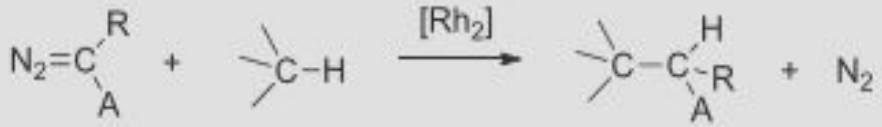
Metal–metal multiple bonded intermediates in catalysis

(for example, Rh_2 and Ru_2 complexes)

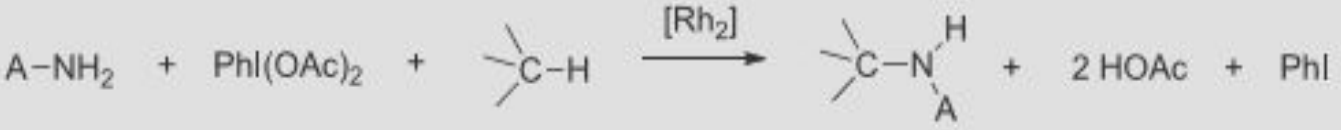
Overview of Rh_2-catalysed C–H functionalization and C–H anination chemistries

Carbenoid C–H functionalization

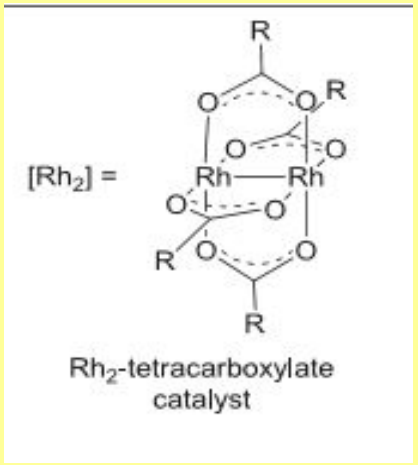


R = Ar, H
A = $COOCH_3$

Nitrenoid C–H amination

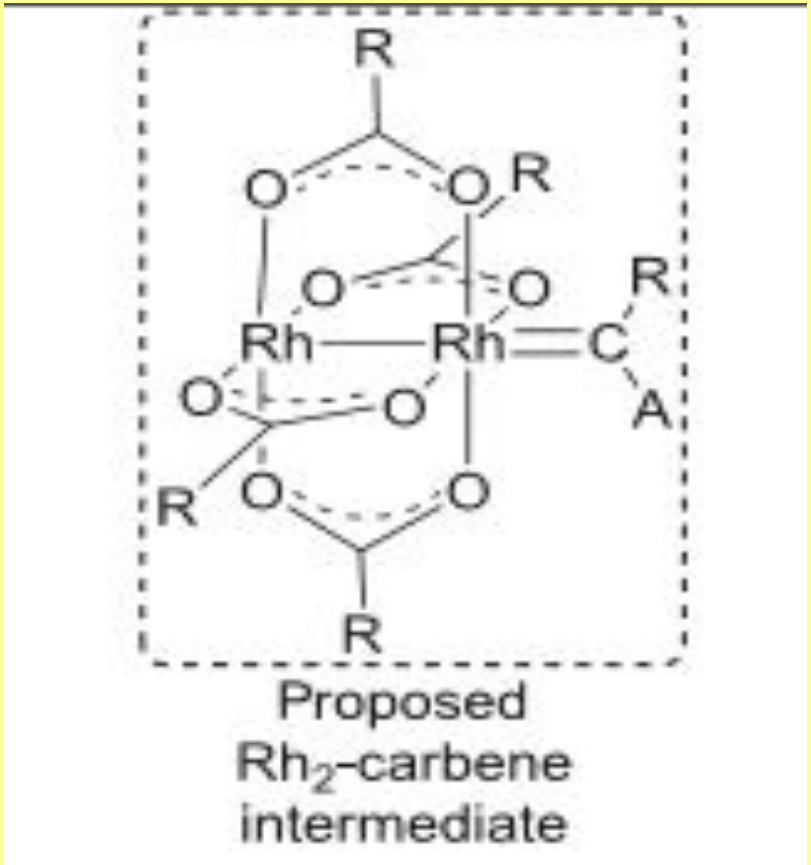


A = SO_3R, COOR



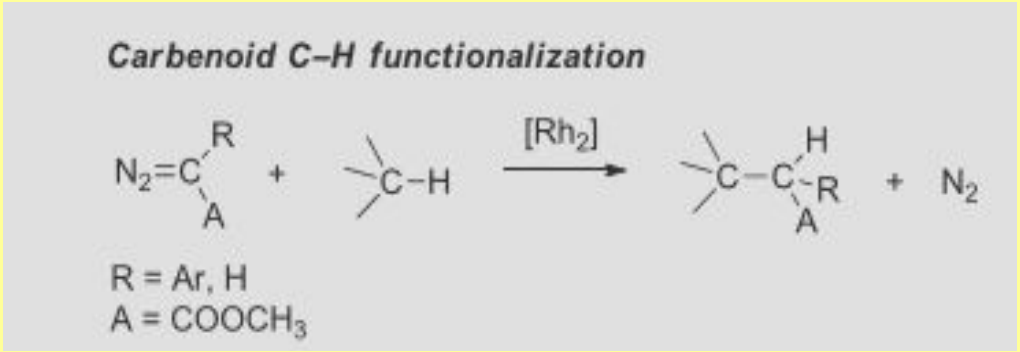
Rh_2-tetracarboxylate catalyst

Rh_2 carbene chemistry

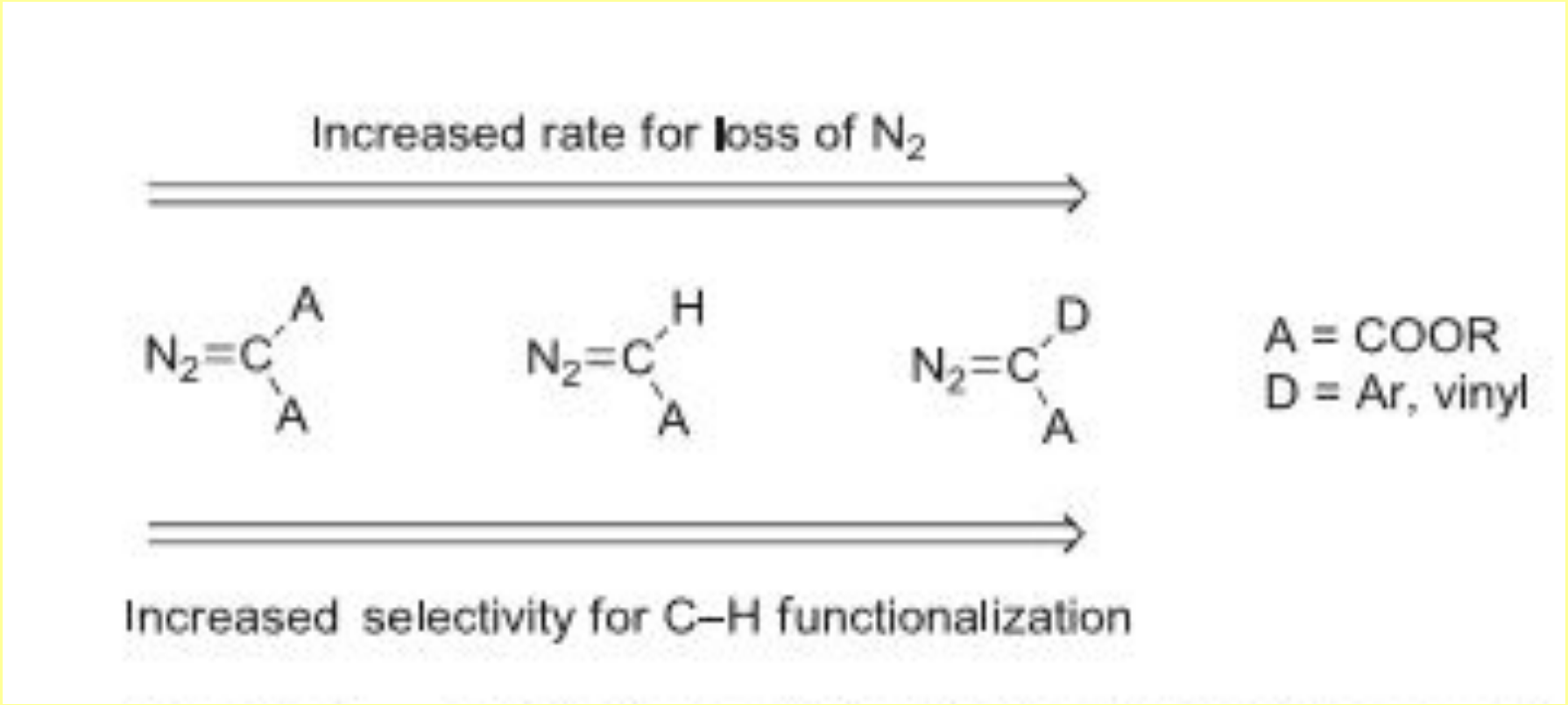


Proposed Rh_2-carbene intermediate

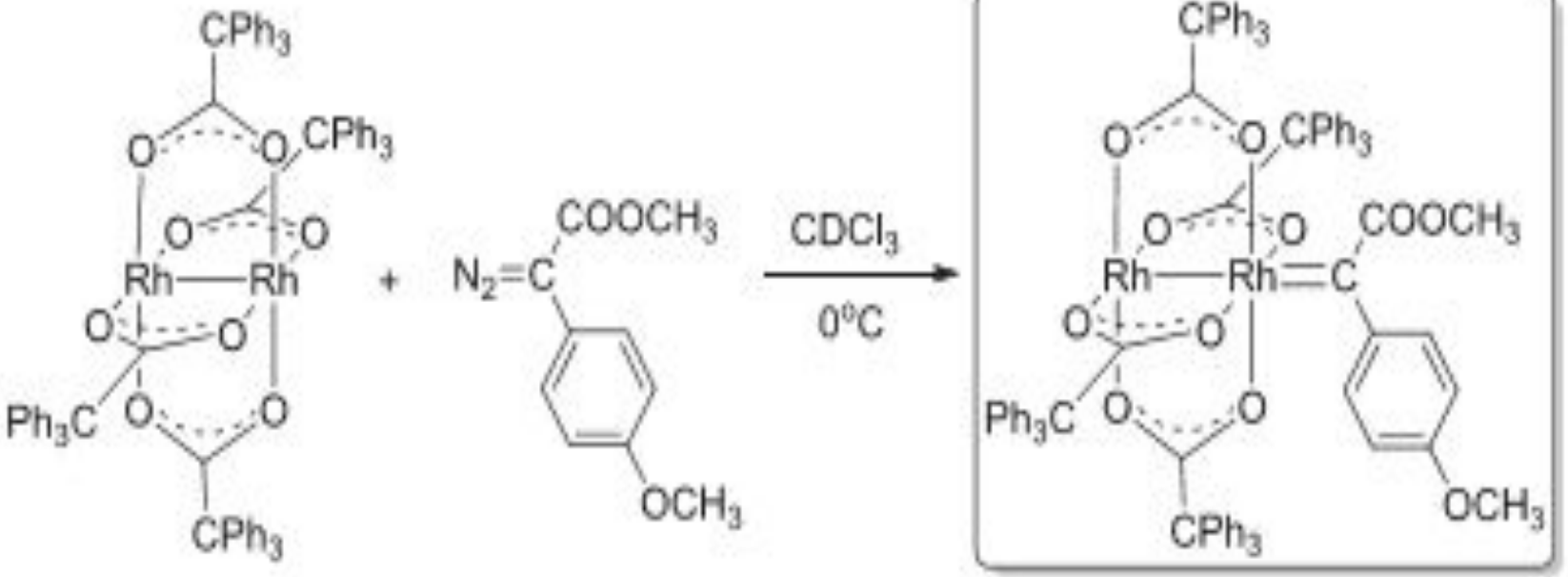
The key electronic feature of this intermediate is delocalized Rh–Rh–C three-centre bonding with appropriate three-centre orbitals of σ and π symmetry



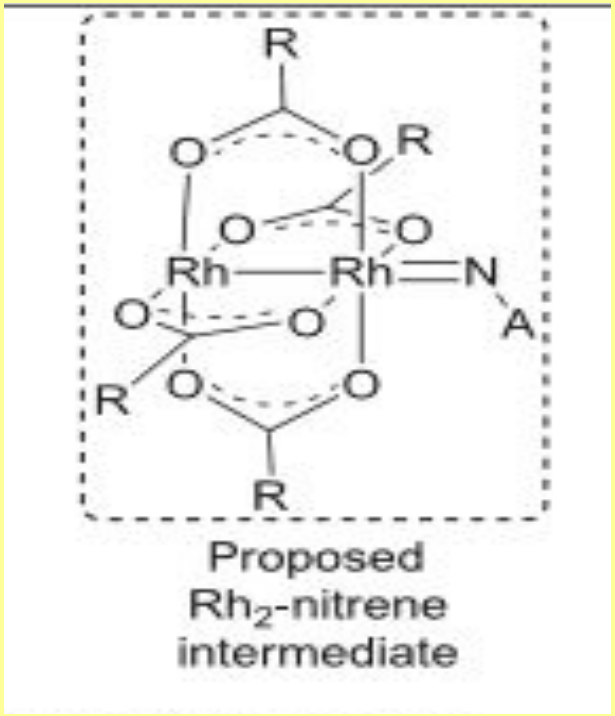
Trends in reactivity for the different classes of organic diazo compounds



Preparation of the first Rh_2 D/A carbene complex



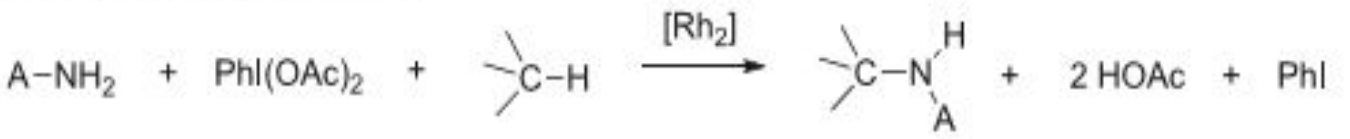
Rh_2 nitrene chemistry



Proposed Rh_2-nitrene intermediate

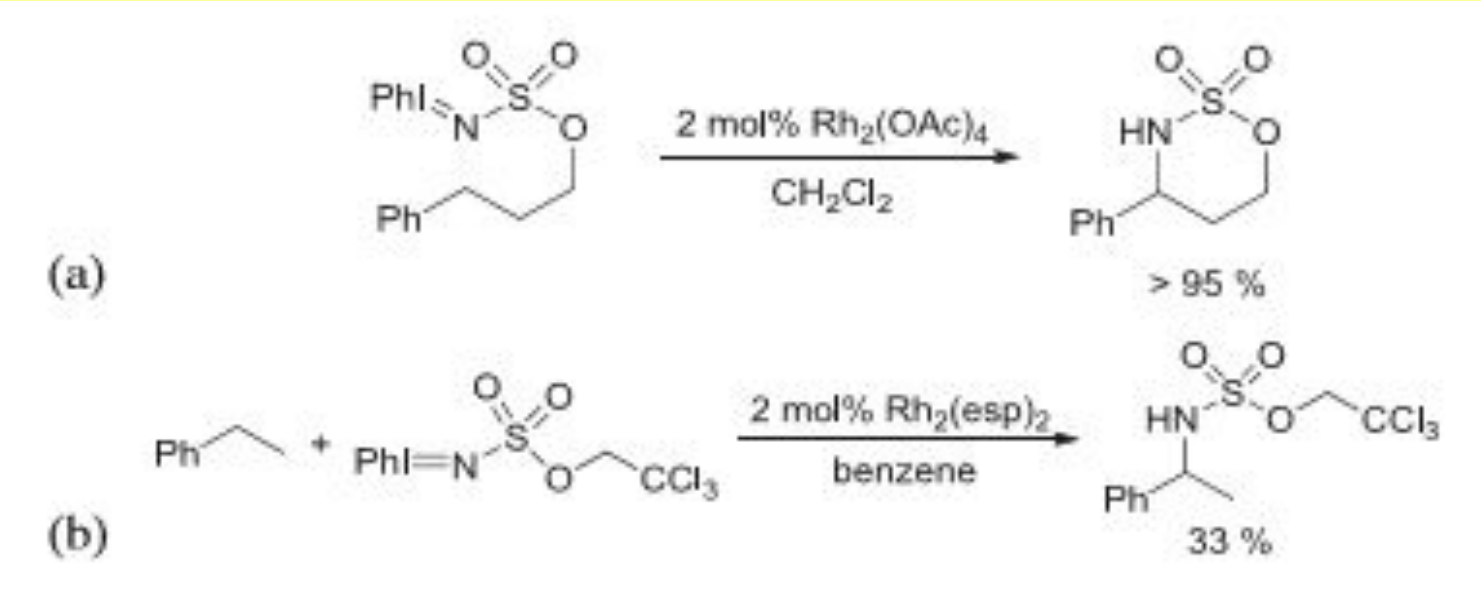
Rh_2-catalysed nitrenoid chemistry is mechanistically more complex than the corresponding carbenoid chemistry

Nitrenoid C–H amination



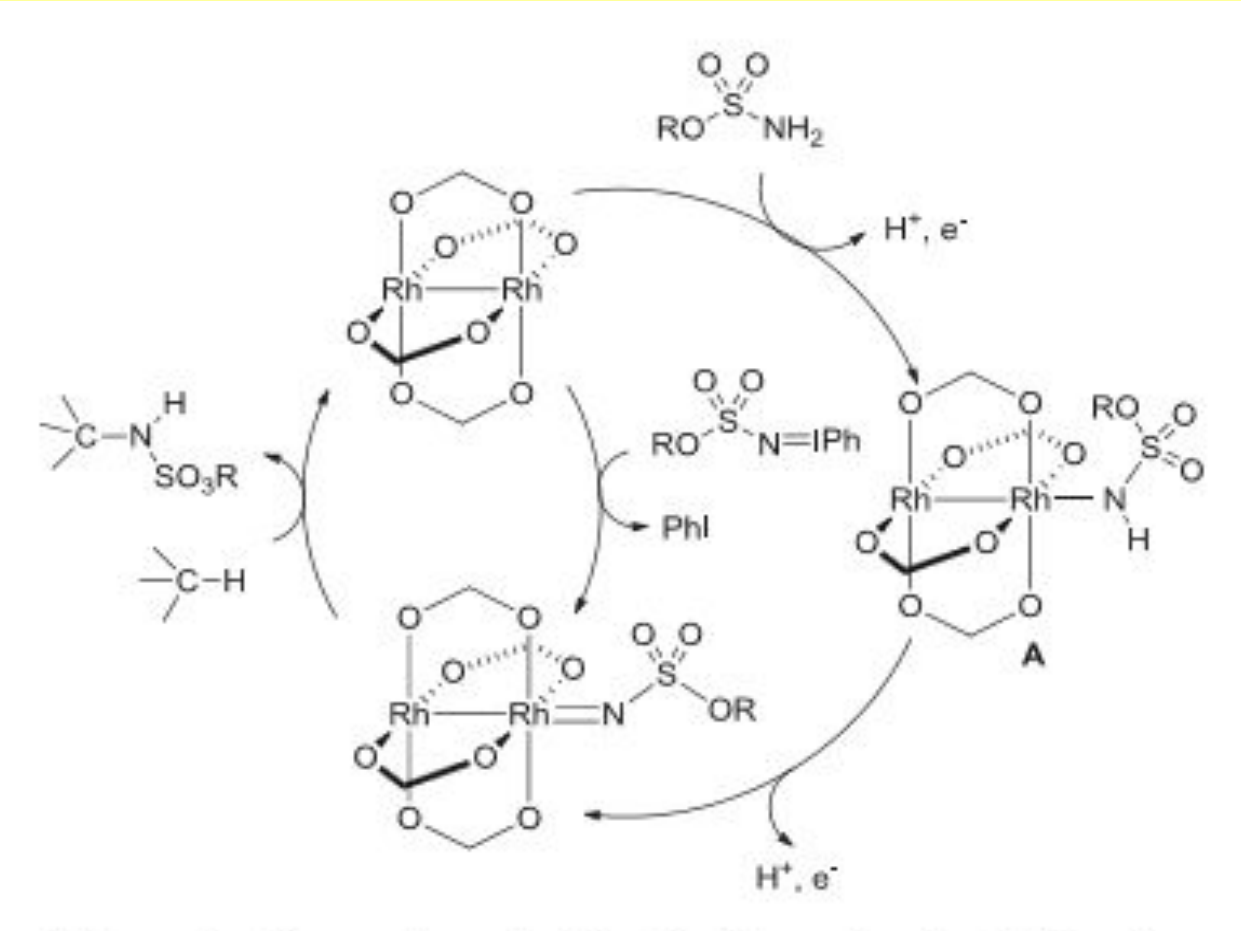
A = SO_3R, COOR

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_2 nitrido chemistry

Rh–Rh=E □ M–M=E □ Ru–Ru≡N

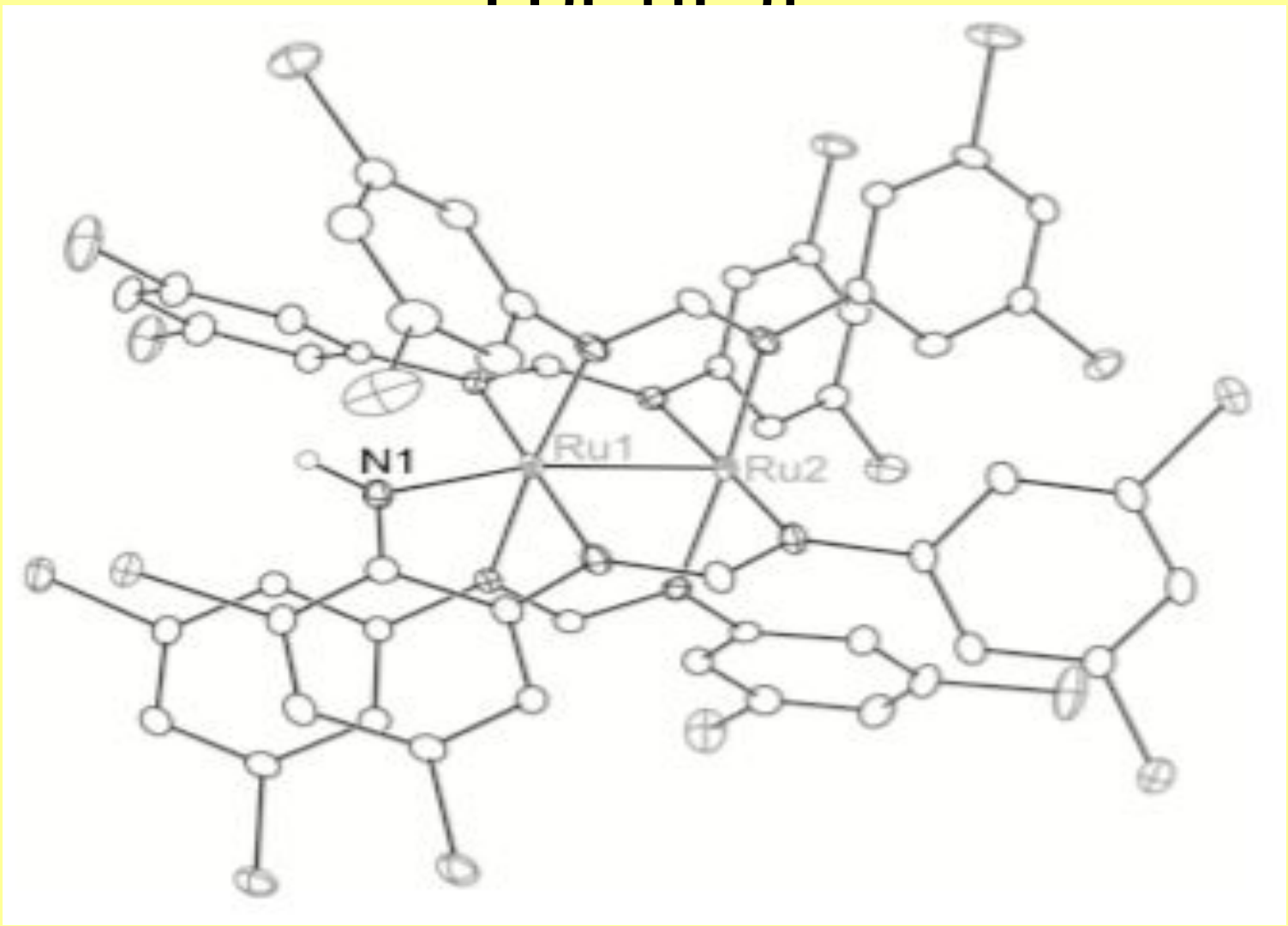
structures structures structure

(E = CR_2/NR)

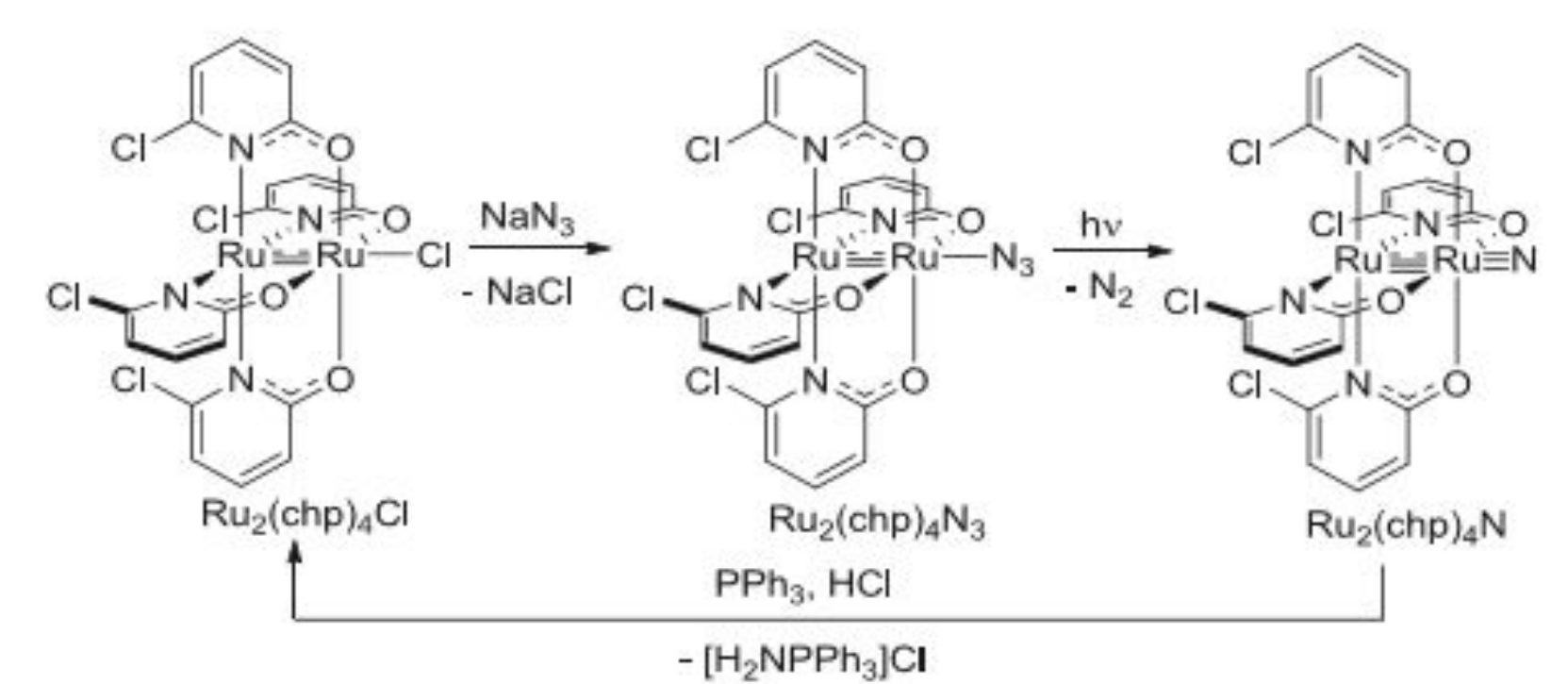
The first Ru_2 nitrido compound –$Ru_2(DPhF)_4N$ (DPhF = N,N′-diphenylformamidinate) – was found to be thermally unstable

In an effort to understand the nature of this instability, the related $Ru_2(D(3,5\text{-}Cl_2)PhF)_4N_3$ azide complex was investigated

Crystal structure of $Ru_2[(D(3,5\text{-}Cl_2)PhF)_3(D(3,5\text{-}Cl_2\text{-}2\text{-}NH)PhF)]$



Synthetic cycle for N-atom transfer using the $Ru_2(chp)_4$ 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≡N core including intramolecular C–H amination as well as intermolecular N atom transfer.

Source

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