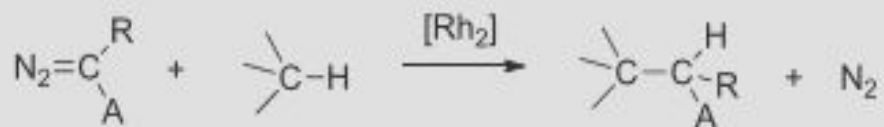


# Metal–metal multiple bonded intermediates in catalysis

(for example,  $\text{Rh}_2$  and  $\text{Ru}_2$  complexes)

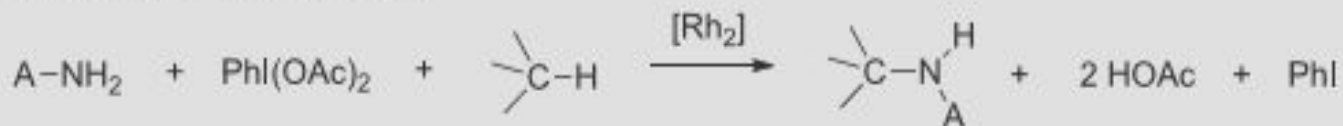
# Overview of Rh<sub>2</sub>-catalysed C–H functionalization and C–H amination chemistries

## *Carbenoid C–H functionalization*

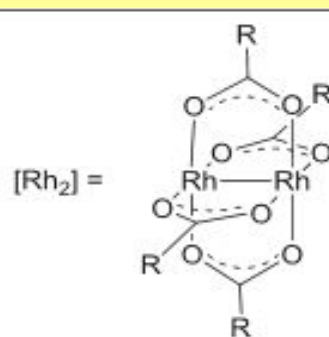


R = Ar, H  
A = COOCH<sub>3</sub>

## *Nitrenoid C–H amination*

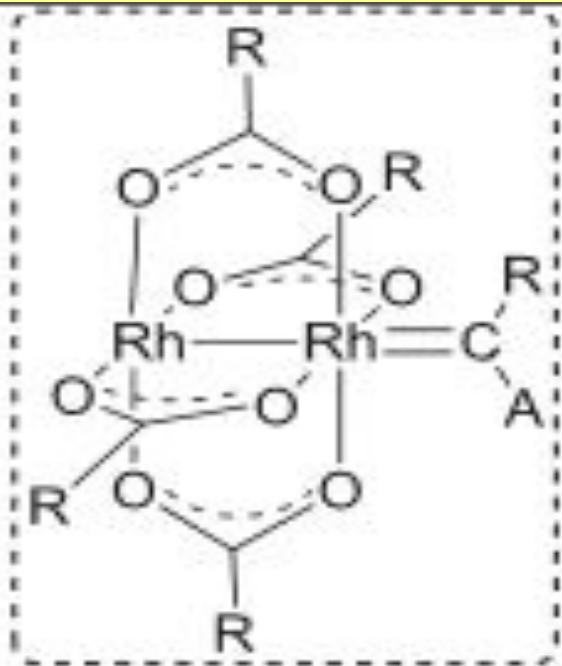


A = SO<sub>3</sub>R, COOR



Rh<sub>2</sub>-tetracarboxylate catalyst

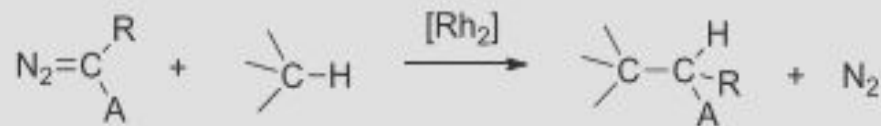
# Rh<sub>2</sub> carbene chemistry



Proposed  
Rh<sub>2</sub>-carbene  
intermediate

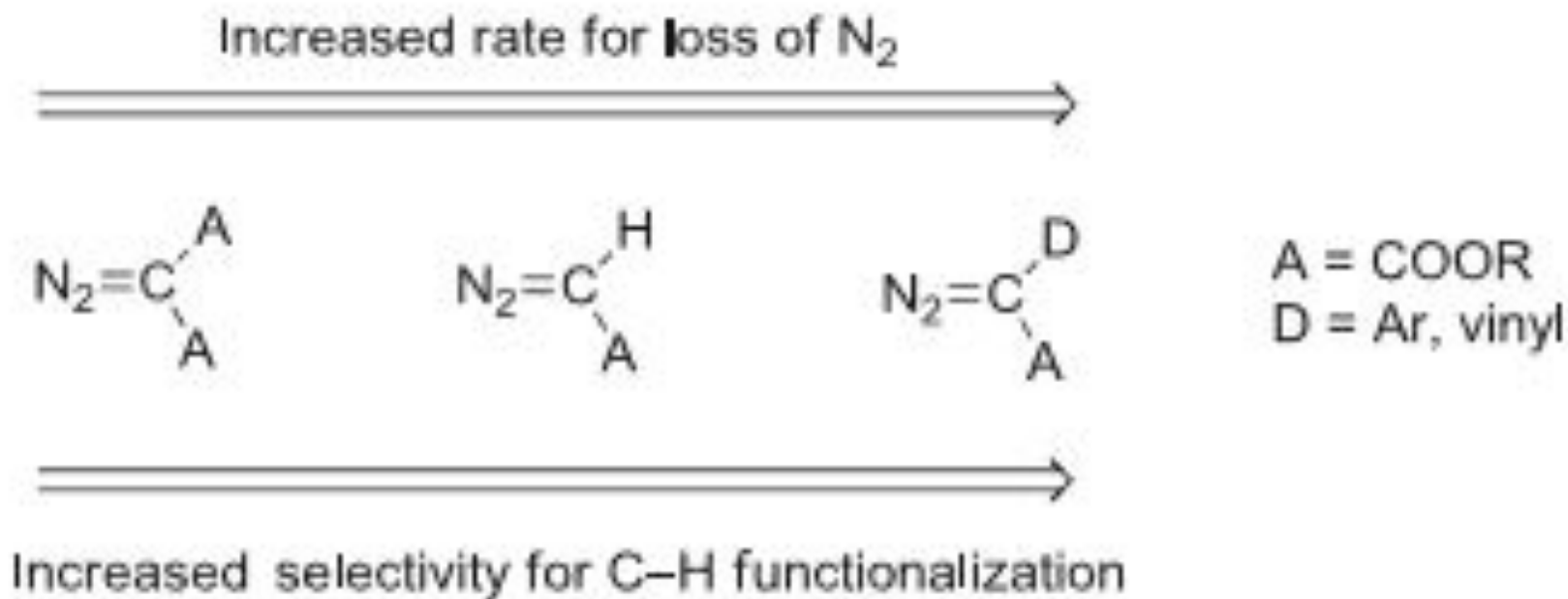
The key electronic feature of this intermediate is delocalized Rh–Rh–C three-centre bonding with appropriate three-centre orbitals of  $\sigma$  and  $\pi$  symmetry

## Carbenoid C–H functionalization

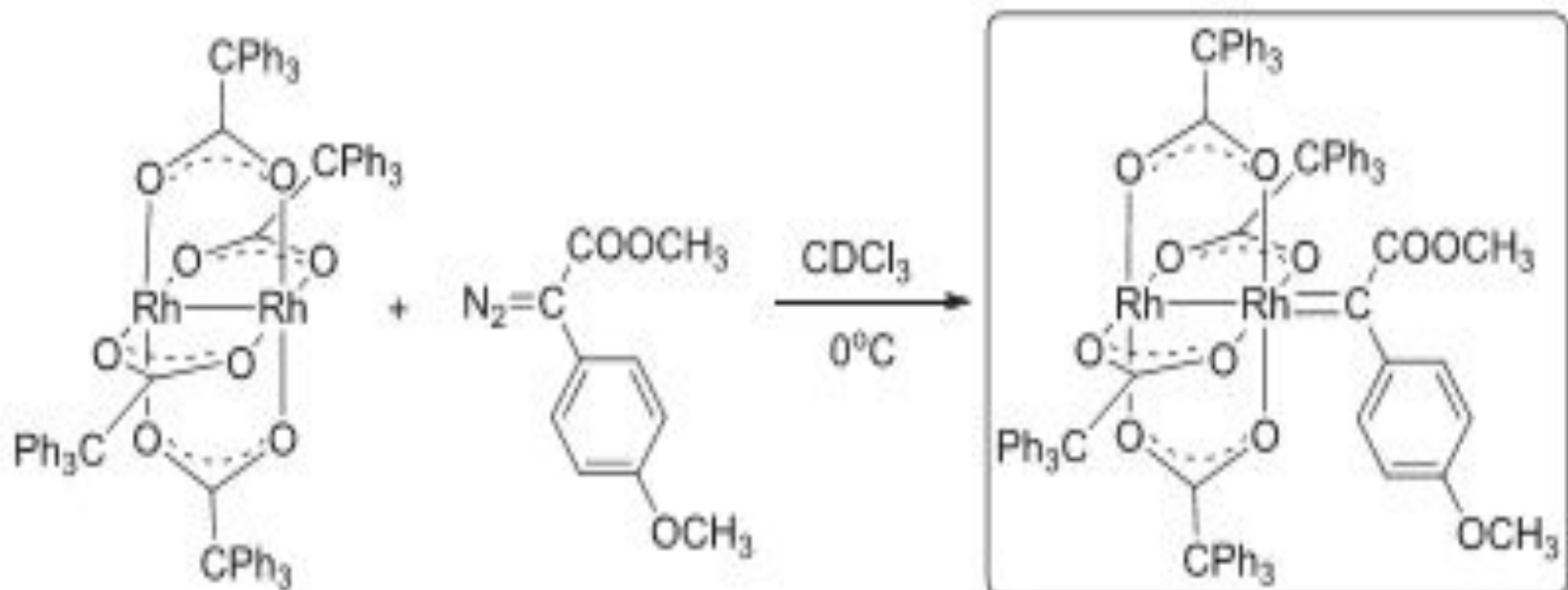


R = Ar, H  
A = COOCH<sub>3</sub>

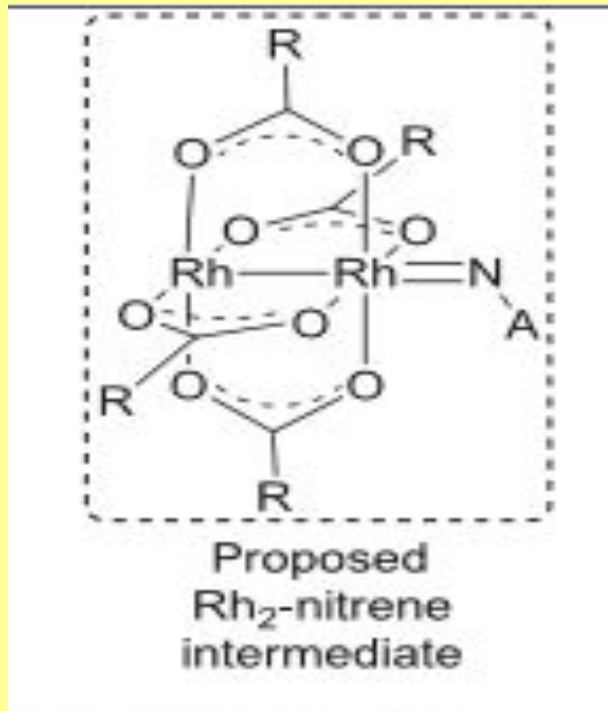
# Trends in reactivity for the different classes of organic diazo compounds



# Preparation of the first Rh<sub>2</sub> D/A carbene complex

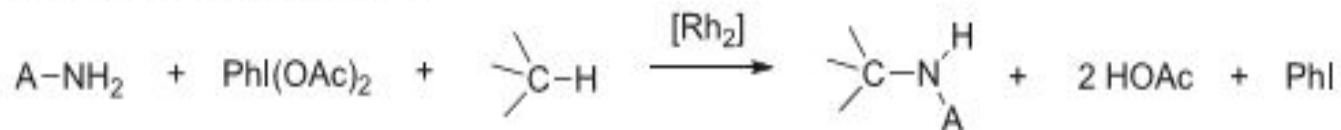


# Rh<sub>2</sub> nitrene chemistry



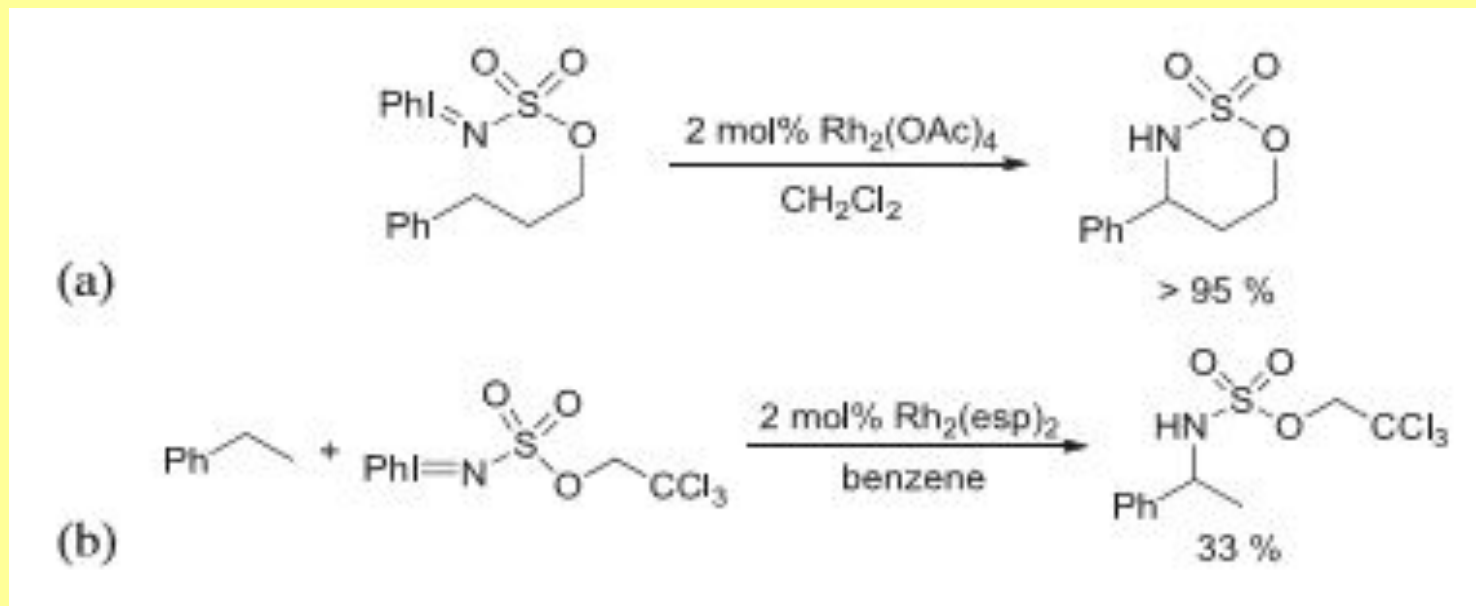
Rh<sub>2</sub>-catalysed  
nitrenoid chemistry  
is mechanistically  
more complex than  
the corresponding  
carbenoid chemistry

## Nitrenoid C-H amination



A = SO<sub>3</sub>R, COOR

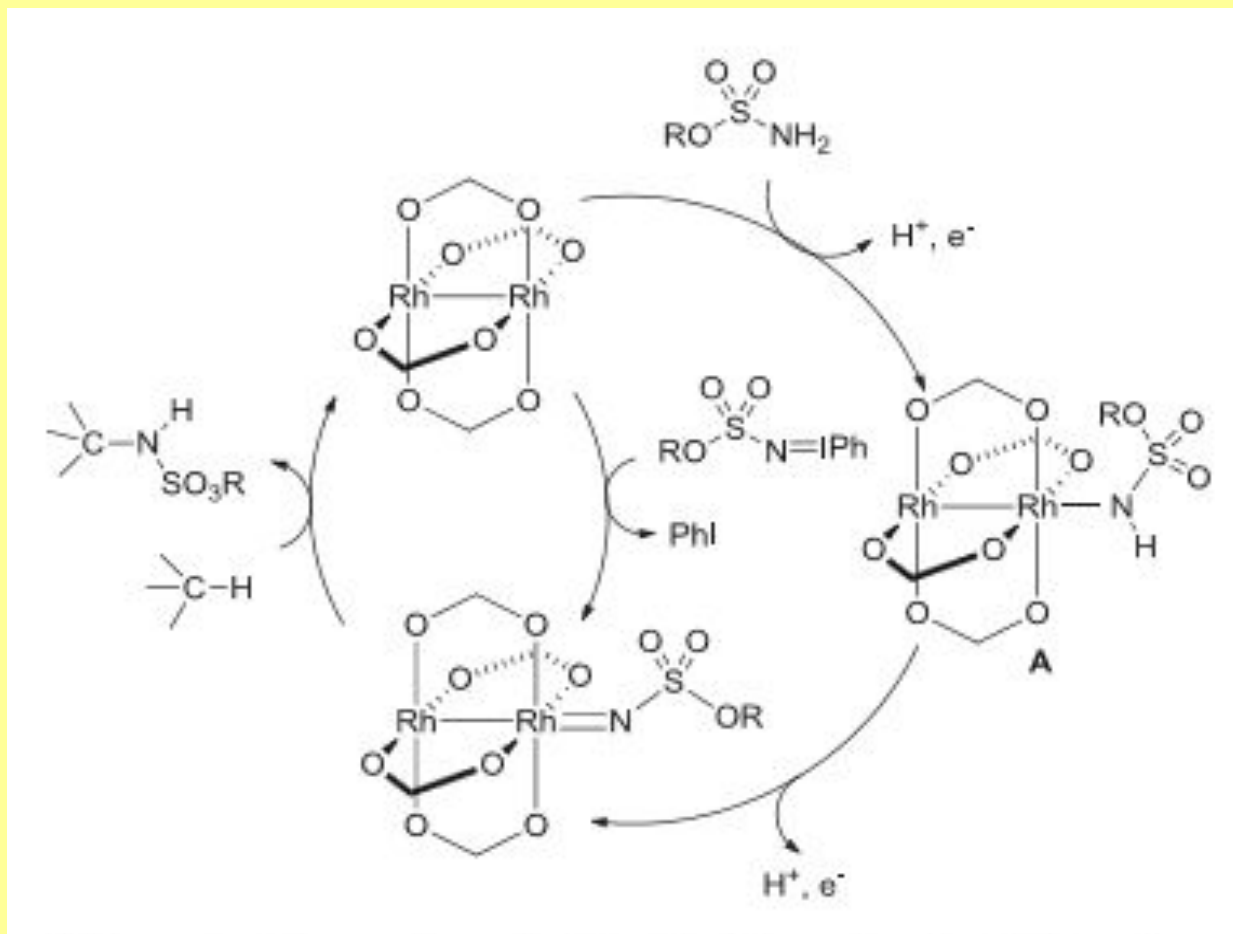
# Reactions using pre-formed iminoiodinane compounds



(a) – intramolecular cyclization

(b) – intermolecular reaction

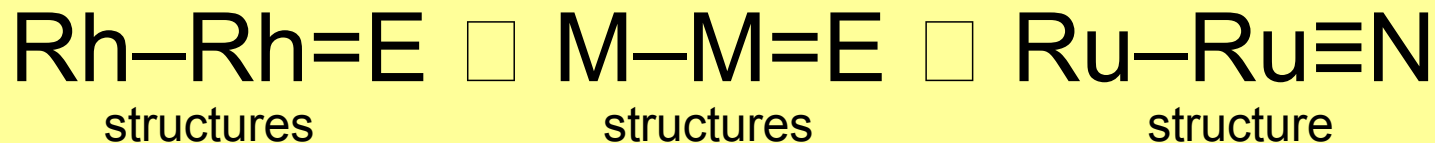
# Proposed mechanism for intermolecular C–H amination



Organic groups on the catalyst are removed for clarity



# Ru<sub>2</sub> nitrido chemistry

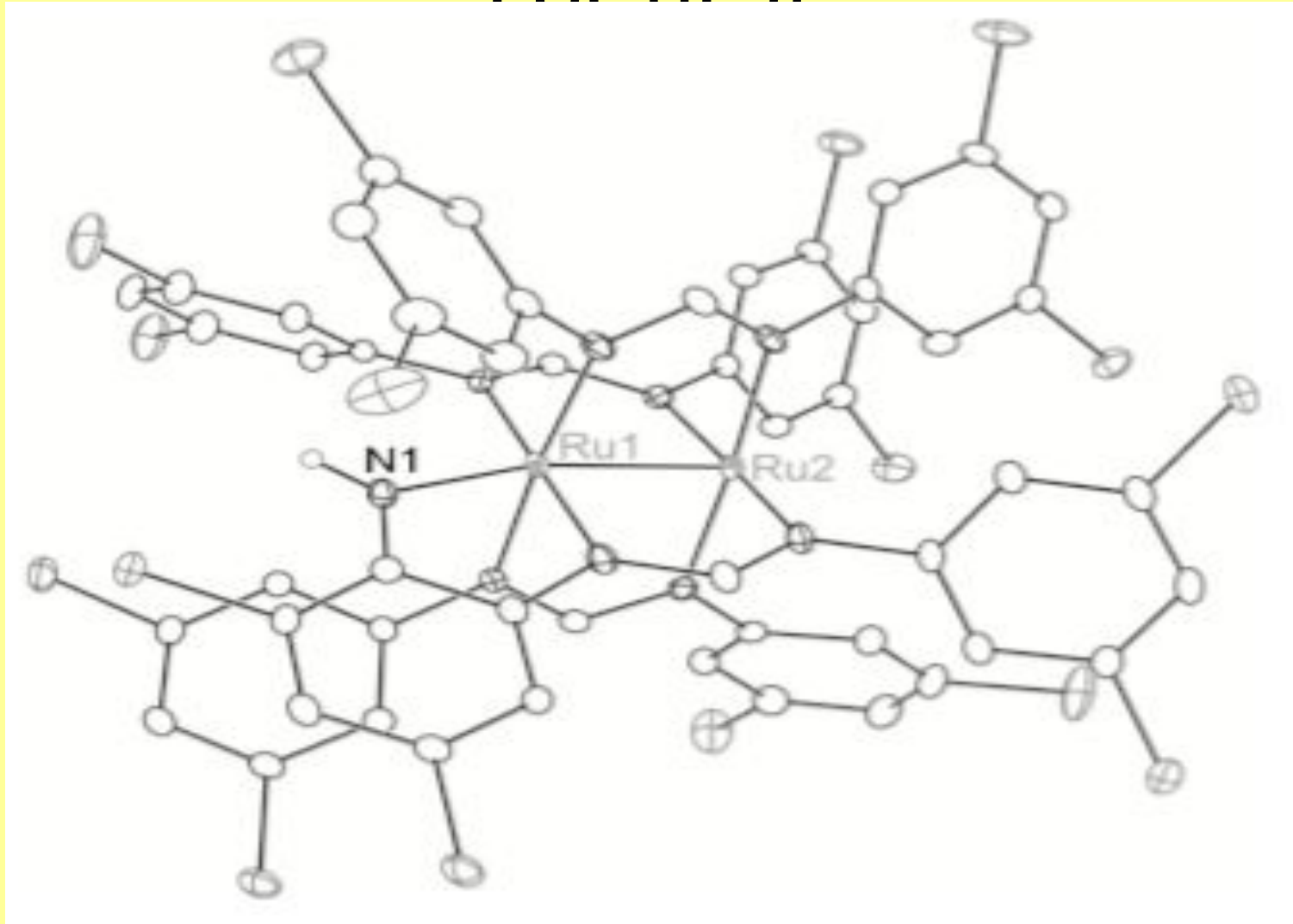


(E = CR<sub>2</sub>/NR)

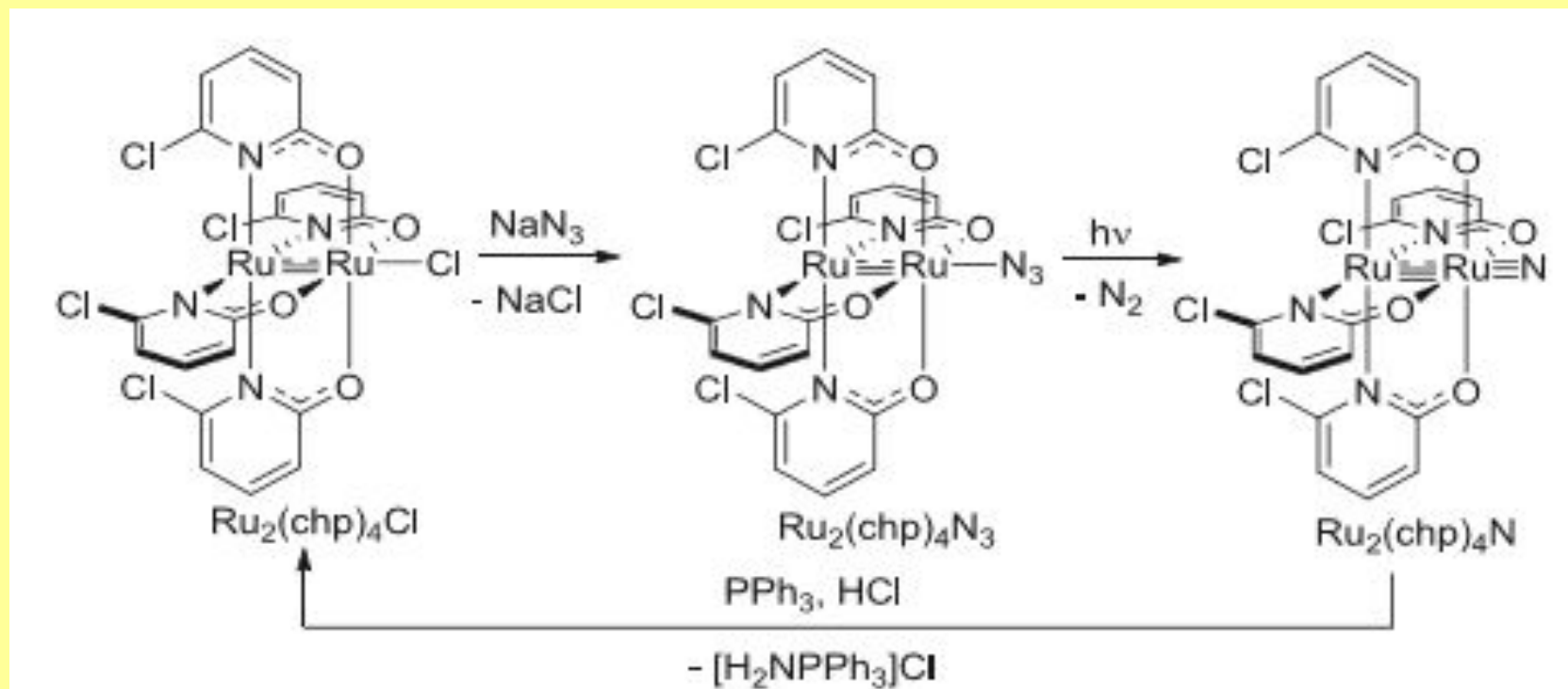
The first Ru<sub>2</sub> nitrido compound  
– Ru<sub>2</sub>(DPhF)<sub>4</sub>N  
(DPhF = N,N'-diphenylformamidinate) – was  
found to be thermally unstable

In an effort to understand the nature of this  
instability,  
the related Ru<sub>2</sub>(D(3,5-Cl<sub>2</sub>)PhF)<sub>4</sub>N<sub>3</sub> azide  
complex was investigated

Crystal structure of  
 $\text{Ru}_2[(D(3,5\text{-Cl}_2)\text{PhF})_3(D(3,5\text{-Cl}_2\text{-2-NH})\text{PhF})]$



# Synthetic cycle for N-atom transfer using the $\text{Ru}_2(\text{chp})_4$ core



# Summary

Efforts to identify reactive metal–metal bonded complexes having a linear  $M-M=E$  structure have led to the observation of important intermediates in  $Rh_2$ -catalysed carbenoid and nitrenoid transformations.

Inspired by the structures of these intermediates, chemists have been able to explore novel reactivity of the  $Ru-Ru\equiv N$  core including intramolecular C–H amination as well as intermolecular N atom transfer.

# Source

J. Chem. Sci. Vol. 127, No. 2, February 2015,  
pp. 209–214. Indian Academy of Sciences. DOI  
10.1007/s12039-015-0773-6

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MS received 19 May 2014; accepted 17 July  
2014

The presentation was prepared by Maxim Pavchenko