

Intramolecular [4+2] Cycloaddition Reactions Catalyzed by Rhodium Catalysts Derived from a Rhodium Anion Precursor

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Development of effective cyclization reactions for the synthesis of carbocycles and heterocycles has been the subject of extensive study because of their relevance to medicines and other functional materials.¹ Among the numerous methods available, the transition metal-promoted cyclization reaction has become one of the most popular.² Although considerable efforts are still being devoted to the development of more efficient and practical catalytic systems,³ identification of true catalysts or utilization of new catalyst precursors is also important since all the key catalytic properties are inherently dependent upon the real catalytic species. Moreover, these studies may lead to development of new catalytic systems.

Recently, we have found generation of an anionic rhodium species, $[\text{Rh}(\text{COD})\text{Cl}_2]^-$, from the reaction of dimeric $[\text{Rh}(\text{COD})\text{Cl}]_2$ with dppe.⁴ Thus, reaction between $[\text{Rh}(\text{COD})\text{Cl}]_2$ and dppe (1 equiv per Rh atom) in THF gave a yellow precipitate, and subsequent heating of the yellow solid above 120 °C led to isolation of the well-known orange solid, $[\text{Rh}(\text{dppe})\text{Cl}]_2$. By the way, the exact composition of the yellow precipitate, a synthetic intermediate for $[\text{Rh}(\text{dppe})\text{Cl}]_2$, had not been reported until we recently solved its molecular structure by an X-ray crystallographic analysis (Figure 1).⁵

Thus, it was revealed that the intermediate yellow solid before heating was an ionic complex of $[\text{Rh}(\text{dppe})_2]^+$ cation and $[\text{Rh}(\text{COD})\text{Cl}_2]^-$ anion. Synthesis of the ionic complex would be attributed to a disproportionation reaction of the starting rhodium dimer. According to the literatures, the first report of this anion with a cation other than the present $[\text{Rh}(\text{dppe})_2]^+$ cation appeared in 1957, but its crystal structure was solved thirty years later.^{6,7} While we studied chemistry of $[\text{Rh}(\text{dppe})_2][\text{Rh}(\text{COD})\text{Cl}_2]$ (**1**), we realized this anion could be used as a catalyst precursor in many catalytic reactions. Herein, we report that [4+2] cycloaddition reactions with catalysts from a $[\text{Rh}(\text{COD})\text{Cl}_2]^-$ anion precursor. The anionic rhodium species was prepared not only by the reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with dppe but also by the reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with PPNCl [PPN = bis(triphenylphosphoranyliene)ammonium] to study catalytic activity of Rh anion precursor.⁷

In order to confirm usefulness of the $[\text{Rh}(\text{COD})\text{Cl}_2]^-$ anion as a catalyst precursor, catalytic intramolecular [4+2] cycloaddition of a diyne was investigated as shown in Table 1.⁸

Both the complex **1** and an initially in-situ generated species from a reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with dppe were inactive as catalyst precursors in the intramolecular [4+2] cycloaddition reaction (entries 1 and 2). However, addition of silver salts to **1** dramatically increased its catalytic activity. The reaction with **1** and AgSbF_6 was completed within 10 min in 93% isolated yield (entry 3). In the catalytic system with **1** and AgSbF_6 , the anionic complex, $[\text{Rh}(\text{COD})\text{Cl}_2]^-$, not the cationic complex, $[\text{Rh}(\text{dppe})_2]^+$, would be responsible for the increased catalytic activity because cationic complex, $[\text{Rh}(\text{dppe})_2]\text{Cl}$ with AgSbF_6 did not show such an increased catalytic activity (entry 4). It was also reported that $[\text{Rh}(\text{diphos})_2]^+$ exhibited a relatively poor catalytic activity in a Diels-Alder reaction.⁹ In the presence of catalysts derived from $[\text{PPN}][\text{Rh}(\text{COD})\text{Cl}_2]$ with AgSbF_6 , the intramolecular [4+2] cycloaddition reaction was completed within 10 min in a quantitative yield (entry 5). Various counteranions of silver salts were also examined to develop a more general reaction (entries 6-8). Because Rh-catalysts from $[\text{Rh}(\text{COD})\text{Cl}]_2$ and AgSbF_6 showed a good catalytic activity, it was assumed that a chemical species, presumably $[\text{Rh}(\text{COD})(\text{solv})_2]^+$, derived from the reaction of anionic $[\text{Rh}(\text{COD})\text{Cl}_2]^-$ with AgSbF_6 would be a real catalytic species (entry 9).

With the best catalytic system in hand, the reaction scopes were expanded to rhodium-catalyzed intramolecular [4+2] cycloaddition of diynes and intermolecular [4+2] cycloaddition between dienophiles and 2,3-dimethylbutadiene. The choice of catalytic system was 4 mol% of $[\text{PPN}][\text{Rh}(\text{COD})\text{Cl}_2]$ and 8 mol% of AgSbF_6 in dichloromethane at room temperature.

Intramolecular [4+2] cycloaddition reactions in the presence of catalysts from a $[\text{Rh}(\text{COD})\text{Cl}_2]^-$ anion precursor were investigated for various diyne substrates as shown in Table 2.

Irrespective of types of diyne substrates, the reactions proceeded very smoothly under the reaction conditions. All the reactions were completed within 10 min with high isolated yields up to 96% and the diastereoselectivity of the intramolecular [4+2] cycloaddition was excellent to produce the sole diastereomer **3**. The intramolecular [4+2] cycloaddition reactions were not so sensitive to substituents on the diene and alkyne termini. A similar result using $[\text{Rh}(\text{C}_{10}\text{H}_8)(\text{COD})]\text{BF}_4$ as a catalyst precursor was also reported in the intramolecular [4+2] cycloaddition reactions.¹⁰

In conclusion, we have developed a new catalytic system of [PPN][Rh(COD)Cl₂]/2AgSbF₆ utilizing anionic rhodium precursor and showed high catalytic activities in Rh-catalyzed intramolecular [4+2] cycloaddition reaction with the anionic rhodium precursor. We are currently investigating uses of this new catalytic system in other rhodium-catalyzed reactions.

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- Single crystals of **1** suitable for a single crystal X-ray analysis were obtained by slow evaporation of a CH₂Cl₂ solution at room temperature. Crystal data for **1**: C₆₀H₆₀Cl₂P₄Rh₂, MW = 1181.75, monoclinic, space group C2/C, a = 23.1885(10), b = 13.2598(5), c = 18.0279(8), α = 90 deg, β = 108.494(2) deg, γ = 90 deg, V = 5256.9(4)³, Z = 8, final R indices [I > 2σ(I)], R1 = 0.0236, wR2 = 0.0339. CCDC reference number: 273787.
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- Representative procedure of the cycloaddition: To a flame-dried schlenk flask, CH₂Cl₂ (5 mL) was injected via a syringe under N₂. [PPN][Rh(COD)Cl₂] (4 mol%) and of AgSbF₆ (8 mol%) were added sequentially. After the Rh catalyst solution was stirred for 10 min, **2a** (0.5 mmol) was added under N₂. After the reactant was disappeared, solvent was removed under a reduced pressure and chromatography on a silica gel eluting with hexane and ethyl acetate (v/v, 10:1) gave the product **3a**.
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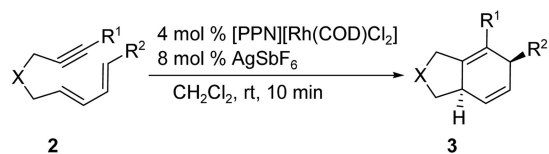
† This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

Table 1. Rh-catalyzed intramolecular [4+2] cycloaddition with various Rh-precursors^a

Entry	Rh-Precursor	Additive	Time (h)	Yield (%) ^b
1	[Rh(COD)Cl ₂] + dppe	–	24	– ^c
2	[Rh(dppe) ₂][Rh(COD)Cl ₂]	–	24	– ^c
3	[Rh(dppe) ₂][Rh(COD)Cl ₂]	2AgSbF ₆	10 min	93
4	[Rh(dppe) ₂]Cl	AgSbF ₆	48	91
5	PPN[Rh(COD)Cl ₂]	2AgSbF ₆	10 min	96
6	PPN[Rh(COD)Cl ₂]	2AgOTf	6	50
7	PPN[Rh(COD)Cl ₂]	2AgClO ₄	10 min	82
8	PPN[Rh(COD)Cl ₂]	2AgBF ₄	10 min	93
9	[Rh(COD)Cl ₂]	2AgSbF ₆	10 min	92

^aReactions were carried out with **2a** (0.5 mmol), 4 mol % of the Rh-precursor, and 8 mol % of the additive in CH₂Cl₂ (5 mL) at room temperature. ^bIsolated yields. ^cNo reactions.

Table 2. Rh-catalyzed intramolecular [4+2] cycloaddition with dienyne^a



Entry	X	R ¹	R ²	Dienyne	Product	Yield (%) ^b
1	O	H	Me	2b	3b	91
2	O	H	Ph	2c	3c	93
3	O	Ph	Me	2d	3d	94
4	TsN	H	Me	2e	3e	96
5	TsN	Me	H	2f	3f	92
6	TsN	H	Me	2g	3g	91

^a Reactions were carried out with **2** (0.5 mmol), 4 mol% of [PPN][Rh(COD)Cl₂], and 8 mol% of AgSbF₆ in CH₂Cl₂ (5 mL) at room temperature. ^b Isolated yields.