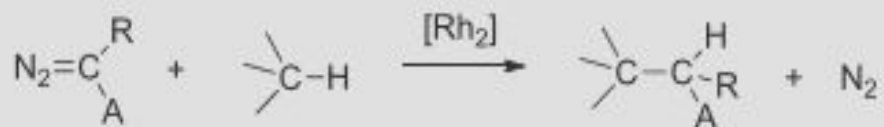


Metal–metal multiple bonded intermediates in catalysis

(for example, Rh_2 and Ru_2 complexes)

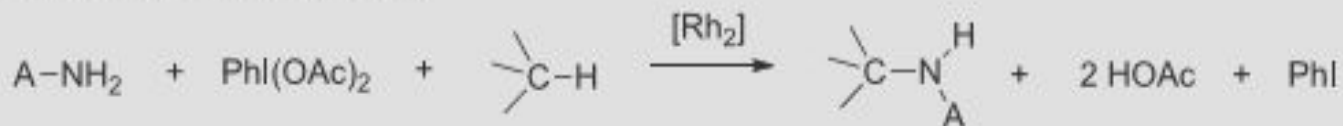
Overview of Rh₂-catalysed C–H functionalization and C–H amination chemistries

Carbenoid C–H functionalization

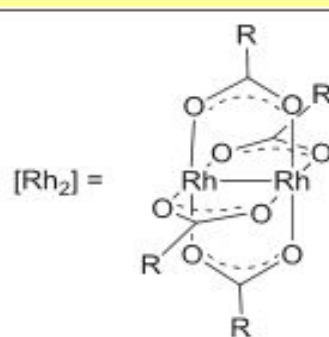


R = Ar, H
A = COOCH₃

Nitrenoid C–H amination

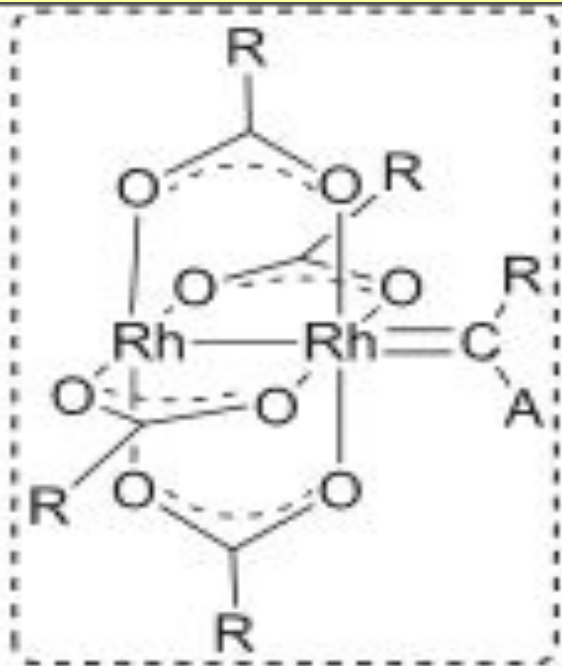


A = SO₃R, COOR



Rh₂-tetracarboxylate catalyst

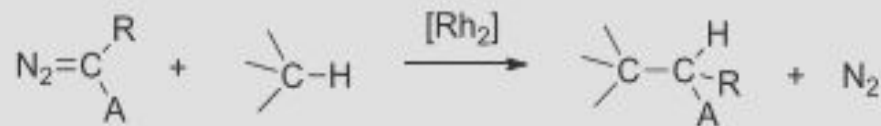
Rh₂ carbene chemistry



Proposed
Rh₂-carbene
intermediate

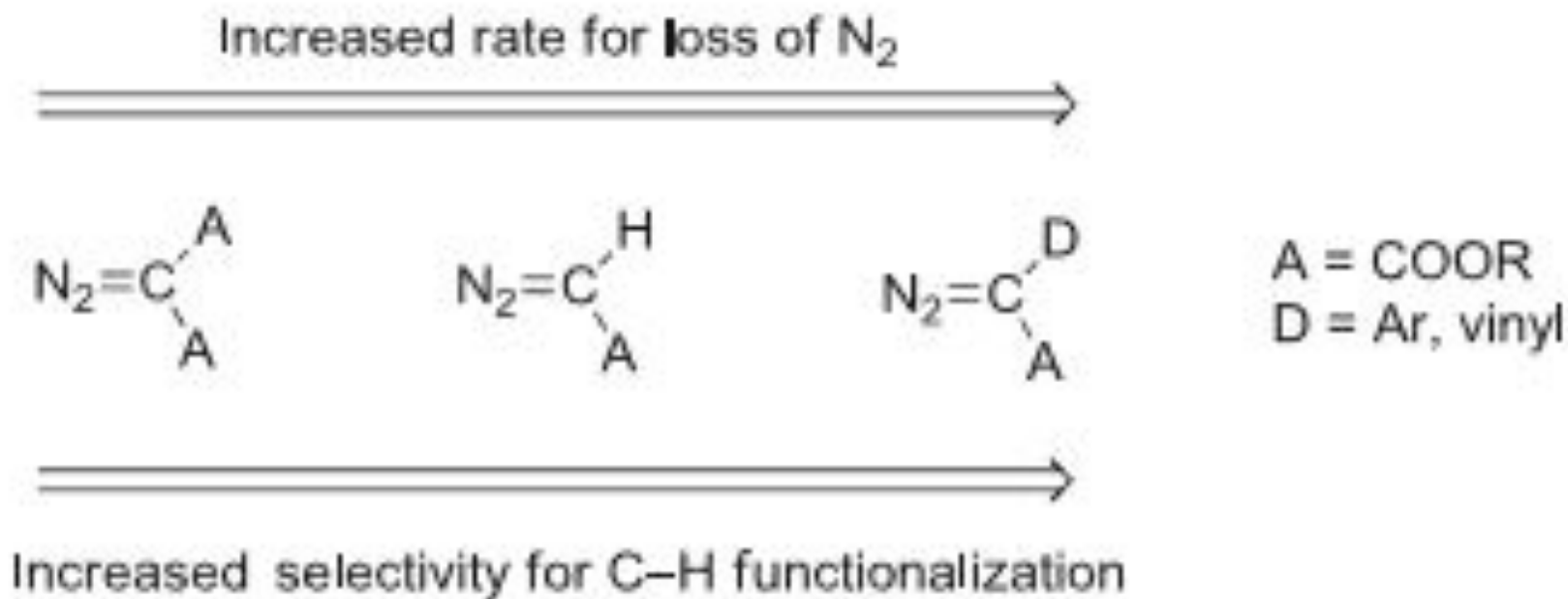
The key electronic feature of this intermediate is delocalized Rh–Rh–C three-centre bonding with appropriate three-centre orbitals of σ and π symmetry

Carbenoid C–H functionalization

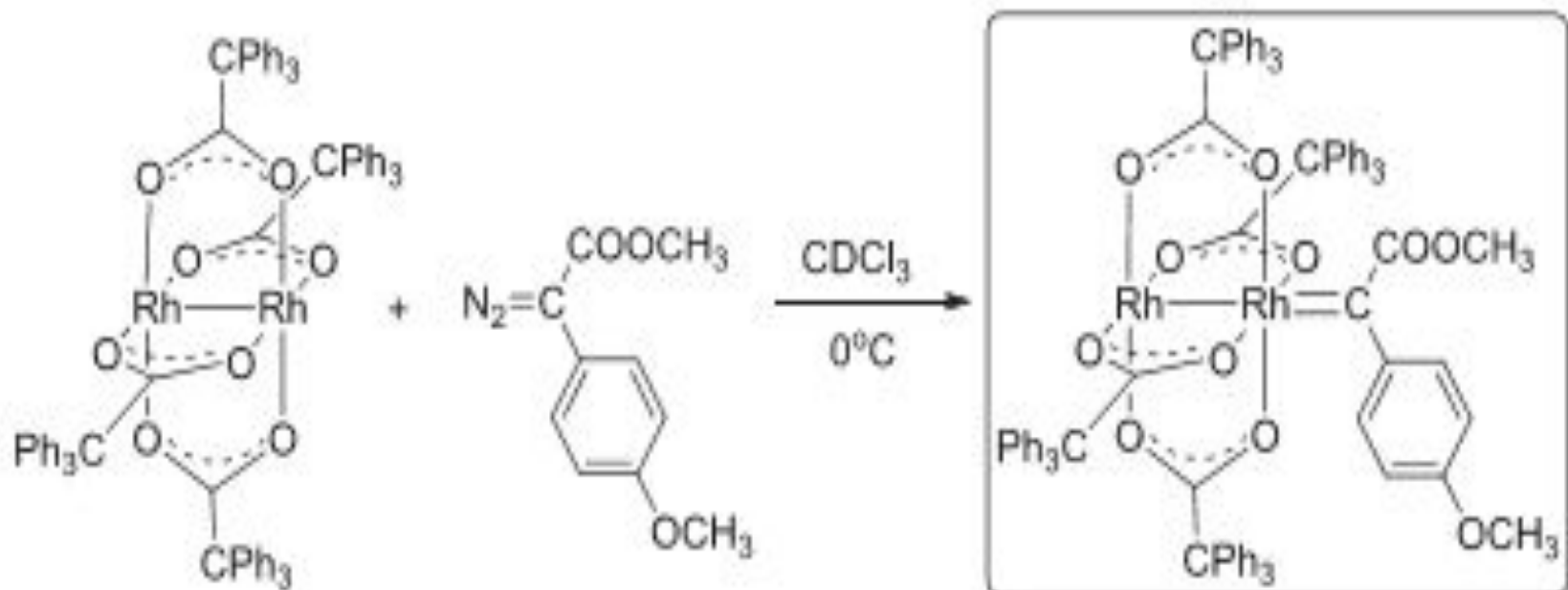


R = Ar, H
A = COOCH₃

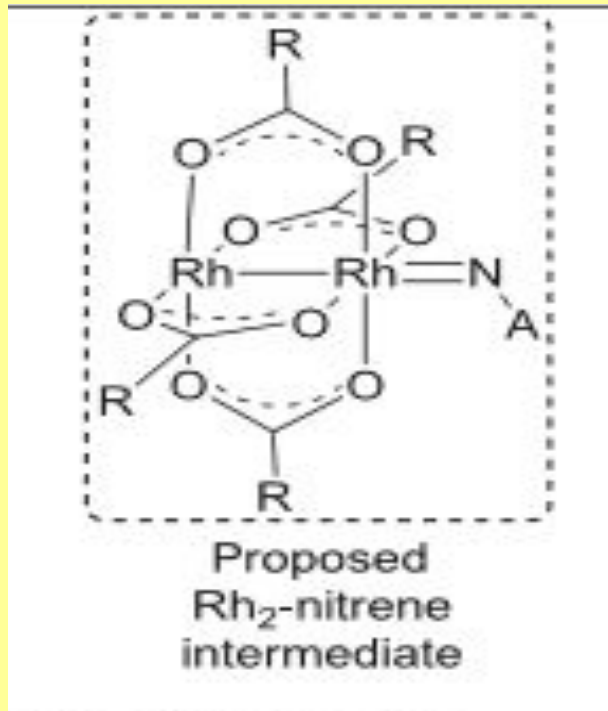
Trends in reactivity for the different classes of organic diazo compounds



Preparation of the first Rh₂ D/A carbene complex

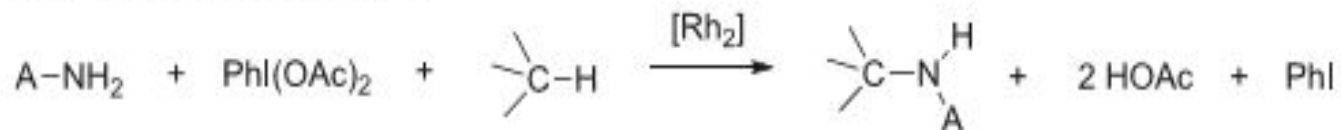


Rh₂ nitrene chemistry



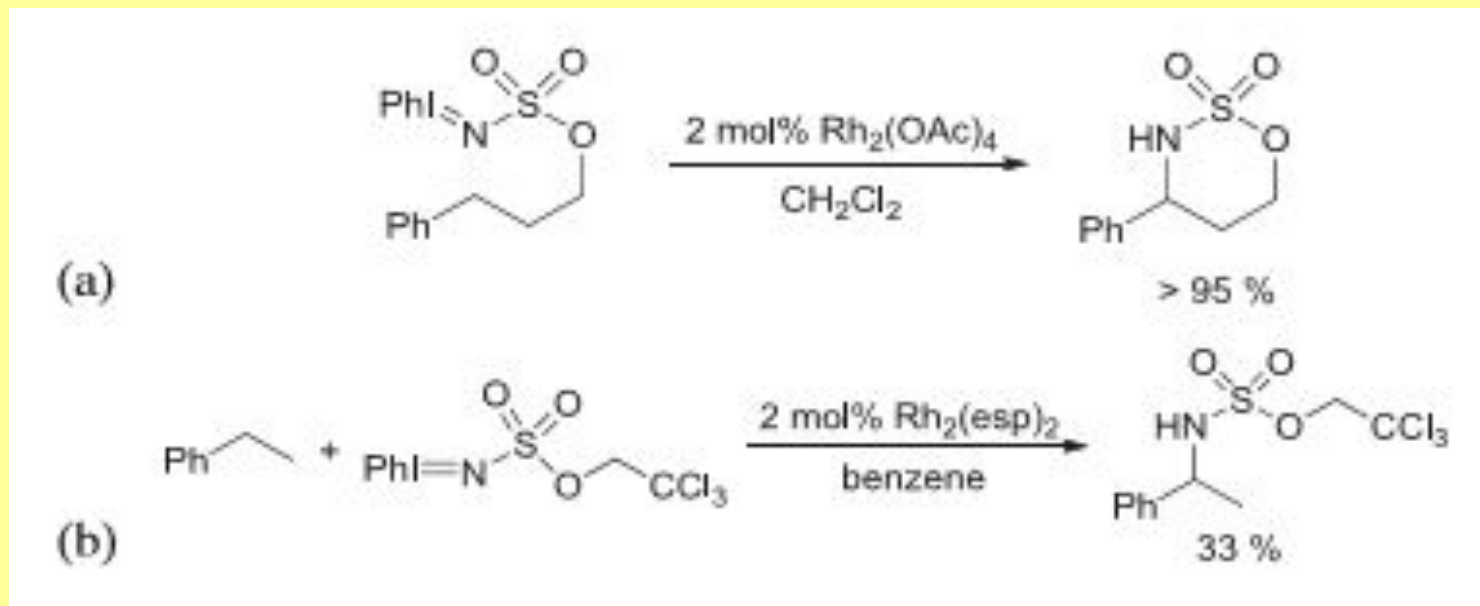
Rh₂-catalysed nitrenoid chemistry is mechanistically more complex than the corresponding carbenoid chemistry

Nitrenoid C-H amination



A = SO₃R, COOR

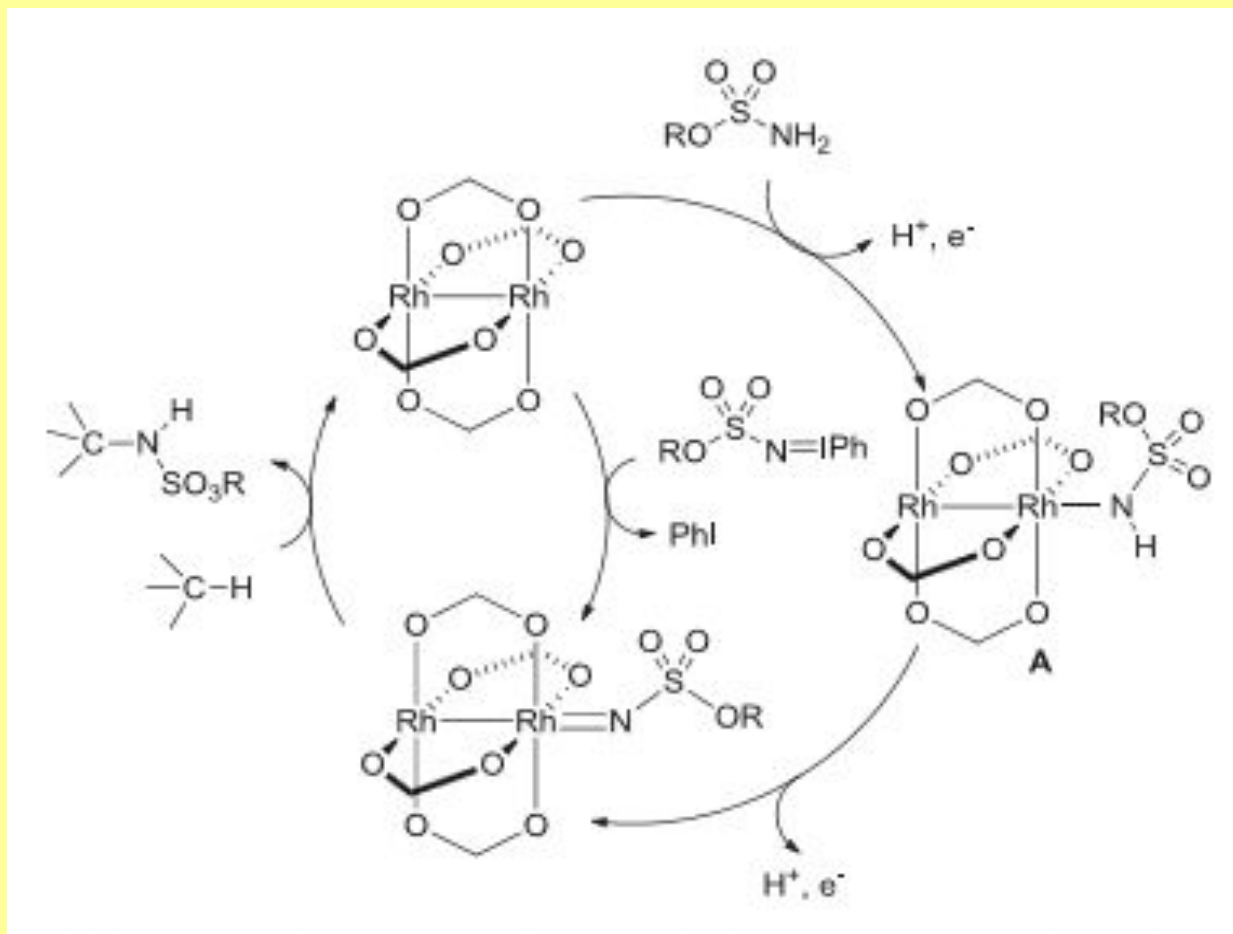
Reactions using pre-formed iminoiodinane compounds



(a) – intramolecular cyclization

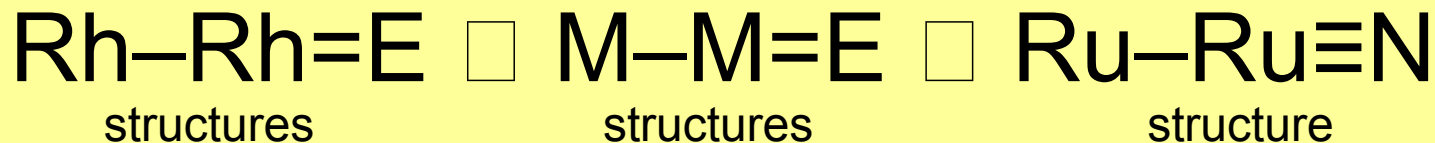
(b) – intermolecular reaction

Proposed mechanism for intermolecular C–H amination



Organic groups on the catalyst are removed for clarity

Ru₂ nitrido chemistry

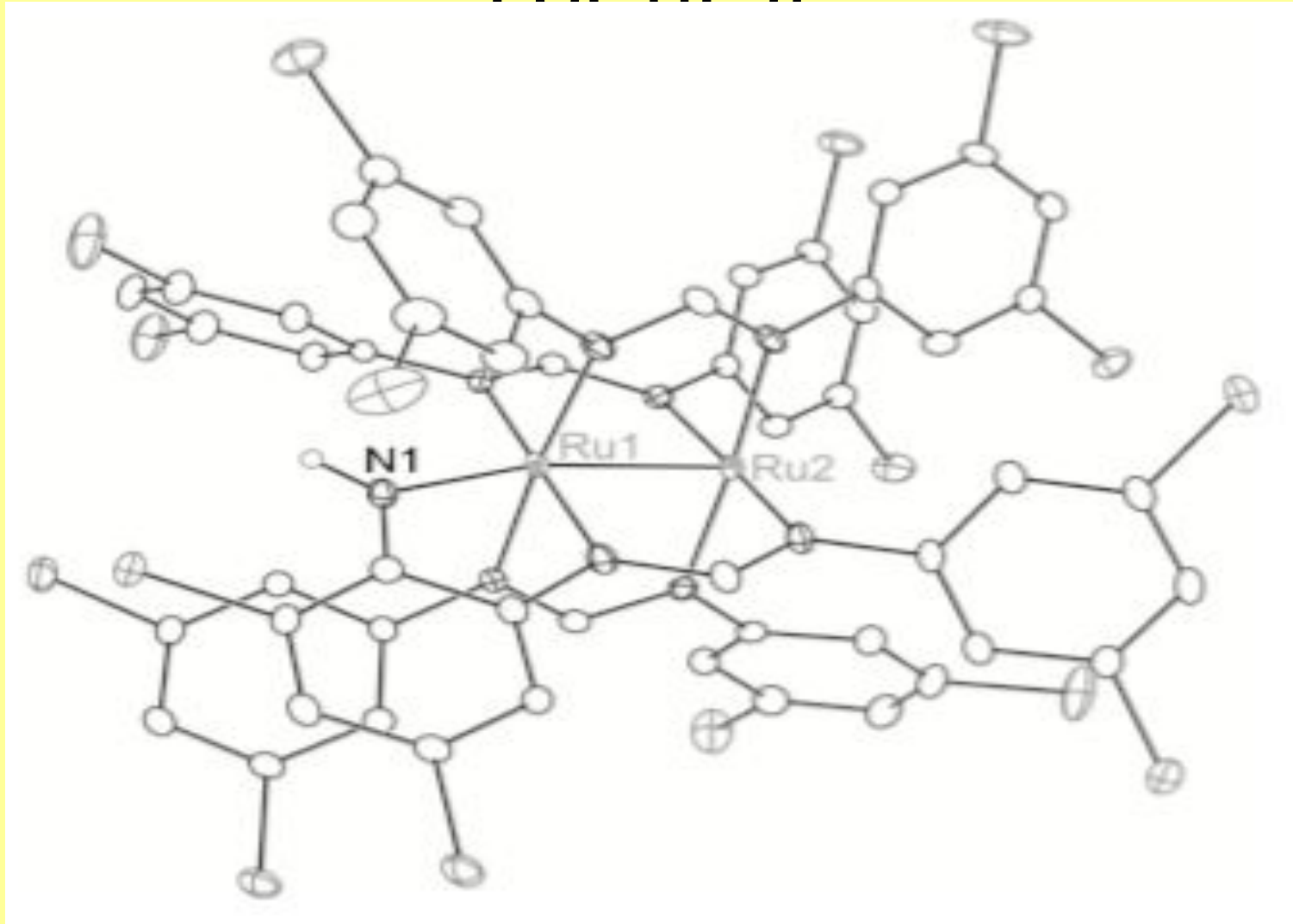


(E = CR₂/NR)

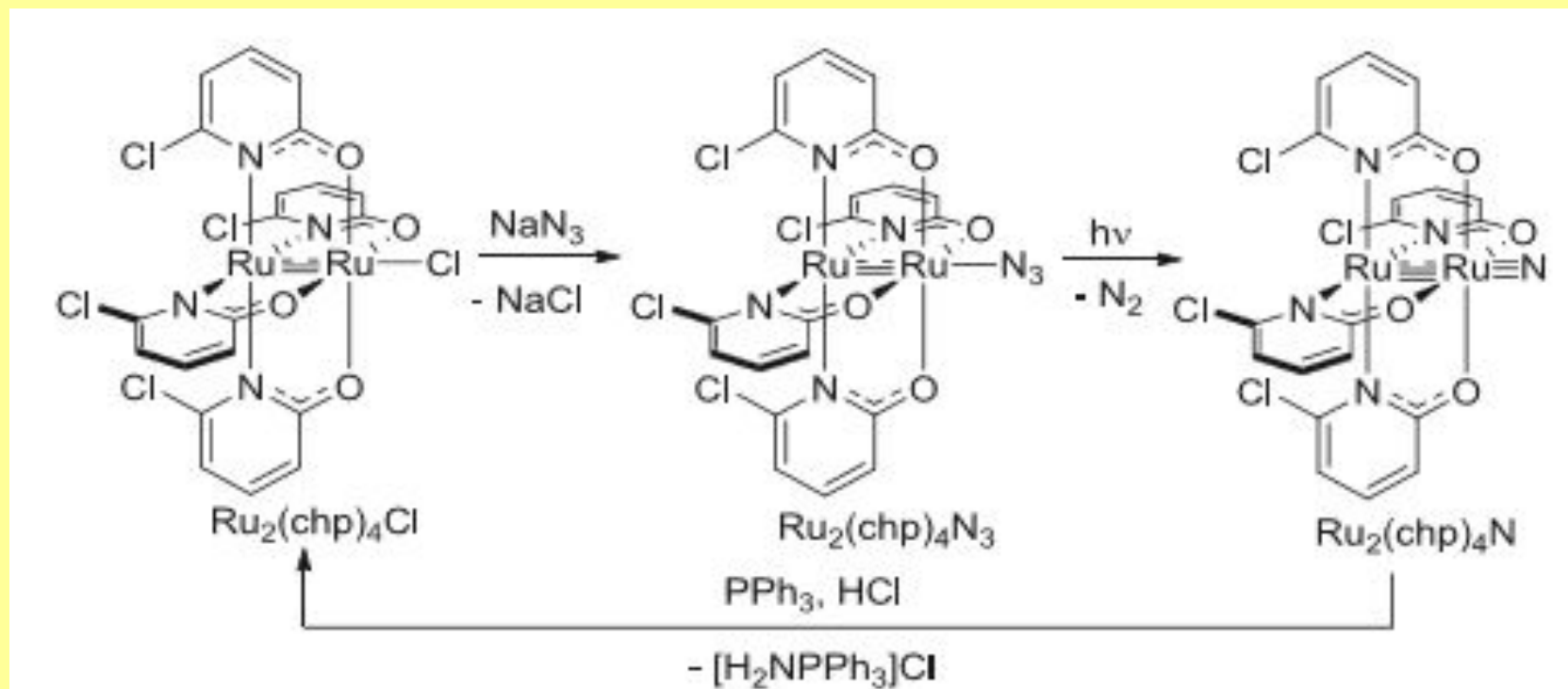
The first Ru₂ nitrido compound
– Ru₂(DPhF)₄N
(DPhF = N,N'-diphenylformamidinate) – was
found to be thermally unstable

In an effort to understand the nature of this
instability,
the related Ru₂(D(3,5-Cl₂)PhF)₄N₃ 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

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