

Rhodium Complexes in Bond Activation and Cyclization Reactions

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Inorganic Literature Seminar

November 2, 2004

Rhodium complexes are often used as homogeneous catalysts. Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$, was prepared in 1966 and used for hydrogenation reactions.¹ Other Rh(I) compounds such as $\text{Rh}(\text{H})(\text{CO})_2(\text{PPh}_3)_2$ and $[\text{Rh}(\text{CO})_2\text{I}_2]$ were synthesized around this time² and used for hydroformylation and the Monsanto acetic acid process respectively. However, Rh(I) complexes have only been recently explored as catalysts for the production of cyclic organic molecules.

The uncatalyzed cyclo-isomerization of non-conjugated enynes occurs at elevated temperatures with poor enantioselectivity.³ Zhang et al. prepared heterocyclic molecules such as chiral γ -lactams and tetrahydrofurans from the corresponding 1,6-enyne derivatives with excellent enantioselectivity using homogeneous Rh(I) complexes (see Figure 1).^{4,5} The catalysts were prepared *in situ* from the reaction of $[\text{Rh}(\text{cod})\text{Cl}]_2$ with AgSbF_6 and chiral phosphines.^{4,5}

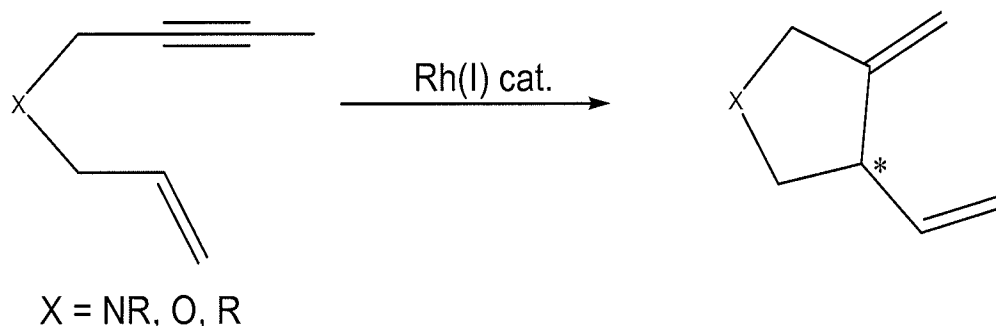


Figure 1: The intramolecular Alder-ene reaction

Krische and co-workers noted similar types of cyclizations with 1,6-diyne. These substrates are reduced with H_2 to the corresponding cyclic 1,3-diene.⁶ Cationic Rh(I) catalysts heterolytically activate hydrogen to form a neutral rhodium hydride.

Messerle et al. prepared a multitude of Rh(I) catalysts to test for intramolecular hydroamination in the preparation of five-membered cyclic imines. The complexes $[\text{Rh}(\text{bim})(\text{CO})_2][\text{BPh}_4]$ (bim = bis(*N*-methylimidazol-2-yl)methane) and $[\text{Rh}(\text{bpm})(\text{CO})_2][\text{BPh}_4]$ (bpm = bis(1-pyrazolyl)methane)⁷, as shown in Figure 2, isomerize aminoalkynes to cyclic imines.^{8,9} There is a large difference in turnover number in refluxing d^8 -THF as opposed to warm (60°C) d^8 -THF.

In comparison of the two N-donor ligands, the bpm ligand is more labile than the bim analog and results in slightly higher TON. A similar reaction was done by Muller in preparing six-membered cyclic imines using $[\text{Rh}(\text{cod})(\text{dipamp})][\text{BF}_4]$ (dipamp = 1,2-ethanediylbis[(2-methoxyphenyl)phenylphosphine]) as catalyst.¹⁰

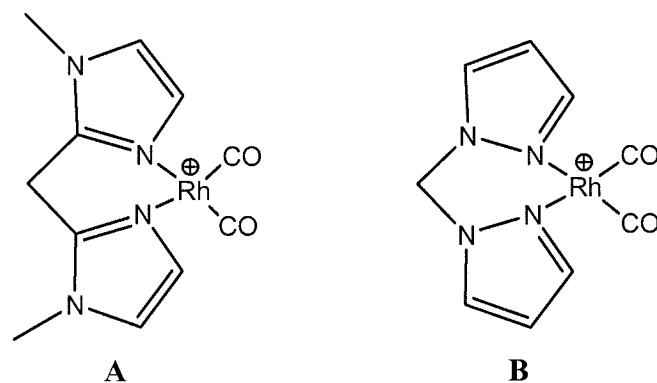


Figure 2: Messerle's catalysts - (A) $[\text{Rh}(\text{bim})(\text{CO})_2]^+$, (B) $[\text{Rh}(\text{bpm})(\text{CO})_2]^+$

Recently, cyclopentenones were made using Rh(I) complexes using two methods. The first involves the reaction of a stoichiometric amount of Cr(0) carbene with electron-poor alkynes using 10 mol% of $[\text{Rh}(\text{cod})(\text{naphthalene})][\text{SbF}_6]$ as catalyst. The chromium complex exchanges both the carbene and CO ligand with rhodium.¹¹ The proposed mechanism is a metalla-Diels-Alder reaction with the carbene ligand as the diene and the alkyne as dienophile. This is not a valid method for the preparation, as it requires stoichiometric amounts of both Cr and Rh. The alternate method, developed by Fu et al., is an isomerization reaction of 4-alkynals into 2-cyclopentenones with the catalyst $[\text{Rh}(\text{dppe})(\text{solv})_2][\text{BF}_4]$, $\text{solv} = \text{CH}_3\text{COCH}_3, \text{CH}_3\text{CN}$, employing no other metals.¹²

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