C-C Bond Cleavage of 8-Quinolinyl Alkyl Ketone by σ,η³-Allyl Rhodium(III) Complex

Dae-Yon Lee, Yeong-Gweon Lim†, and Chul-Ho Jun*

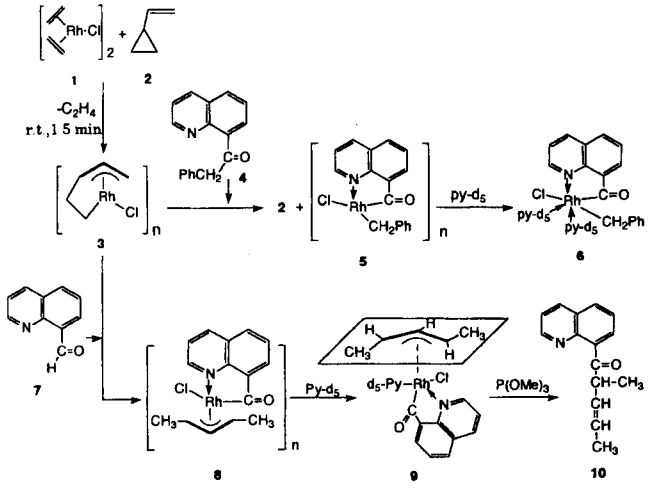
Department of Chemistry, Yonsei University, Seoul 120-749, Korea
†Agency for Defense Development, Yuseong 305-600, Korea

Bis(ethylene)rhodium(I) chloride dimer reacted with vinylcyclopropane to give σ,η³-allylrhodium(III) complex **3**. Complex **3** underwent C-C bond cleavage of 8-quinolinyl ethyl ketone **11**, to form η³-1,3-dimethylallyl-rhodium(III) complex **8**, which was reductively eliminated by trimethyl phosphite to give 8-quinolinyl-1-methylbut-2-enyl ketone (**10**). More sterically hindered 8-quinolinyl alkyl ketones were allowed to react with complex **3** to afford corresponding alkenes as well as a mixture of complex **8** and η³-1-ethylallyl rhodium(III) complex **19**, identified as **10** and 8-quinolinyl-pent-2-enyl ketone (**20**) after reductive elimination. 8-Quinolinyl alkyl ketone bearing a sterically hindered alkyl group showed less reactivity for C-C bond cleavage and higher **20/10** ratio compared with those having a less sterically hindered alkyl group, such as 8-quinolinyl ethyl ketone (**11**).

Introduction

Vinylcyclopropanes could be transformed into cyclopentenes[1] and dienes[2] by transition metal complexes. Vinylcyclopropanes particularly undergo an epimerization in the presence of rhodium(I) complexes as catalyst.[3] This transformation can be explained by reversible formation of σ,η³-allylrhodium(III) intermediate through oxidative addition of a strained C-C σ-bond of the three membered ring in vinylcyclopropane to rhodium(I). The σ,η³-allyl metal complexes have been prepared by many different methods and well characterized.[4] We have previously reported the preparation of the σ,η³-allylrhodium(III) complex **3** from the reaction of bis(ethylene)rhodium(I) chloride dimer (**1**) and vinylcyclopropane (**2**) (Scheme 1).[5]

Treatment of complex **3** with 8-quinolinyl benzyl ketone (**4**) induced reductive elimination of **3** to generate vinylcyclopropane, and subsequent C-C bond cleavage of **4** to give **5**, which was identified with addition of pyridine-d_5 as **6**.[5] When 8-quinolinecarboxaldehyde (**7**) was applied to this reaction in place of **4**, η³-1,3-dimethylallylrhodium(III) complex **8** was obtained, which was identified as *syn, anti*-η³-1,3-dimethylallylrhodium(III) complex **9** after addition of pyridine-d_5.[6] Ligand-promoted reductive elimination of **9** by trimethyl phosphite produced β,γ-unsaturated ketone **10**. This report explains C-C bond cleavage of various 8-quinolinyl alkyl ketones bearing β-hydrogens by σ,η³-allylrhodium(III) complex **3**.



Scheme 1. Formation of σ,η³-allyl rhodium(III) chloride (**3**) from vinylcyclopropane (**2**) and bis(ethylene) rhodium(I) chloride dimer (**1**), and its application into C-C bond and C-H bond cleavgae of 8-quinolinyl acyl derivatives, **4** and **7**.

Experimental

All reactions were carried out under nitrogen. Vinylcyclopropane,[14] chlorobis(cyclooctene)rhodium(I),[15] 8-quinolinyl alkyl ketones[9] were prepared by published procedures. Bis(ethylene)rhodium(I) chloride dimer, 1,3-pentadiene, trimethyl phosphite, pyridine-d_5, benzene-d_6 were purchased from Aldrich Chemical Co. and used without further purification. All solvents were distilled and stored over a molecular sieve (4Å). NMR spectra were recorded with either a Bruker AC 300 MHz or a Bruker Avance/DPX250 (250 MHz) spectrometer.

Reaction of 3 with 11. To 20 mg (0.05 mmol) of bis(ethylene)rhodium(I) chloride dimer (**1**) in a screw-capped vial, 72 mg (1.00 mmol) of vinylcyclopropane (**2**) was added at ambient temperature under nitrogen with loss of ethylene. After the reaction mixture was stirred for an additional 15 minutes, excess vinylcyclopropane was completely removed *in vacuo* to provide a yellow precipitate **3**.[5] To this suspension was rapidly added 19 mg (0.103 mmol) of 8-quinolinyl ethyl ketone (**11**) in 1 mL of benzene. The reaction was allowed to proceed at 100 °C for two hours. The dark brown precipitate was dissolved in 120 mg (0.960 mmol) of trimethyl phosphite to give a brown solution which was evaporated to dryness at 80 °C under reduced pressure. The crude residue was purified by column chromatography (n-hexane : ethyl acetate=5 : 2) to give 15.7 mg (68% yield) of 8-quinolinyl-1-methyl but-2-enyl ketone (**10**) (a trace (<1%) of **20** was also determined).[12]

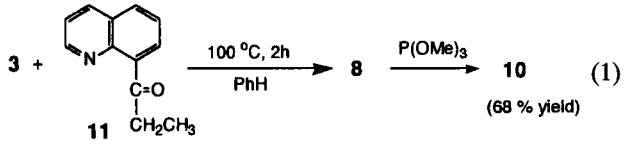
General Procedure of the reaction of 3 and 18 in C_6D_6. To 20 mg (0.05 mmol) of bis(ethylene)rhodium(I) chloride dimer (**1**) in a screw-capped vial, 72 mg (1.00 mmol) of vinylcyclopropane (**2**) was added at ambient temperature under nitrogen with loss of ethylene. After the reaction mixture was stirred for additional 15 minutes, excess vinylcyclopropane was completely removed *in vacuo* to provide a yellow precipitate **3**. To this suspension was added 0.103 mmol of 8-quinolinyl alkyl ketone **18**, in 1 mL of C_6D_6. The reaction was allowed to proceed at 100 °C for two hours. After cooling the reaction mixture, the solution was filtered to give alkene in C_6D_6, determined by ^1H NMR. The dark brown precipitate was dissolved in 120 mg (0.960 mmol) of trimethyl phosphite to give a brown solution, which was evaporated to dryness at 80 °C under reduced pressure. The crude residue was purified by column chromatography to give a mixture of **10** and 8-quinolinyl-pent-2-enyl ketone (**20**)[12] in which ratio was determined from the ^1H NMR spectra.

Isomerization of 3 into 1,3-pentadiene. To 14 mg (0.036 mmol) of bis(ethylene)rhodium(I) chloride dimer (**1**) in a screw-capped vial, 72 mg (1.00 mmol) of vinylcyclopropane (**2**) was added at ambient temperature under nitrogen with loss of ethylene. The reaction mixture was stirred for additional 15 minutes, excess vinylcyclopropane was completely removed *in vacuo* to provide a yellow precipitate **3**. To **3** was added 0.6 mL of C_6D_6. The resulting suspension was heated at 100 °C for 15 minutes. After cooling, 0.2 g of pyridine-d_5 and one drop of trimethyl phosphite were added to give a mixture of vinylcyclopropane and 1,3-pentadiene in a 74/26 ratio, determined by ^1H NMR spectra.

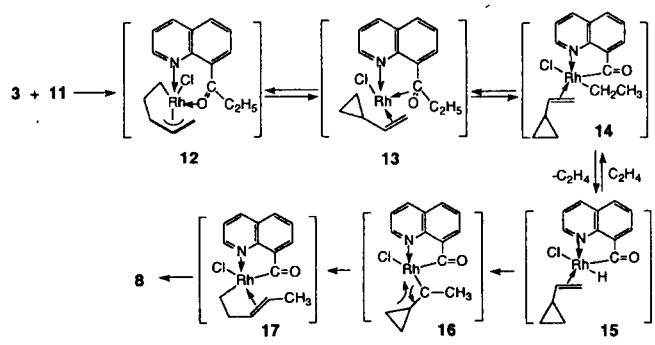
Reaction of 21 with 8-quinolinyl n-hexyl ketone (18b). To 30.0 mg (0.042 mmol) of chlorobis(cyclooctene)rhodium(I) (**25**) in a screw-capped vial, 80 mg of 1,3-pentadiene was added at ambient temperature under nitrogen. After the reaction mixture was stirred for additional 30 minutes, excess 1,3-pentadiene and cyclooctene were completely removed *in vacuo* to provide a yellow precipitate **21**.[12,13] To this suspension was rapidly added 20.0 mg (0.083 mmol) of 8-quinolinyl *n*-hexyl ketone (**18b**) in 1.5 mL of benzene. The reaction was allowed to proceed at 100 °C for two hours. The dark brown precipitate dissolved in 120 mg (0.960 mmol) of trimethyl phosphite, to give a brown solution which was evaporated to dryness at 80 °C under reduced pressure. The crude residue was purified by column chromatography to give 4.0 mg (21% yield) of a mixture of **10** and **20** in a 9/1 ratio, and 51% unreacted **18b** was recovered.

Results and Discussion

Complex **3**, prepared from **1** and **2**, was allowed to react with 8-quinolinyl ethyl ketone (**11**) in benzene at 100 °C for two hours to give an insoluble precipitate **8**. Ligand-promoted reductive elimination of the resulting reaction mixture with trimethyl phosphite led to **10** in 68% isolated yield after chromatographic isolation (eq. 1).



(1)

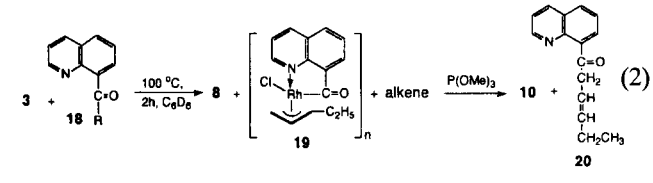


Scheme 2. Reaction mechanism of σ,η^3-allyl rhodium(III) complex **3** and 8-qionolinyl ethyl ketone (**11**) to produce complex **8**.

Complex **8** could be isolated with pentane and identified by addition of pyridine-d_5 as **9**.[6] The formation of **8** from the reaction of **11** with **3** is explained in Scheme 2.

The first step may form vinylcyclopropane[7] from the σ,η^3-allylrhodium(III) complex by coordination of the acylquinolinyl group as in **12** to give **13**. There is a report about the formation of vinylcyclopropane from the σ,η^3-allylrhodium (III) complex. With reductive elimination of **12**, Rh(III) might be reduced to Rh(I) in **13**. An intermediate **13**, Rh(I) might oxidatively add to an α-C-C bond of the ketone to generate **14**. The Rh(I) species have been known to undergo C-C bond cleavage of **11** under very mild conditions.[8] Complex **14** bearing β-hydrogens might undergo β-elimination to give **15** as a transient intermediate. During the process for β-elimination of **14**, ethylene, the β-elimination product should be formed, but barely detectable due to its volatility. β-Elimination of the metal alkyls bearing β-hydrogens is the common process in organotransition metal chemistry, especially in 8-acylquinolinyl rhodium(III) alkyls.[9] The hydride insertion into vinylcyclopropane in **15** according to Markovnikoff's rule and the subsequent ring opening in **16** produced alkenyl rhodium(III) intermediate **17**. Complex **17** underwent olefin-isomerization by allyl-hydrido mechanism to give **8**, which has already been studied.[10]

Some other kinds of 8-quinolinyl alkyl ketone **18** having β-hydrogens were applied for this C-C bond cleavage by **3** to identify the generation of the β-elimination product, alkene (eq. 2).



(2)

Reaction of **18** with **3** at 100 °C for two hours in C_6D_6 produced the corresponding alkenes, determined by ^1H NMR spectra, as well as **8** and a small amount of **19**. The yields and ratios of **8** to **19** were determined as **10** and **20** after ligand-promoted reductive elimination with trimethyl phosphite as shown in Table 1.

In the reaction of 8-quinolinyl sec-butyl ketone (**18c**), 8-quinolinyl cyclopentyl ketone (**18d**) and 8-quinolinyl cy-

Table 1. Reaction of **18** and **3** at 100 °C for 2 h in C_6D_6 and reductive elimination of the resulting complex by $P(OMe)_3$

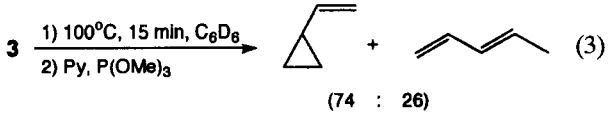
Entry	R	alkene[a]	Ratio of **10/20**[b]	Isolated Yield of **10** & **20**
1	*n*-butyl (**18a**)	2-butene	95/5	64%
2	*n*-hexyl (**18b**)	2-hexene	97/3	62%
3	*sec*-butyl (**18c**)	2-butene	94/6	48%
4	cyclopentyl (**18d**)	cyclopentene	93/7	44%
5	cyclohexyl (**18e**)	cyclohexene	92/8	46%
6	*t*-butyl (**18f**)			0%
7	α,α-dimethylbenzyl (**18g**)			0%

[a] Alkenes were determined by ^1H NMR spectra. [b] Ratios were determined by ^1H NMR spectra.

clohexyl ketone (**18e**) with **3**, expected β-elimination products, 2-butene, cyclopentene and cyclohexene were determined by ^1H NMR spectra (Table 1, entry 3-5). However, the reaction of 8-quinolinyl *n*-butyl ketone (**18a**) and 8-quinolinyl *n*-hexyl ketone (**18b**) with **3** afforded 2-butene and 2-hexene instead of 1-butene and 1-hexene (Table 1, entry 1-2). Initially generated 1-butene and 1-hexene might be isomerized into 2-butene and 2-hexene by rhodium complexes. Isomerization of the terminal alkene into the more stable internal alkene by transition metals has been studied in detail.[11]

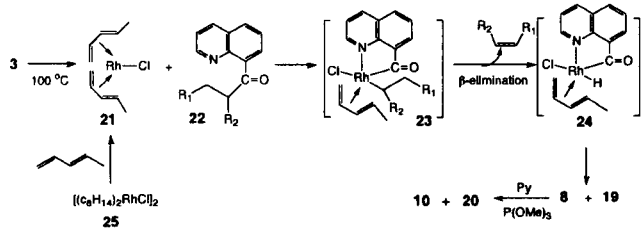
Complex **8** was contaminated with a small amount of **19**, in which the ratios of **8/19** were also determined as those of reductive elimination products, **10** and **20**. The mechanism for the formation of **19** is explained in Scheme 3.

At high temperature, complex **3** may partially decompose to chlorobis(1,3-pentadiene)rhodium(I) (**21**), which reacts with **22** to give the C-C bond cleavage complex **23**, followed by β-elimination to form **24**. There are some reports about conversion of σ,η^3-allyl complex into 1,3-pentadiene.[2] On heating **3** in C_6D_6 at 100 °C for 15 minutes, 26% of **3** was transformed into 1,3-pentadiene, determined by ^1H NMR spectra (eq. 3).



(3)

It has been reported that a hydride addition into 1,3-pentadiene in **24** produced a mixture of **8** and **19** in an 80/20



Scheme 3. Plausible mechanism of the formation of **19** from the reaction of 8-quinolinyl alkyl ketone (**22**) bearing β-hyrogens and **21**, partially decomposed from **3**.

ratio[12] while reaction of 8-quinolinecarboxaldehyde (**7**) with σ,η^3-allylrhodium(III) complex **3** afforded **8** exclusively.[6] To identify partial formation of **19** from complex **21** and **22**, 8-quinolinyl hexyl ketone (**18b**) was allowed to react with complex **21**,[13] prepared *in situ* by addition of 1,3-pentadiene to chlorobis(cyclooctene)rhodium(I) dimer (**25**), at 100 °C for two hours. Ligand-promoted reductive elimination by pyridine and trimethyl phosphite produced **10** and **20** in a 90/10 ratio in 21% isolated yield.

When R group in **18** was changed as *primary, secondary* and *tertiary* alkyl in this reaction, the isolated yield of **10** and **20** was dramatically decreased, and no product was obtained for 8-quinolinyl *tertiary* alkyl ketones (Table 1, entry 6-7). These trends can be explained by proposing the increasing steric hindrance of the alkyl group by changing the *primary* alkyl group to the *tertiary* alkyl group in **18**. It is not clear whether the accessibility problem is generated between the metal center and the nitrogen in quinoline or between the nitrogen-coordinated metal center and the α-ketone C-C bond. Since the steric hindrance problem of the alkyl group makes C-C bond cleavage more difficult, complex **3** might have more time for isomerization into **21** as in the primary alkyls to secondary alkyls. Therefore, as the steric hindrance of alkyl group increases as in **11, 18b**, and **18e**, the product ratio of **20/10** also increases as 0/100, 3/97 and 8/92.

In conclusion, various 8-quinolinyl alkyl ketones bearing β-hydrogens were applied for C-C bond cleavage by σ,η^3-allylrhodium(III) complex **3**. C-C bonds of 8-quinolinyl alkyl ketone having *primary* alkyls and *secondary* alkyls could be cleaved by **3**, while those of 8-quinolinyl *tertiary* alkyl ketones resisted cleavage due to the steric hindrance.

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Cobalt(III) Complexes of 1,3-Diaminopropane-N,N'-di-α-(β-methyl)-pentanoic Acid

Hyeyoung Ham, Young-Joon Park, and Moo-Jin Jun*

Department of Chemistry, Yonsei University, Seoul 120-749, Korea
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A novel ONNO-type tetradentate ligand, 1,3-diaminopro-pane-N,N'-di-α-(β-methyl)-pentanoic acid (H_2apmp) and its cobalt(III) complexes, $[Co(apmp)X_2]^{n+}$, (X=Cl^-, NO_2^-, H_2O, X_2=CO_3^{2-}, en, L-phenylalanine) have been synthesized. During the preparation of the dichloro cobalt(III) complex of apmp, $[Co(apmp)Cl_2]^-$, the ligand has coordinated to the cobalt(III) ion in a geometric selectivity to give only the *uns-cis* isomer and, during the substitution reaction between L-phenylalanine and $[Co(apmp)Cl_2]^-$, the L-phenylalanine has coordinated to the cobalt(III) ion in a geometric selectivity to give only an *uns-cis*-meridional isomer. It is of interest that this is a rare case of the $[Co(ONNO\ ligand)X_2]^{n+}$-type complex preparations, which gives only an *uns-cis* isomer with geometric selectivity.

Introduction

A linear flexible tetradentate ligand of the type ONNO in the donor atom array such as edda (ethylenediamine-N,N'-diacetic acid, $HOOCCH_2NHCH_2CH_2NHCH_2COOH$) can occupy four coordination sites in an octahedral geometry to give three possible geometric isomers: *s-cis* (symmetric *cis*), *uns-cis* (unsymmetric *cis*), and trans (Figure 1). A number of ONNO-type ligands have been prepared, and many studies have been directed toward the stereospecificity of these complexes and the isolation of various isomers.[1-10] The *s-cis* and *uns-cis* geometric isomers have usually been isolated in the preparation of the metal complexes, but no trans isomers have been obtained to date.

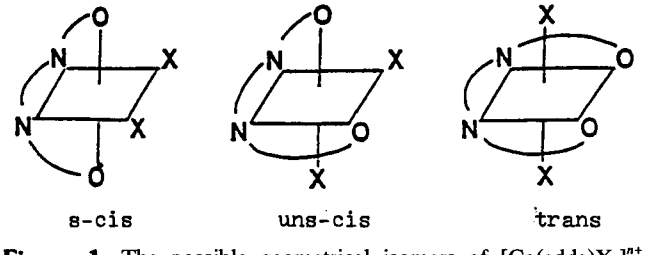
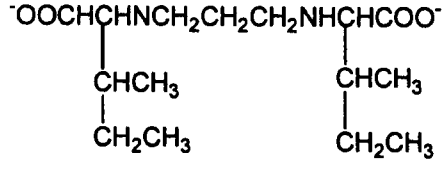


Figure 1. The possible geometrical isomers of $[Co(edda)X_2]^{n+}$ complexes.



1,3-diaminopropane-di-α-(β-methyl)-pentanoate ligand, apmp

In order to study the relative stabilities of the *s-cis* and *uns-cis* isomers during the preparation process of the metal complexes of an ONNO-type ligand, a novel bulky 1,3-diaminopropane-N,N'-di-α-(β-methyl)-pentanoate (apmp) ligand and the cobalt(III) complexes of this apmp ligand have been prepared.

It is of particular interest to observe what isomers would be formed from the preparation of $[Co(apmp)X_2]^{n+}$-type (X=Cl^-, H_2O, NO^{2-}, X_2=CO_3^{2-}, en, L-phenylalanine) complexes. It will be shown that only the *uns-cis* geometric isomer is obtained in the preparation of $[Co-(apmp)X_2]^{n+}$ com-

*To whom correspondence should be addressed