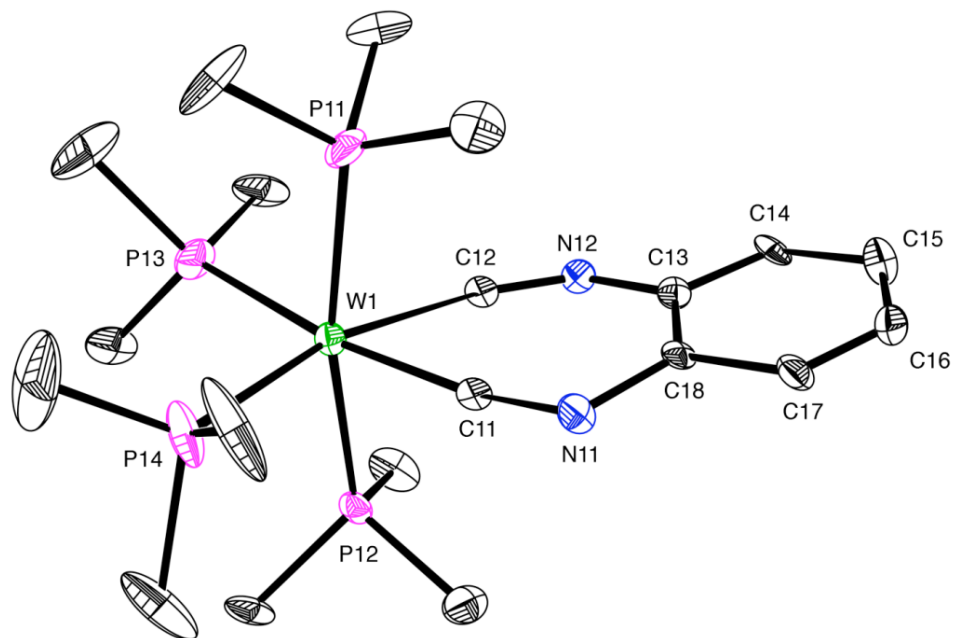
(n<sup>4</sup>-C<sub>2</sub>N<sub>2</sub>-Qox<sup>Me<sup>2</sup></sup>H)W(PMe<sub>3</sub>)<sub>3</sub>H<sub>2</sub> -- 38% yield



# Some Reasons Why Cleaving a C-C Aromatic Bond is Awesome...

- A C-C aromatic bond is a significantly stronger bond to cleave.
- More instances of cleaving the C-N bond on pyridine exist than cleaving an aromatic C-C bond.



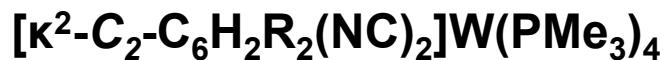
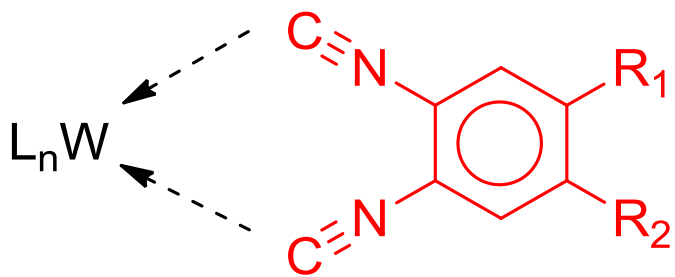


## Two interesting features:

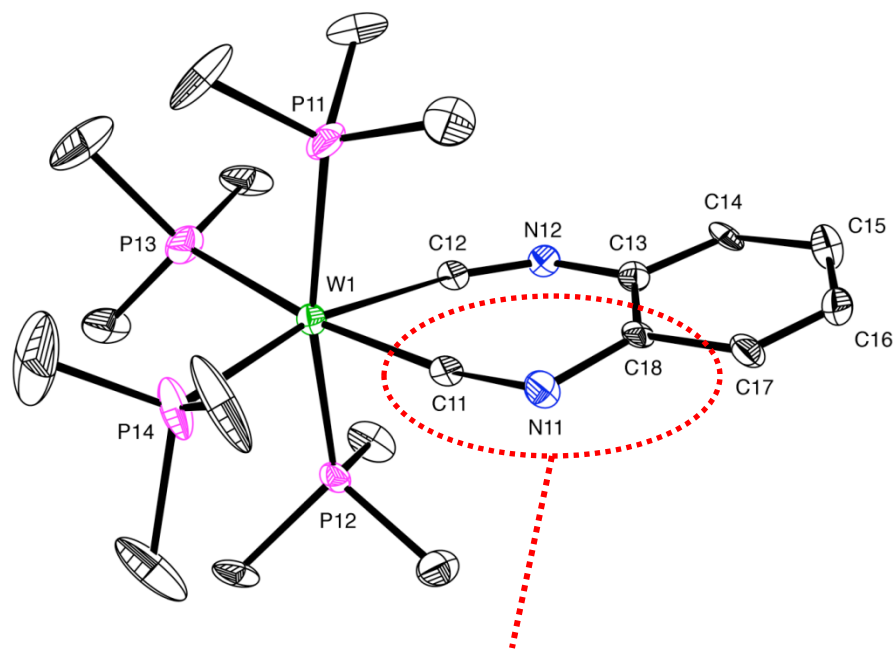
- $W \rightarrow C$  backbonding
- 7-membered metallocycle

# Interesting Features of $[\kappa^2\text{-C}_2\text{-C}_6\text{H}_2\text{R}_2(\text{NC})_2]\text{W}(\text{PMe}_3)_4$

$W \rightarrow C$  Backbonding



...can be thought of as an isocyanide ligand...

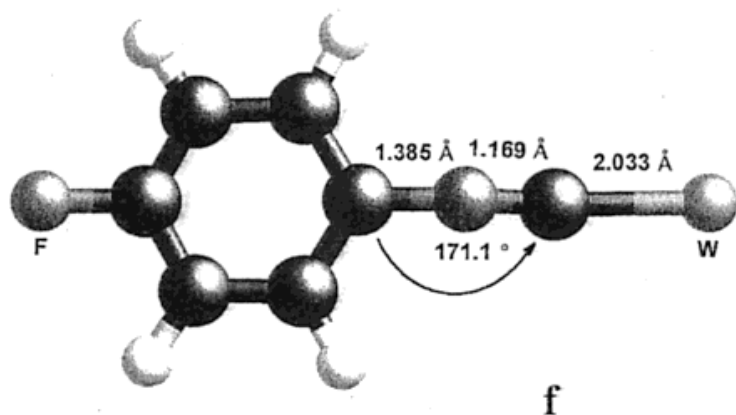


...but X-ray crystallography shows the C-N-C angle is 125-128°, not 180°...

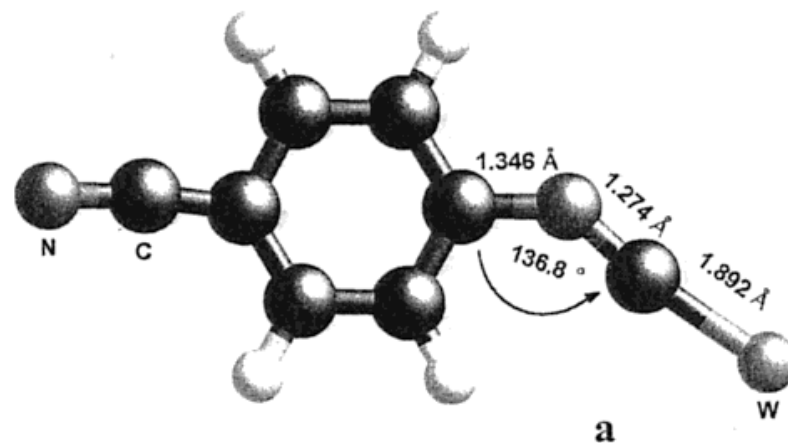
# Interesting Features of $[\kappa^2\text{-C}_2\text{-C}_6\text{H}_2\text{R}_2(\text{NC})_2]\text{W}(\text{PMe}_3)_4$

## $W \rightarrow C$ Backbonding

Such C-N-C bending is indicative of metal-to-ligand  $\pi$ -backbonding, as seen in some monodentate isocyanide complexes.



Less  $W \rightarrow C$   $\pi$ -backbonding

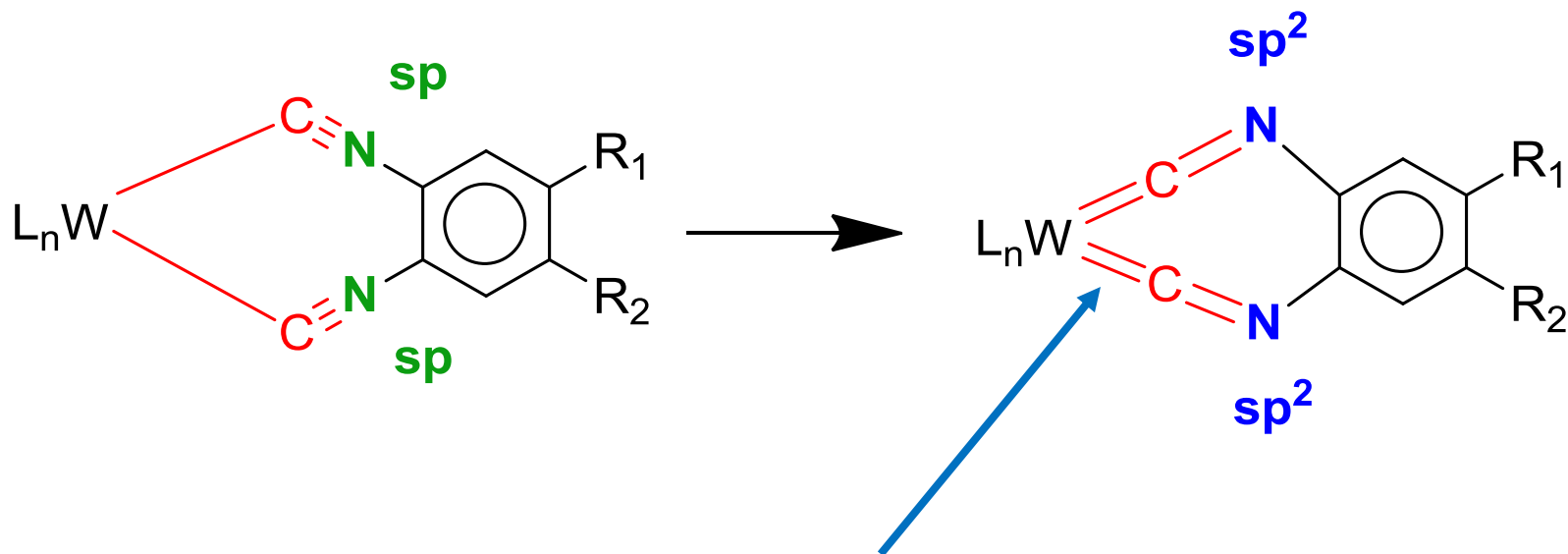


Greater  $W \rightarrow C$   $\pi$ -backbonding

# Interesting Features of $[\kappa^2\text{-C}_2\text{-C}_6\text{H}_2\text{R}_2(\text{NC})_2]\text{W}(\text{PMe}_3)_4$

## $W \rightarrow C$ Backbonding

Why? *Rehybridization and change in bond order!!!*



The W-C bond distance is 1.93 Å, similar to 1.98 Å found for a  $\text{W}=\text{CR}_2$ . This is shorter than a W-C single bond length of 2.23 Å.

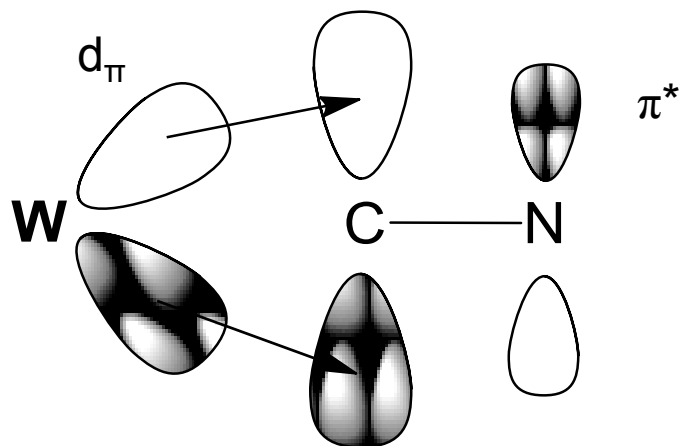
The degree of  $W \rightarrow C$   $\pi$ -backbonding can be monitored using physical methods we learned in class...

## IR Spectroscopy

$$\nu(\text{CN}) \text{ for } \kappa^2\text{-C}_2\text{-C}_6\text{H}_2\text{R}_2(\text{NC})_2\text{]W(PMe}_3)_4 = 1,698 - 1,709 \text{ cm}^{-1}$$

$$\nu(\text{CN}) \text{ range for isocyanide complexes} = 1,670 - 2,310 \text{ cm}^{-1}$$

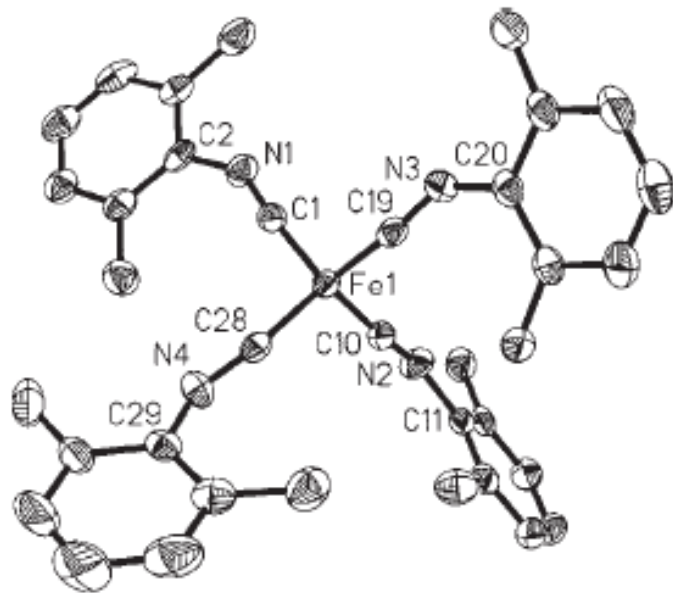
\*\*corresponds to metal-ligand backbonding\*\*



# $^{13}\text{C}$ NMR

## **Trends:**

- $\nu(\text{CN})$  decreases in energy with greater metal-to-ligand backbonding.
- $^{13}\text{C}$  NMR isocyanide carbon signal shifts downfield (deshielding) as backbonding increases.



$$^{13}\text{C} (\text{C-N}) \delta = 238.7 \text{ ppm}$$

$$\text{C-N-C angle} = 144^\circ$$

$$\nu(\text{CN}) = 1,670 \text{ cm}^{-1}$$

Would assume greater  $\pi$ -backbonding due to the formal negative charge on  $\text{Fe}^{2-}$

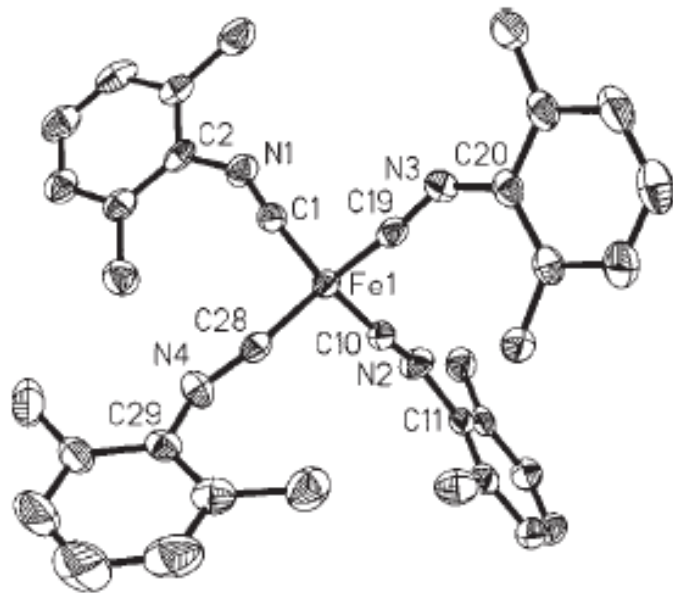
Also would assume greater backbonding due to its physical characteristics

$$^{13}\text{C} (\text{C-N}) \delta \text{ range} = 151.8 - 238.7 \text{ ppm}$$

# $^{13}\text{C}$ NMR

## **Trends:**

- $\nu(\text{CN})$  decreases in energy with greater metal-to-ligand backbonding.
- $^{13}\text{C}$  NMR isocyanide carbon signal shifts downfield (deshielding) as backbonding increases.

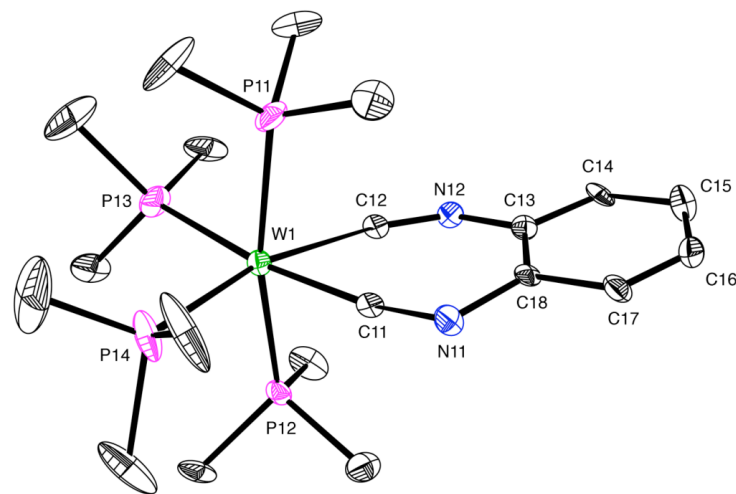


**$[\text{Fe}(\text{CNXyl})_4]^{2-}$**

$^{13}\text{C}$  (C-N)  $\delta$  = 238.7 ppm

C-N-C angle =  $144^\circ$

$\nu(\text{CN})$  =  $1,670\text{ cm}^{-1}$



**$[\kappa^2\text{-C}_2\text{-C}_6\text{H}_2\text{R}_2(\text{NC})_2]\text{W}(\text{PMe}_3)_4$**

$^{13}\text{C}$  (C-N)  $\delta$  = 211.4 ppm

C-N-C angle =  $125 - 128^\circ$

$\nu(\text{CN})$  =  $1,703\text{ cm}^{-1}$

# Interesting Features of $[\kappa^2\text{-C}_2\text{-C}_6\text{H}_2\text{R}_2(\text{NC})_2]\text{W}(\text{PMe}_3)_4$

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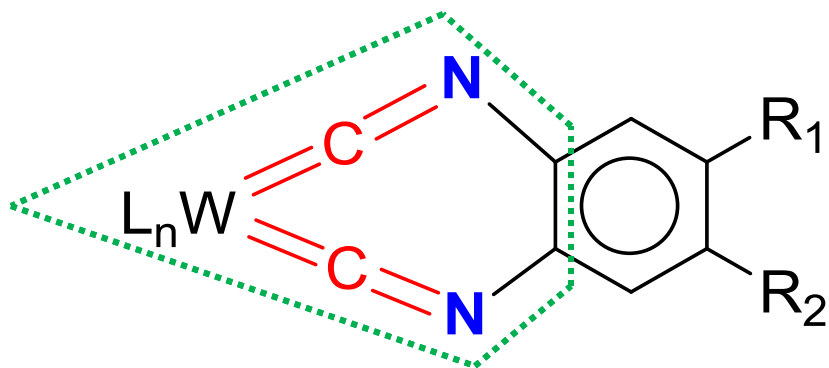
*W → C Backbonding*

## Summary:

- Non-linear C-N-C angle and shorter W-C bond distance is indicative of increased W→C backbonding.
- Low  $\nu(\text{CN})$  in comparison with other isocyanide ligands is evidence for C≡N bond weakening.
- Downshifted  $^{13}\text{C}$  NMR isocyanide resonance signifies backbonding in this complex.

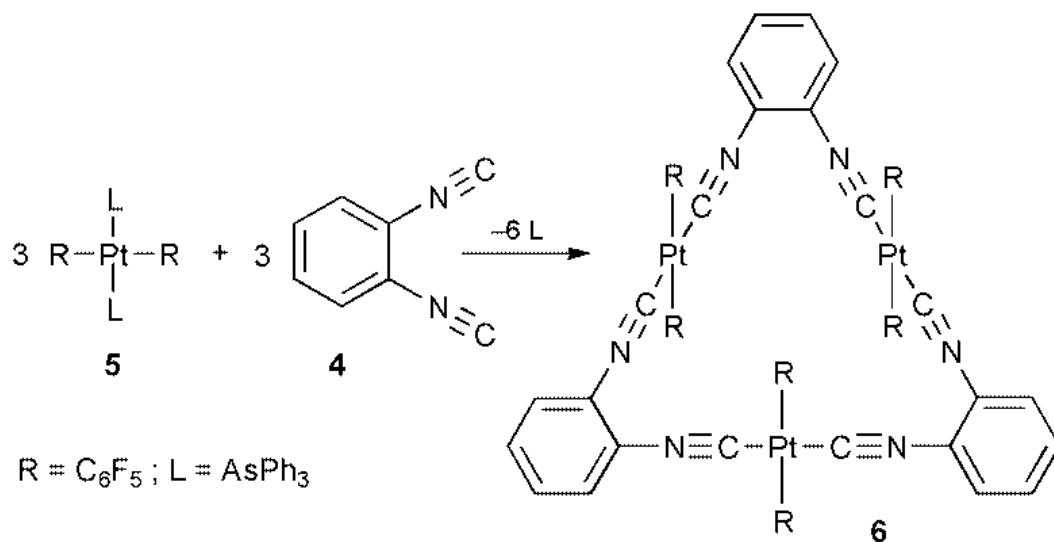
# Interesting Features of $[\kappa^2\text{-C}_2\text{-C}_6\text{H}_2\text{R}_2(\text{NC})_2]\text{W}(\text{PMe}_3)_4$

*7-membered metallocycle = totally nuts*



But...chelating isocyanide ligands W-C-N-R prefer to adopt linear geometries at C and N!

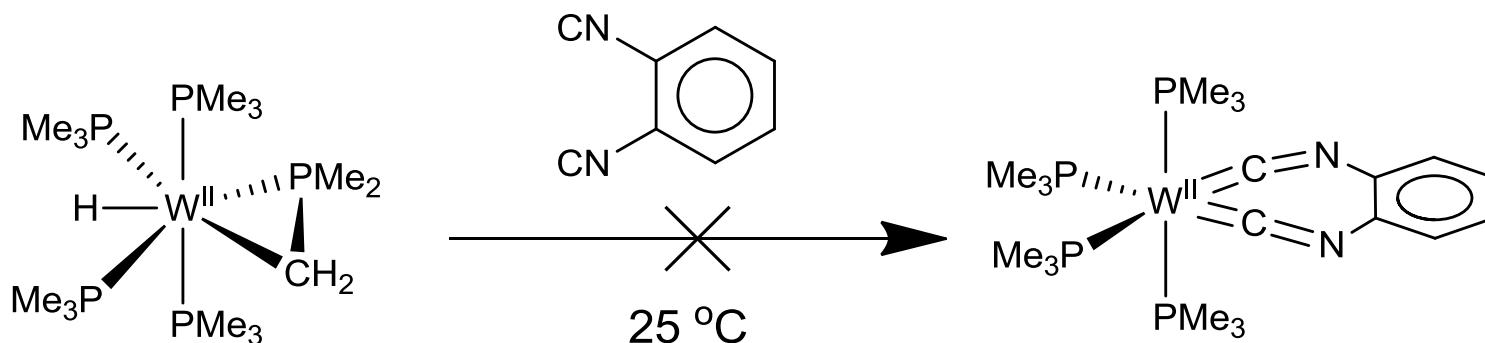
- This can be seen when  $o\text{-(CN)}_2\text{C}_6\text{H}_4$  is used as a stand-alone ligand...it prefers to act as a bridging ligand.
- Because of this, the smallest ring size using bidentate isocyanide ligands is 12.



# Interesting Features of $[\kappa^2\text{-C}_2\text{-C}_6\text{H}_2\text{R}_2(\text{NC})_2]\text{W}(\text{PMe}_3)_4$

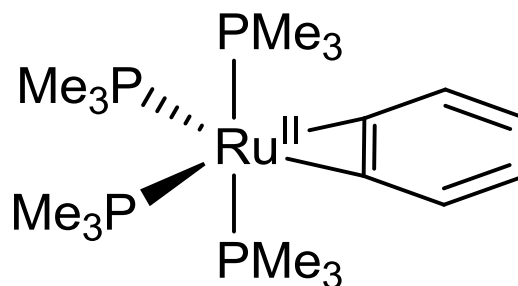
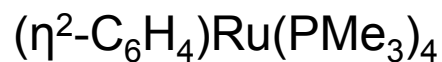
*7-membered metallocycle = it's okay*

**Explanation:** mechanism includes insertion of W into the aromatic ring allows for a smaller metallocycle.

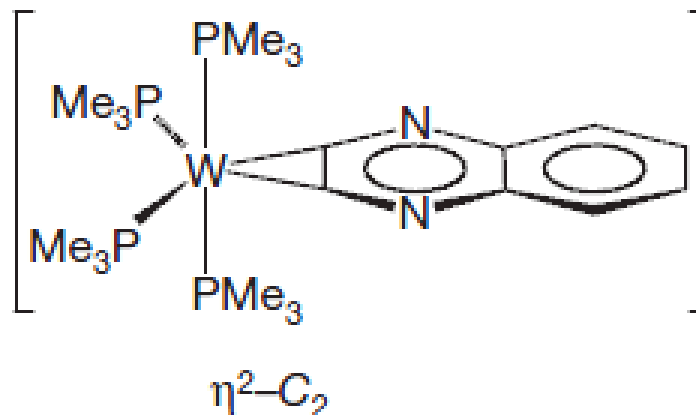


# Proposed Mechanism

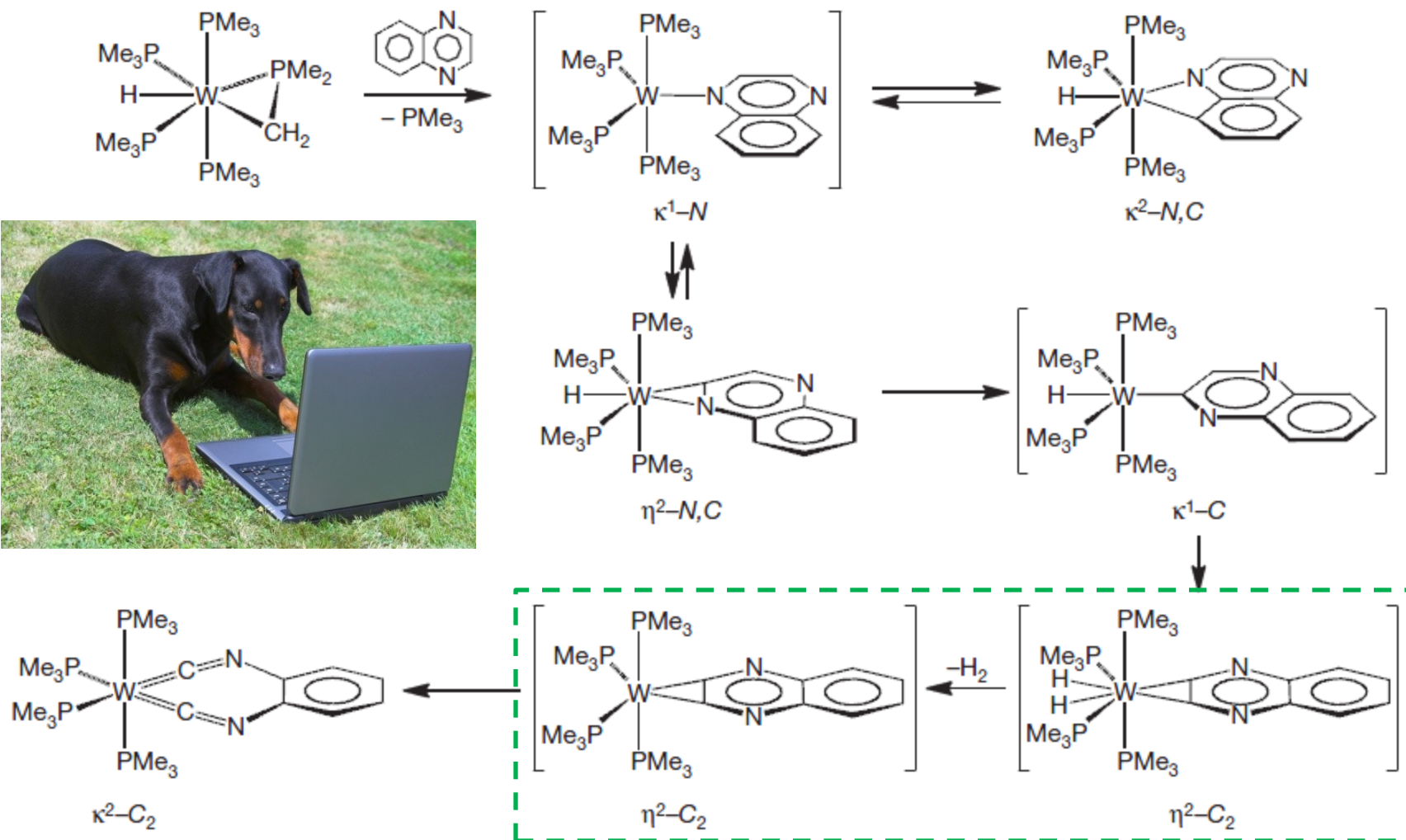
The authors base their mechanism off a benzyne intermediate seen in a recently reported Ru complex.



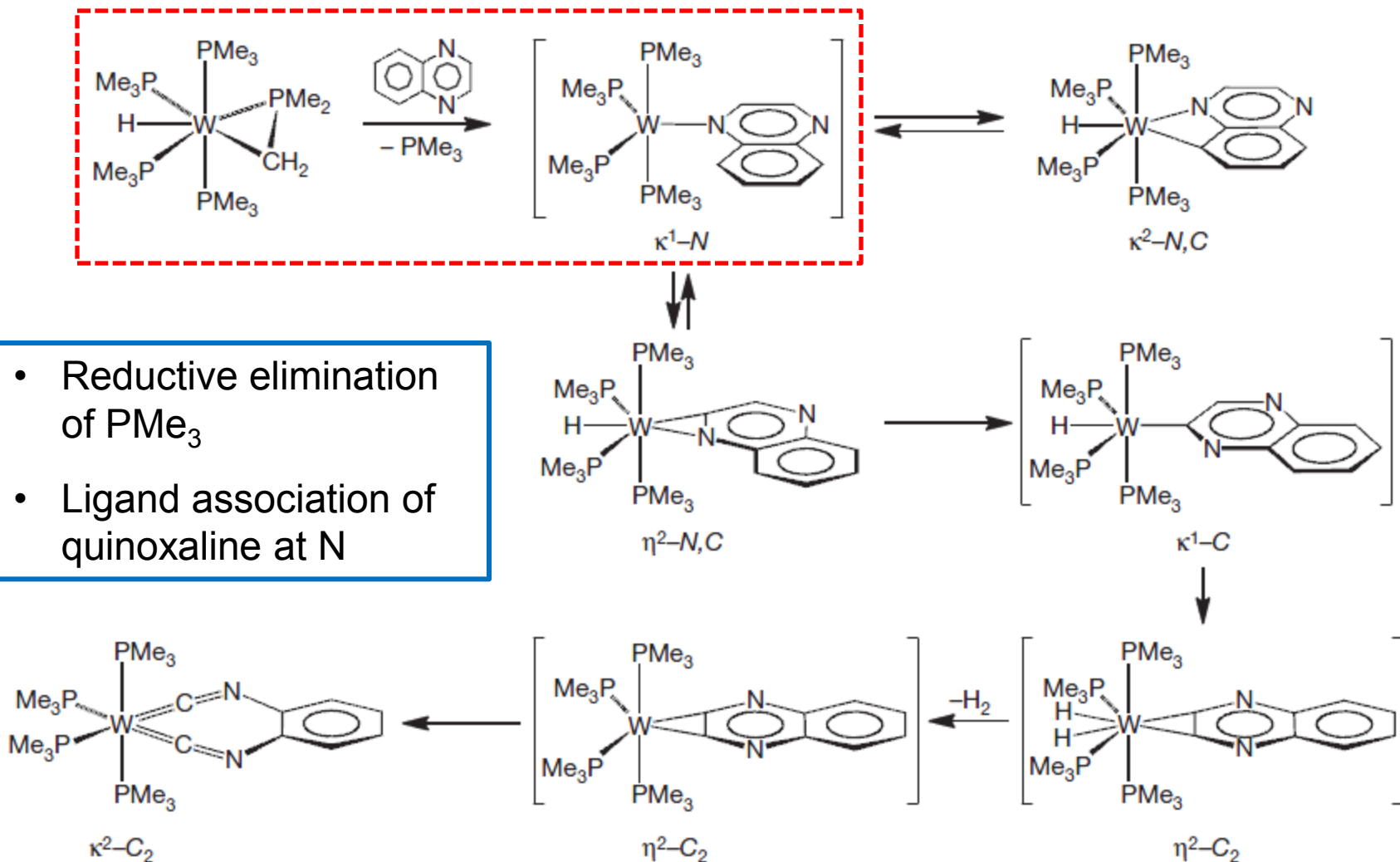
Benzyne intermediate



# Proposed Mechanism

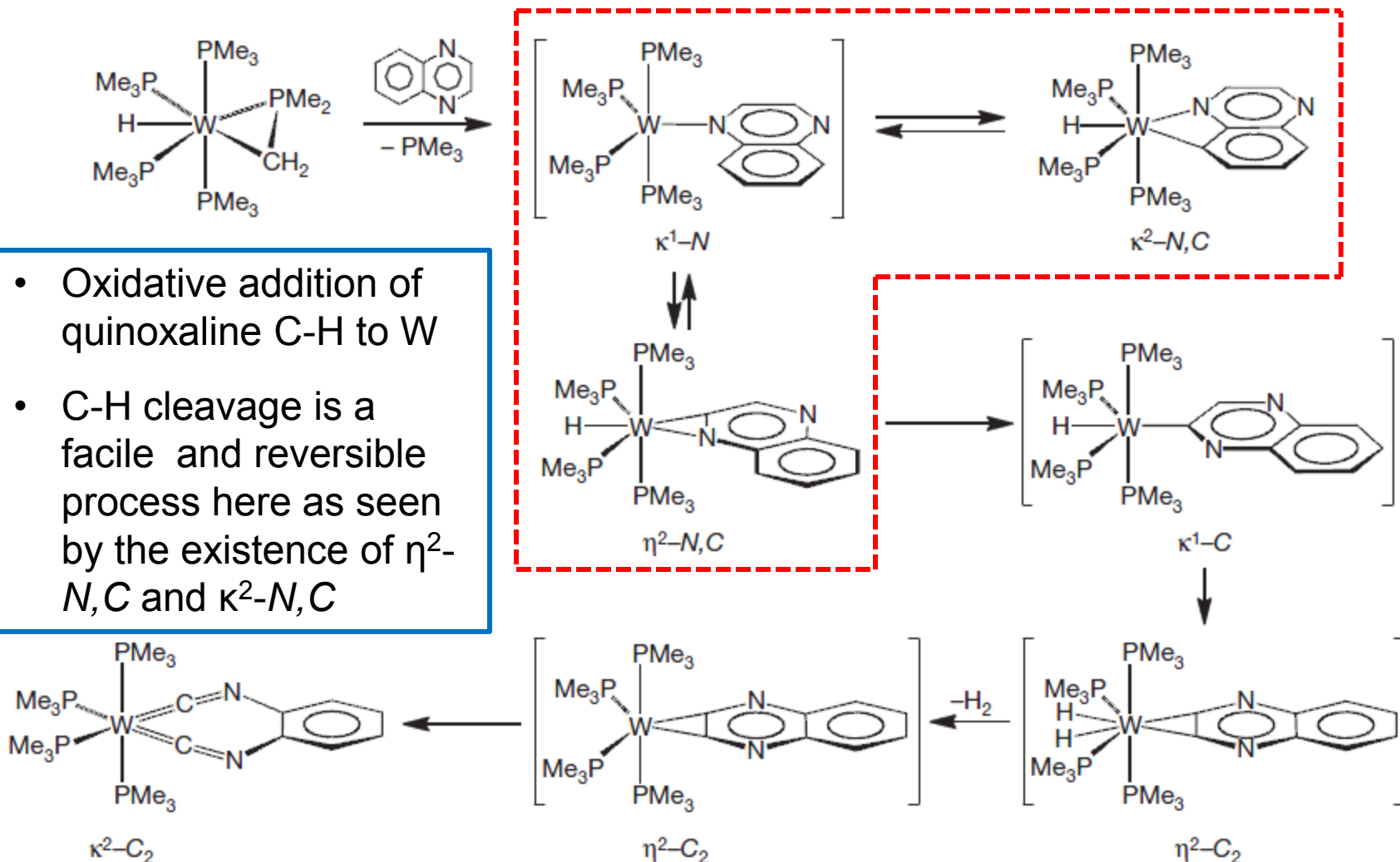


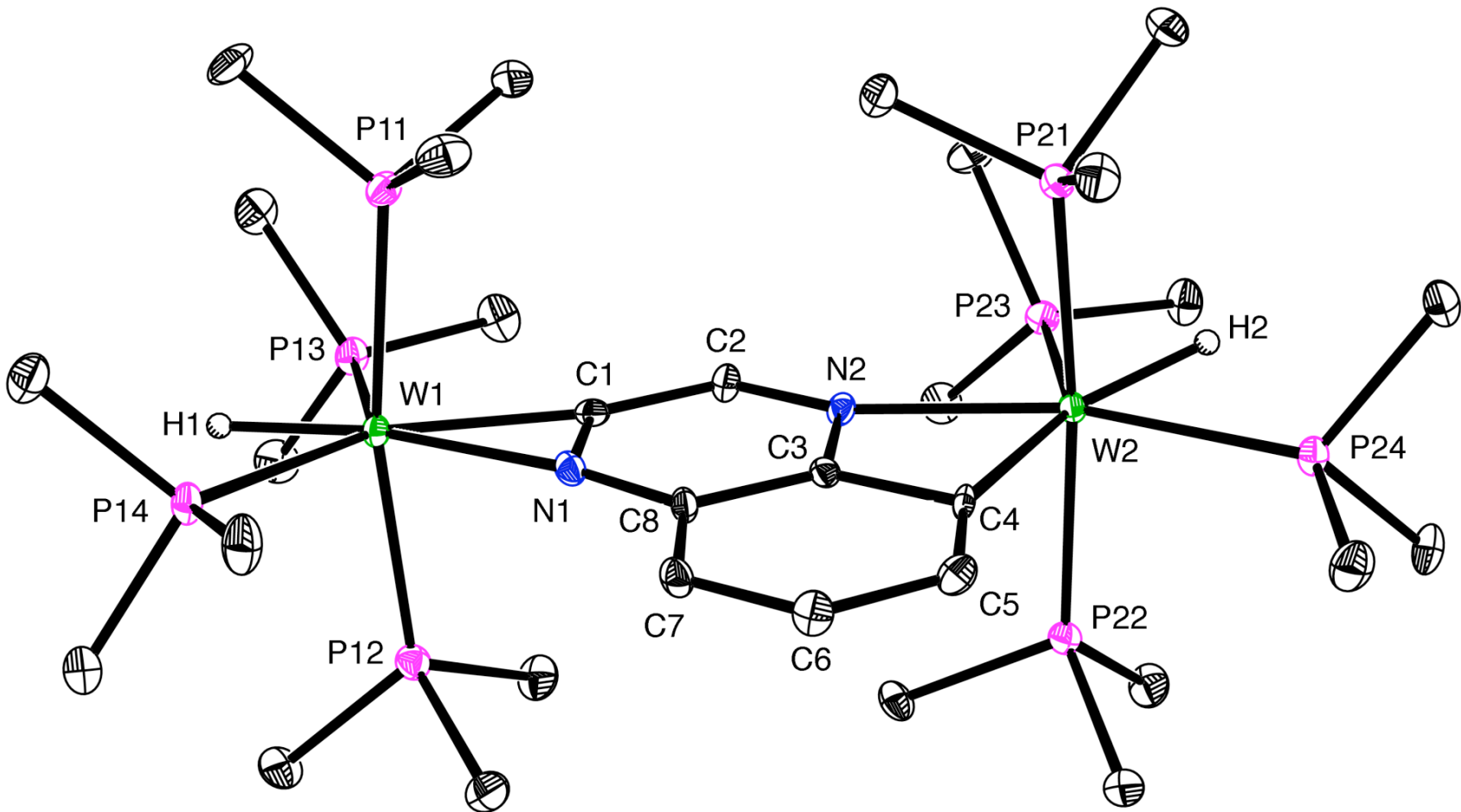
# Proposed Mechanism



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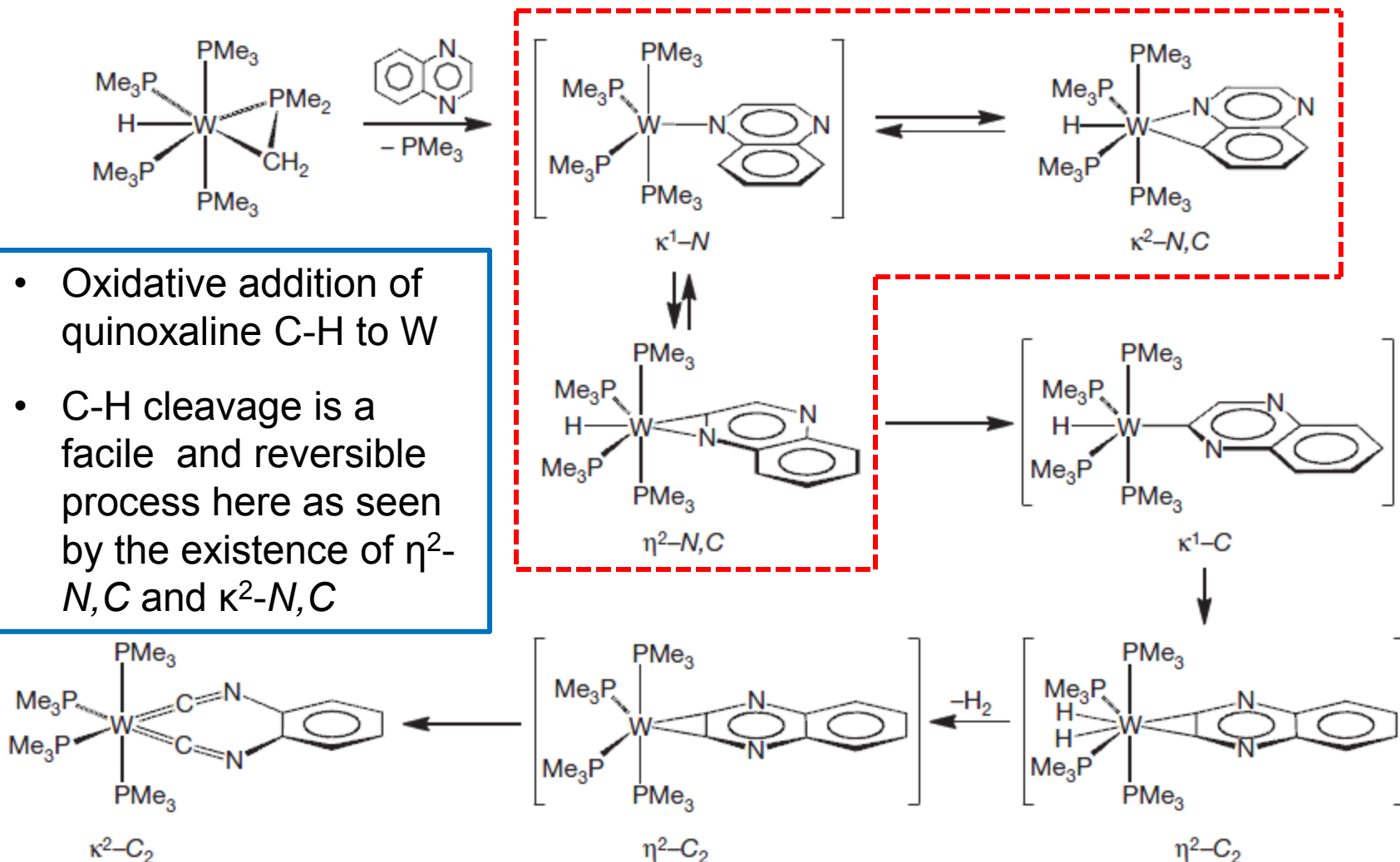
- Oxidative addition of quinoxaline C-H to W
- C-H cleavage is a facile and reversible process here as seen by the existence of  $\eta^2-N,C$  and  $\kappa^2-N,C$



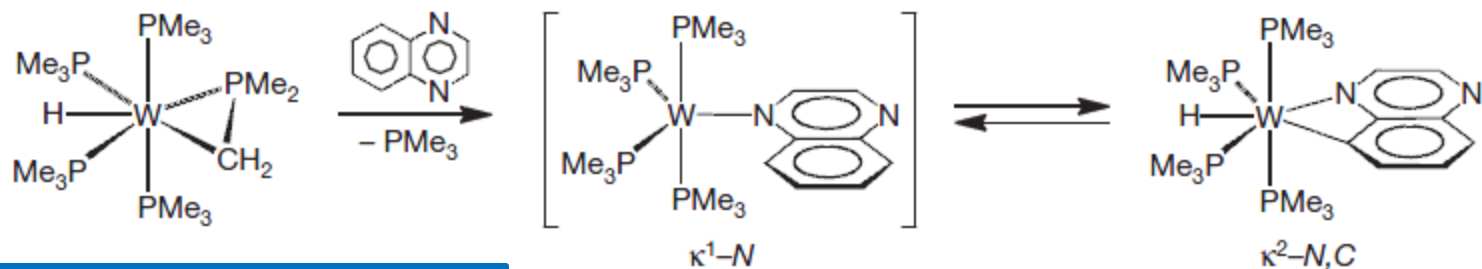


# Proposed Mechanism

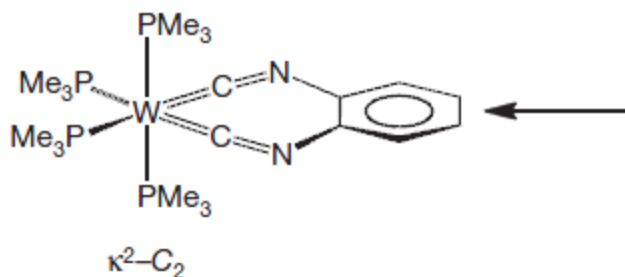
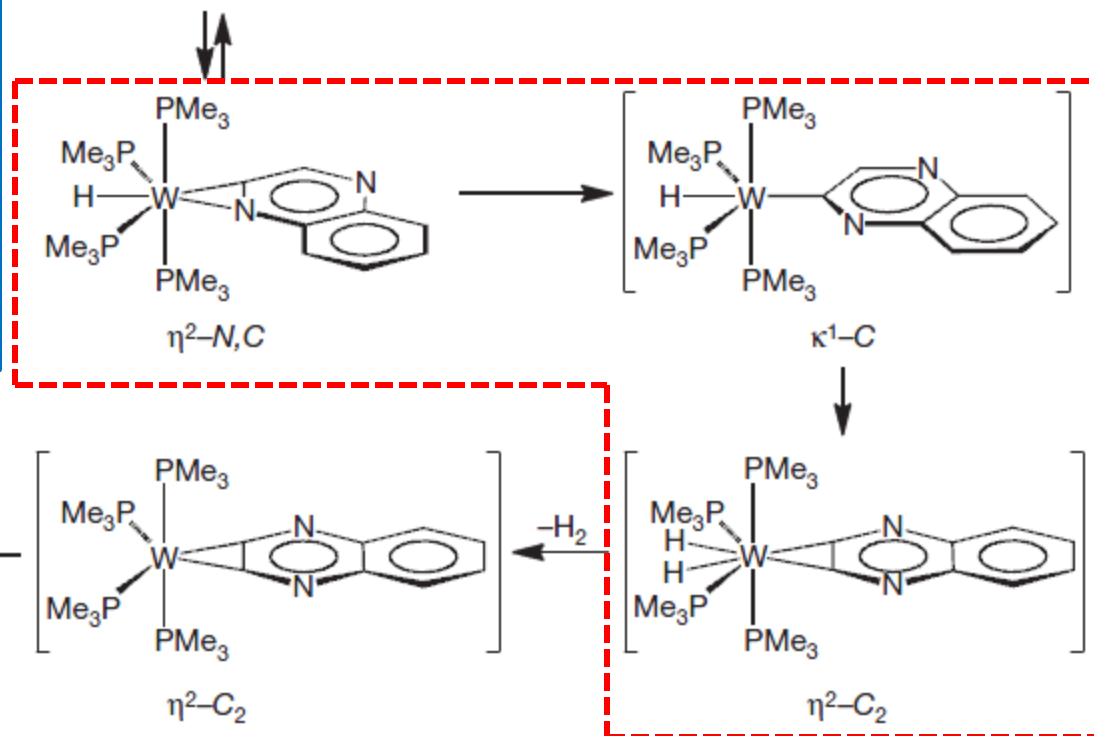
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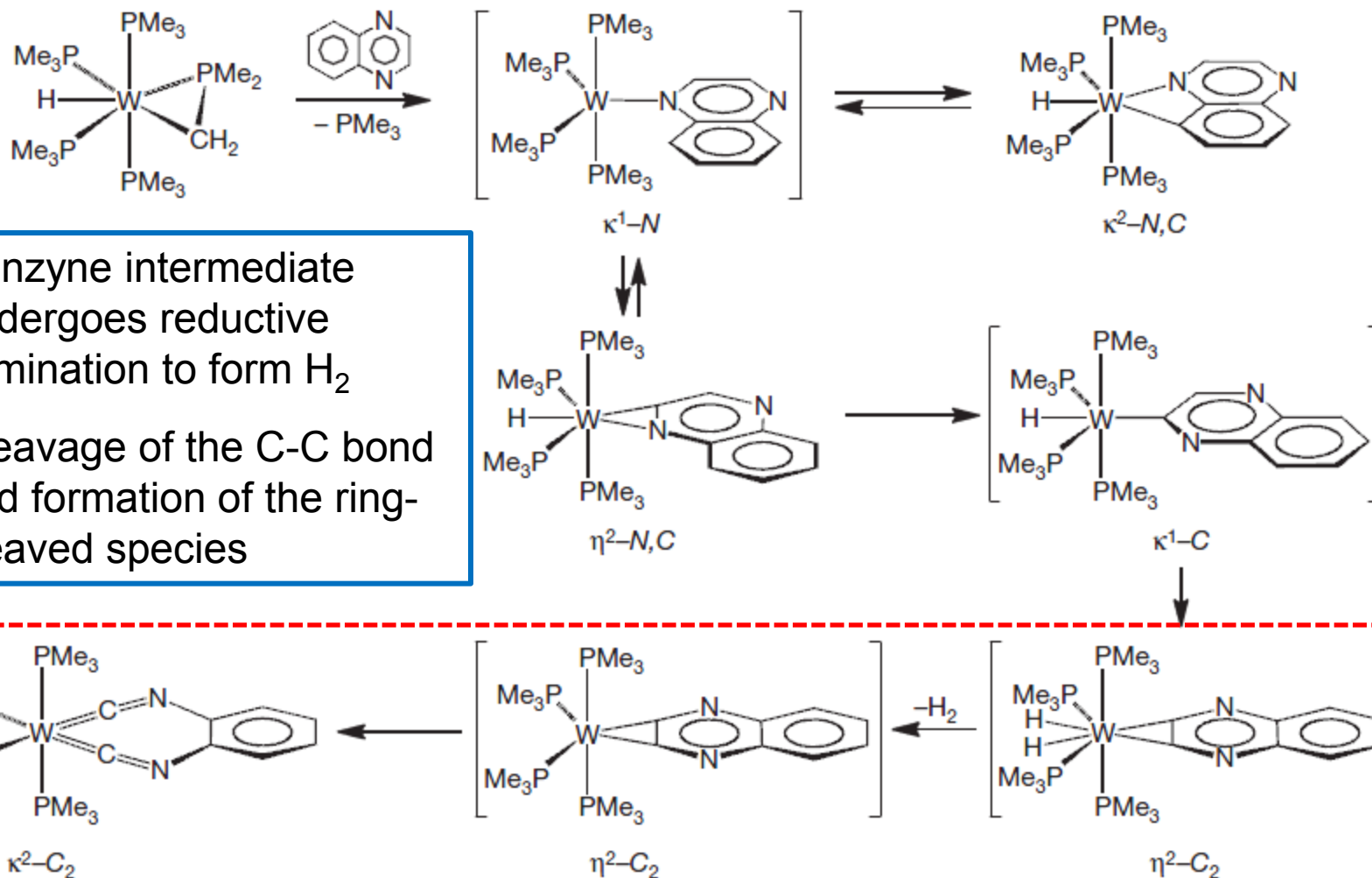
# Proposed Mechanism



- Ligand dissociation of the quinoxaline N maintains +2 formal charge on W
- Oxidative addition of quinoxaline C-H oxidizes W from +2 to +4.



# Proposed Mechanism



- Benzyne intermediate undergoes reductive elimination to form H<sub>2</sub>
- Cleavage of the C-C bond and formation of the ring-cleaved species

# Conclusions...

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Developed a new method for functionalizing aromatic molecules

Successfully cleaved a C-C bond from an aromatic system using tungsten metal center

The extension of this method could potentially be used in the hydrodenitrogenation industry!



# Questions...

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