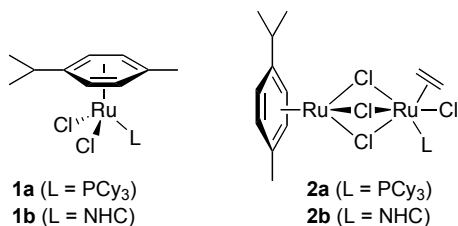


Ruthenium-Arene Complexes Bearing N-Heterocyclic Carbene Ligands as Catalysts for Olefin Metathesis

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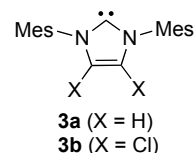
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Ruthenium-arene complexes are versatile and efficient catalyst precursors for various important organic transformations. This is due in part to the lability of the η^6 -arene ligand that can be easily removed upon thermal or photochemical activation to release highly active, coordinatively unsaturated species. During the 1990s, we demonstrated that $[\text{RuCl}_2(\textit{p}\text{-cymene})(\text{PR}_3)]$ complexes bearing basic and bulky phosphine ligands such as tricyclohexylphosphine (**1a**) were highly effective precatalysts for the ring-opening metathesis polymerization (ROMP) of strained and low-strain cycloolefins.¹ The past decade also witnessed the experimental reality of stable nucleophilic N-heterocyclic carbenes (NHCs). We have adopted this class of ancillary ligands instead of phosphines to generate $[\text{RuCl}_2(\textit{p}\text{-cymene})(\text{NHC})]$ species (**1b**), either preformed or in situ, that displayed a remarkable activity for initiating ROMP under visible light illumination.²



In 2005, Severin and co-workers reported a new type of molecular scaffold, in which a $\text{RuCl}(\eta^2\text{-C}_2\text{H}_4)(\text{PCy}_3)$ fragment was connected via three μ -chloro bridges to a ruthenium-(*p*-cymene) moiety (**2a**).³ In view of the enhancements brought by the replacement of phosphines by NHCs in monometallic ruthenium-arene catalyst

precursors of type **1**, we have investigated the effect of similar modifications on the catalytic activity of complexes of type **2**. Two new homobimetallic ruthenium-arene complexes bearing NHC ligands **3a** and **3b** were isolated in high yields upon heating a toluene solution of $[\text{RuCl}_2(\textit{p}\text{-cymene})]_2$ with 1 equivalent of carbene ligand under an ethylene atmosphere. Contrary to monometallic ruthenium-arene complexes of type **1**, these new catalyst precursors did not require the addition of a diazo compound nor visible light illumination to initiate the ROMP of norbornene or cyclooctene. Cross-coupling experiments with various styrene derivatives and ring-closure of α,ω -dienes or -enynes confirmed their outstanding aptitude to catalyze olefin metathesis reactions.⁴ Thus, they provide a valuable alternative to preformed ruthenium-alkylidene catalysts for initiating metathetical transformations in polymer chemistry and fine organic synthesis.



References:

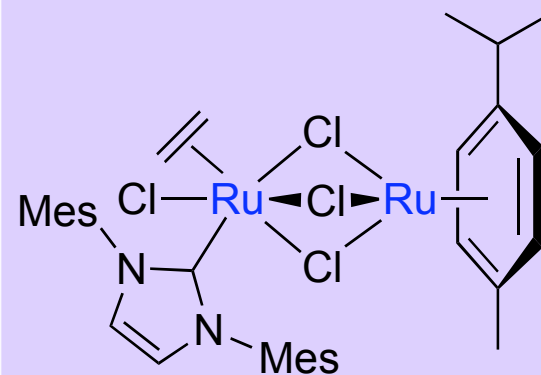
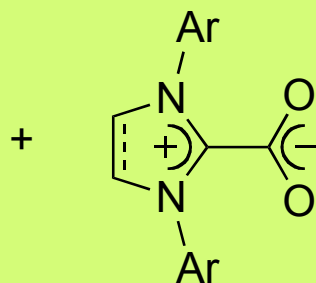
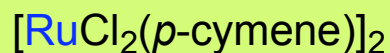
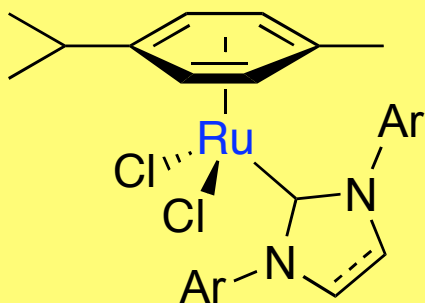
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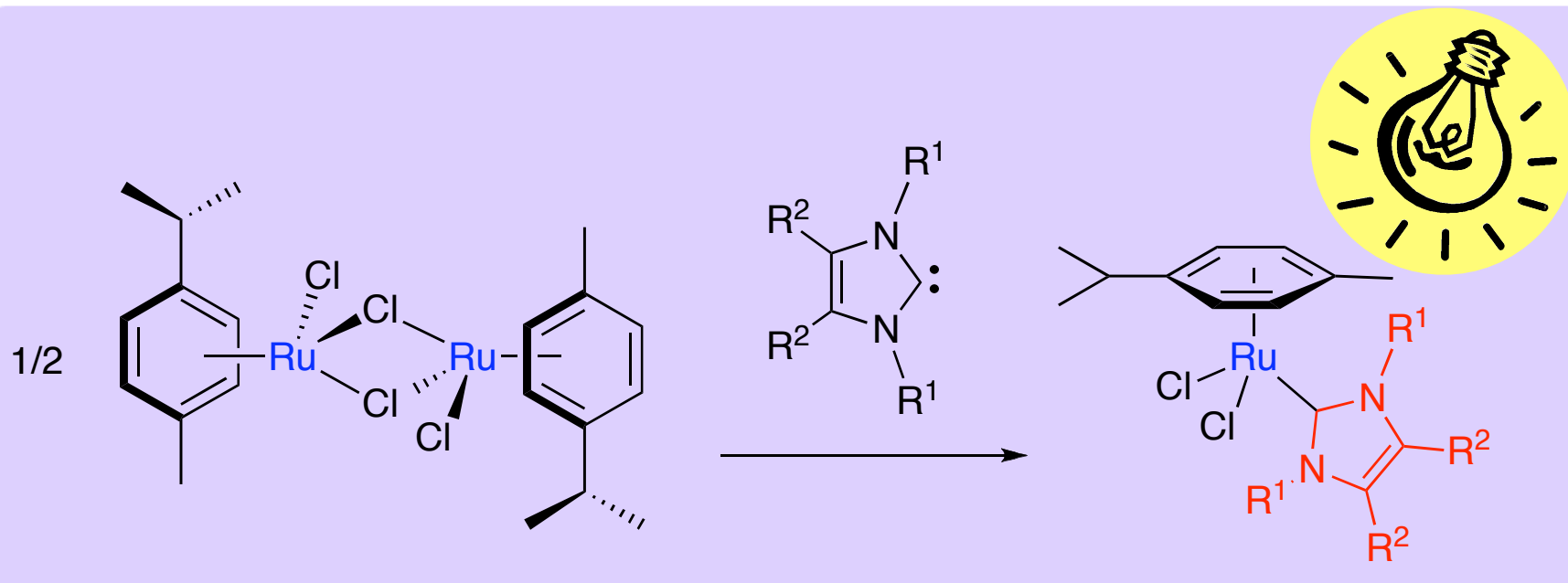
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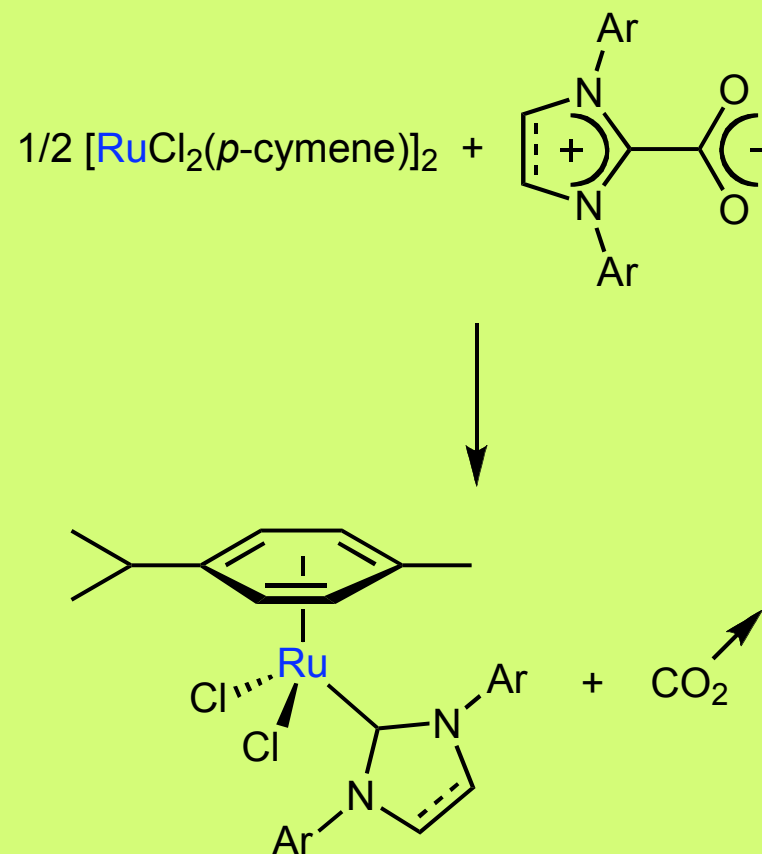
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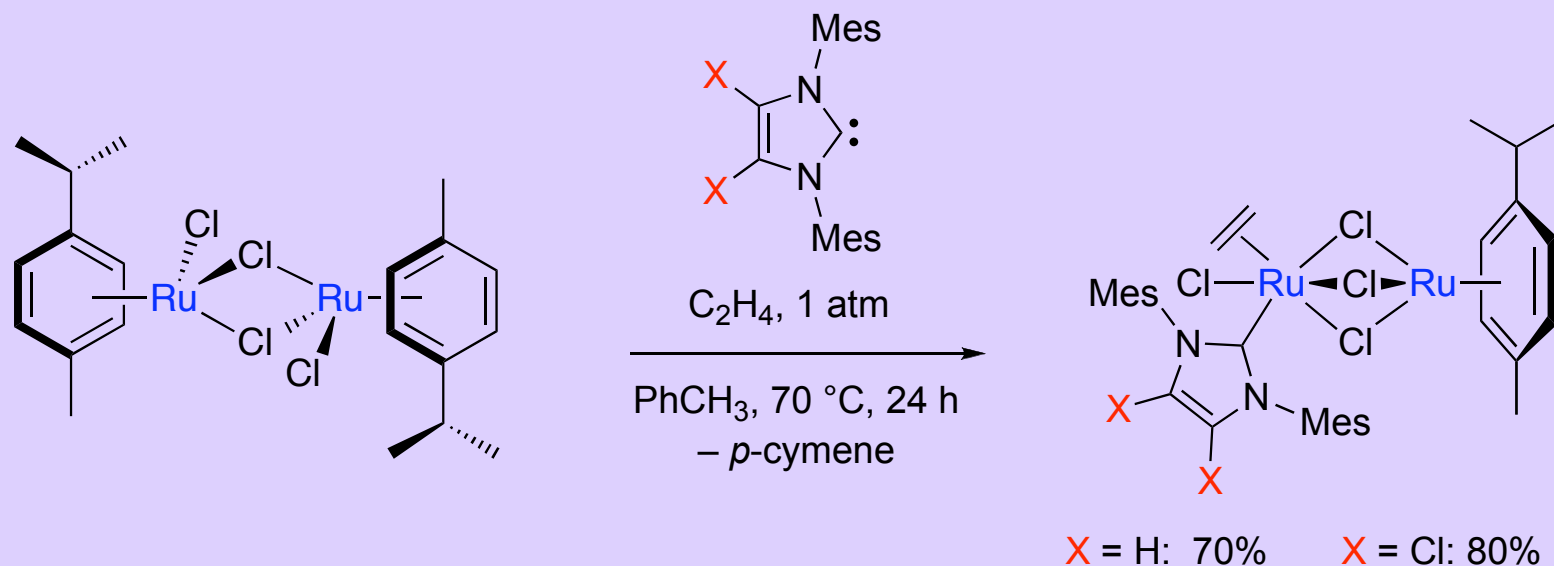




Monometallic Complexes

NHC•CO₂ Adducts





Homobimetallic Complexes