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C–H bond activation by rhodium(I) and the mechanism of the olefin isomerization: new synthesis of β,γ-unsaturated ketones via η^1- or η^3-alkylallylrhodium(III) complexes by reductive elimination

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Abstract

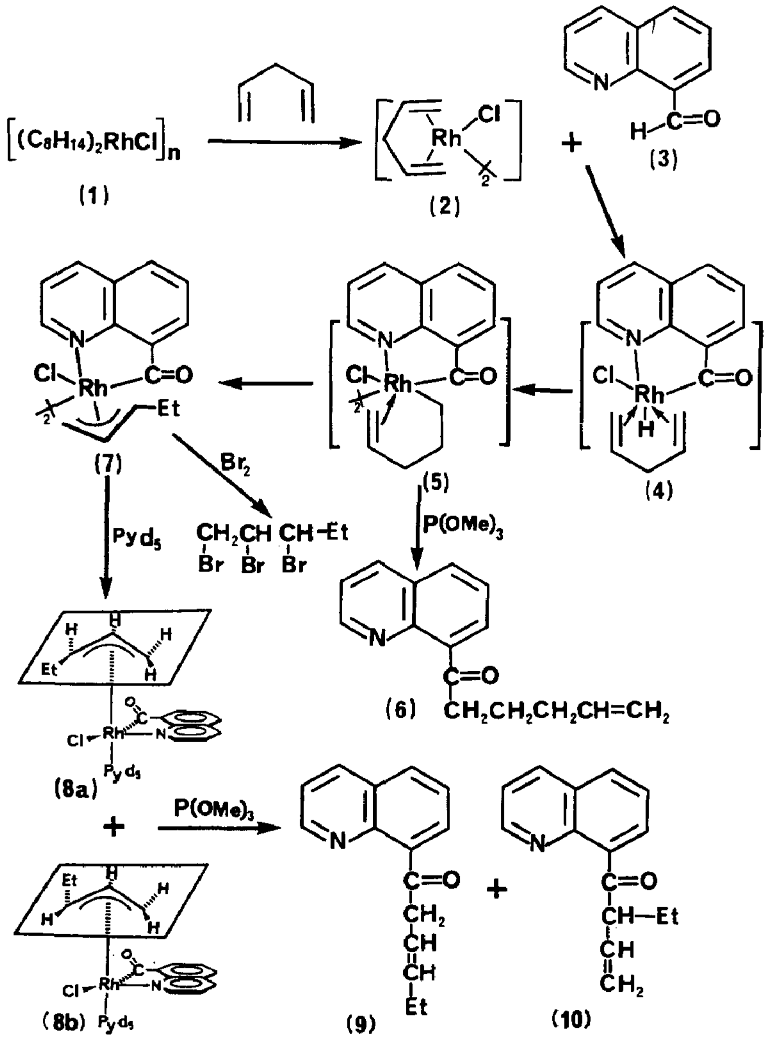
Acylrhodium(III)-η^3-1-ethylallyl complex (7) was prepared by the reaction of 8-quinolinecarboxaldehyde (3) and 1,4-pentadienerhodium(I) chloride (2) by C–H bond activation, followed by hydrometallation, and double bond migration. Higher concentrations of pyridine as coordinating ligand transforms η^3-1-ethylallylrhodium(III) complexes (**8a,8b**) into η^1-pent-2-enylrhodium(III) complex (**11a**). Acylrhodium(III)-η^3-*syn,anti*-1,3-dimethylallyl complex (**14**) was also prepared from 1,3-pentadienerhodium(I) chloride (**16**) and **3**. The reductive elimination of acylrhodium(III)-η^1- and -η^3-1-alkylallyl complexes by trimethylphosphite gives various β,γ-unsaturated ketones.

Introduction

The activation of the C–H bond by transition metal complexes has recently received much interest in organometallic chemistry [1]. The C–H bond of aldehyde can be readily cleaved by transition metals such as Wilkinson's complex. Subsequent decarbonylation of the acylmetal hydride and reductive elimination of the resulting alkylmetal hydride gives alkane [2]. This undesired decarbonylation can be prevented by cyclometallation, since a five-membered ring is the right size for a stable metallacycle complex [3]. The cyclometallation permits facile oxidative-addition into C–C [4] or C–H bonds to yield acylmetal alkyls [5]. The C–C bond activation of 8-quinolinyl alkyl ketone by rhodium(I) produces acylrhodium(III) alkyls directly whereas the C–H bond activation of the corresponding aldehyde by Wilkinson's complex gives a stable acylrhodium(III) hydride [6]. When the olefin-coordinated rhodium(I) complexes were used in place of Wilkinson's complex, the acylrhodium(III) hydride generated as a transient intermediate, hydrometallates the coordinate olefins, to give acylmetal alkyls. Treatment of these acylmetal alkyls with bases such as phosphine or phosphite induces ligand-promoted reductive-elimination to give the corresponding ketones under very mild conditions [5,7]. It has been reported that reductive-elimination of the acylmetal allyl complexes formed from the reaction of allylmetal complexes and acyl chloride give β,γ-unsaturated ketones [8]. Here we describe a facile new organic synthesis of β,γ-unsaturated ketones by reductive-elimination of acylrhodium(III)η^1- and η^3-alkyl-substituted allyl complexes derived from the reaction of 8-quinolinecarboxaldehyde and diene-coordinated rhodium(I) complexes.

Results and discussion

It has been reported that many dienes can readily coordinate to Rh by olefin exchange under mild conditions [9]. 1,4-Pentadienerhodium(I) chloride complex (2) can be generated in situ from the reaction of bis(cyclooctene)rhodium(I) chloride (1)

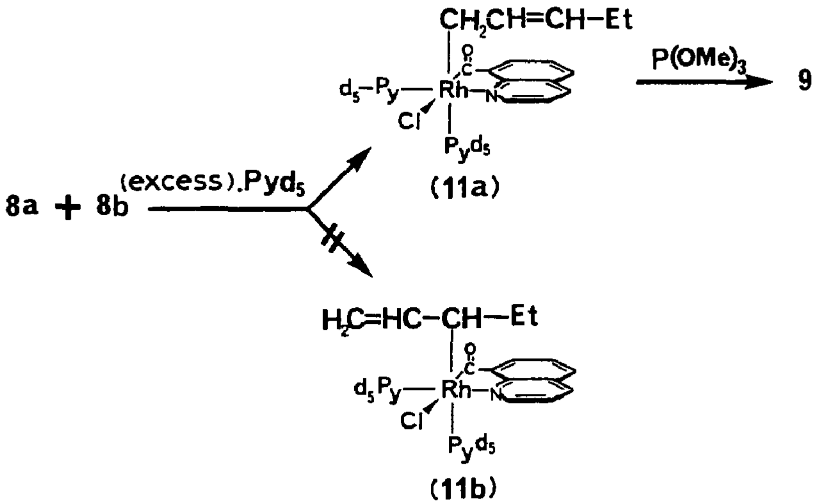


Scheme 1

and 1,4-pentadiene (Scheme 1) [9b]. Compound **3** (8-quinolinecarboxaldehyde) [10] was allowed to react with a solution of **2** in ether at room temperature for 10 min and gave a yellow precipitate. Reductive-elimination of this yellow solid precipitate by trimethylphosphite gave 8-quinolinyl pent-4′-enyl ketone (**6**) in 42% yield. Although the yellow solid could not be characterized because of complication of the ^{1}H NMR spectra, the structure of the acylrhodium(III)pent-4′-enyl complex (**5**) was inferred from the reductive-elimination product **6**. The hydride in **4**, formed from the C–H bond activation of **3** by **2**, inserts into the 2-position of 1,4-pentadiene to form a stable intramolecularly coordinated ω-alkenyl complex **5**. Many cyclometallated π-complexes with a five and a half membered ring have been reported [11]. Ether was used as the solvent to retard double bond isomerization owing to rapid precipitation as soon as **5** is formed.

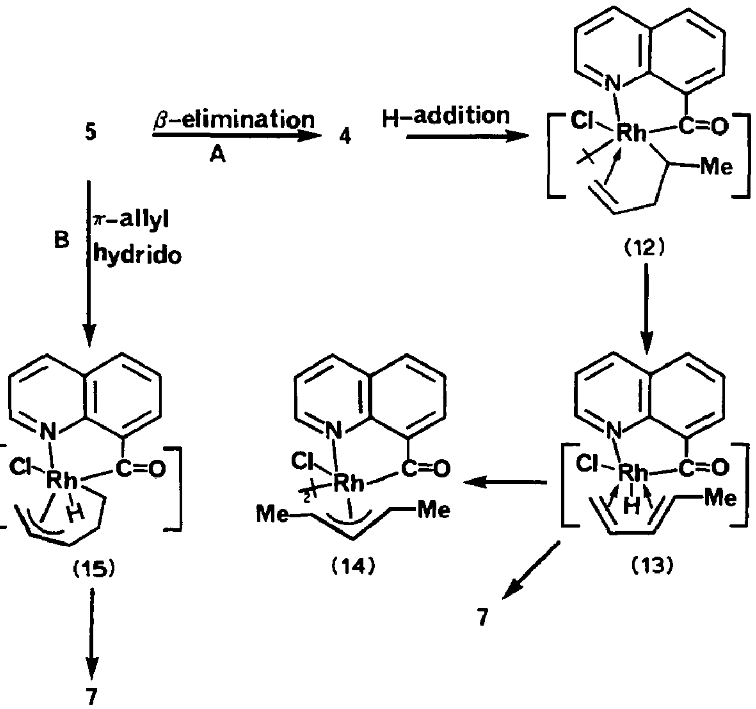
For longer reaction times in chloroform, a better solvent than ether or pentane, the reaction yielded **6** contaminated with **9**, an olefin-isomerized compound, after reductive-elimination of the resulting complexes. Under prolonged reaction times (24 hr) to allow complete isomerization of **5**, the reaction of **2** and **3** in $CHCl_3$ at room temperature affords a chlorine-bridged dimer **7**, which was isolated with pentane in 85% yield. Treatment of **7** with Br_2 gives 1,2,3-tribromopentane, as determined from its ^{1}H NMR spectra. The addition of two equivalents of pyridine-d_5 to **7** in $CDCl_3$ solution gives acylrhodium(III)-η^3-1-ethylallyl complexes, which are five-coordinate species, which consisting of two isomers, *anti*-η^3-1-ethylallyl rhodium(III) complex (**8a**) and the syn-isomer (**8b**) in a 2:1 ratio as determined by ^{1}H NMR spectroscopy [12]. The IR band of the carbonyl group in **3** at 1690 cm^{-1} is shifted to 1630 cm^{-1} in a mixture of **8a** and **8b**. Trimethylphosphite causes ligand-promoted reductive-elimination of a mixture of **8a** and **8b** to give two different β,γ-unsaturated ketones, **9** and **10** in 78% yield in a 10:3 ratio. The higher yield of **9** compared with that of **10** is due to the more difficult reductive-elimination of the sterically hindered secondary carbon (C-1 carbon) than of the less hindered primary carbon (C-3) in the unsymmetrically alkyl substituted η^3-1-ethylallyl group in the mixture of **8a** and **8b**.

A twenty-fold excess of pyridine-d_5 in $CDCl_3$ solution tranforms a mixture of **8a** and **8b** into six-coordinate **11a**, for which signals from two diastereotopic protons of α-methylene group [4b] to Rh in **11a** appear at 2.5 and 3.3 ppm as a doublet of triplets and each doublet of the CH_2 of η^3-*anti*- and *syn*-1-ethylallyl group disappears in the spectrum of the mixture of **8a** and **8b** (Scheme 2). The ^{13}C NMR spectrum of the α-methylene group in **11a** showed only one doublet (J(Rh–C) 23.4 Hz) at 19.3 ppm and the disappearance of the η^3-allylic three doublets for **8a** and **8b**. The result can be explained by assuming that excess pyridine-d_5 not only cleaves the chlorine bridge but also displaces the olefinic π-bond in η^3-1-ethylallyl group in **7** to keep the 18 electron rule. When the η^3-acylrhodium(III)-ethylallyl complexes of **8a** and **8b** rearrange to the η^1-acylrhodium(III) alkenyl complex by addition of an excess pyridine-d_5, two possible positional isomers such as **11a** and **11b** may be formed. However only **11a** was detected after this rearrangement, probably because of the higher stability of **11a** owing to primary C–Rh bond compared with that of **11b** which has a secondary C–Rh bond which causes more steric congestion. Reductive-elimination of **11a** gave **9** exclusively in 86% yield thus it is possible to retard the contamination of **10** by addition of excess pyridine to **7** in the synthesis of β,γ-unsaturated ketone.

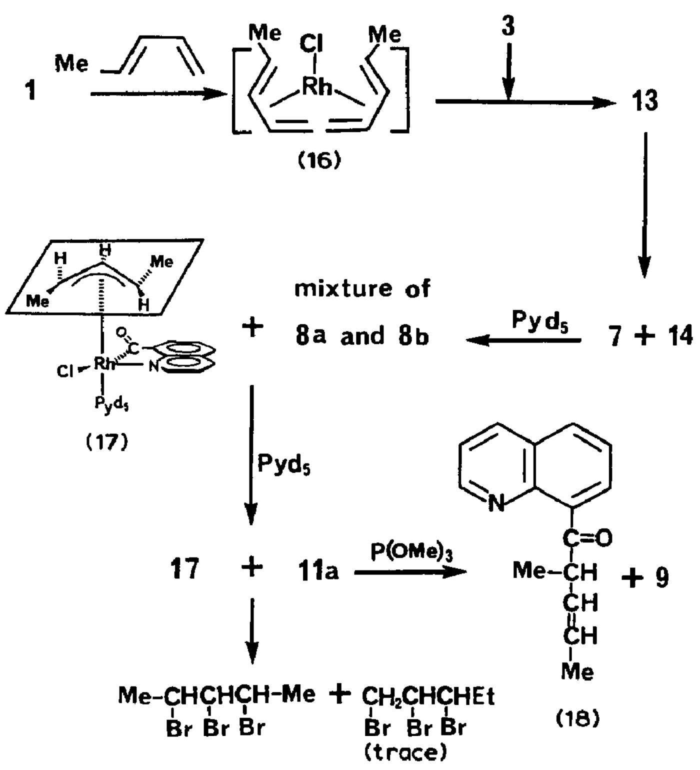


Scheme 2

Two possible mechanisms should be considered for the isomerization of **5** to **7** [13]; a hydride addition–elimination mechanism, A [14] (β-hydride elimination), and a π-allyl hydrido mechanism, B [15] (Scheme 3). Many olefin-isomerization process can be explained in terms of the hydride addition–elimination mechanism. The hydride addition–elimination mechanism allows **5** to form intermediate **13** via **4** and **12**. A subsequent hydride addition into the conjugate diene in **13** should form



Scheme 3



Scheme 4

two different allylrhodium(III) complexes, **7** and **14** by hydride addition to the 4-position and the 1-position in the coordinated 1,3-pentadiene. Many examples of hydride addition to coordinated conjugate dienes have given **14** rather than **7** [16]. However no **14** was isolated from the isomerization of **5** formed by the reaction of **2** with **3**. To confirm the mechanism, the hydride addition into the coordinated conjugate diolefin in **13** was examined by using 1,3-pentadiene.

The 1,3-pentadiene rhodium complex (**16**) was also generated in situ by the reaction of **1** and 1,3-pentadiene (Scheme 4) [9a]. Compound **3** reacts with a solution of **16** in $CHCl_3$ at room temperature to give yellow, chlorine-bridged, dimeric complexes in 84% yield, which consist of **7** and **14** in a 2 : 8 ratio determined by the following procedure. Addition of two equivalents of pyridine-d_5 to a suspension of the yellow complexes in $CDCl_3$ gives acylrhodium(III)-η^3-*anti,syn*-1,3-dimethylallyl complex **17**, and a mixture of **8a** and **8b** in a 8 : 2 ratio, as determined from its ^{1}H NMR spectrum [12]. The ^{1}H NMR chemical shifts for the *anti*-methyl and the *syn*-methyl group in **17** appear at 0.6 (J 6.2 Hz) and 1.7 ppm (J 6.1 Hz), respectively as doublets. The ^{13}C NMR chemical shifts for the allyl group in **17** appear at 114 (d, J(Rh–C) 6.6 Hz, C-2 of the allyl group), 66.8 (d, J(Rh–C) 9.96 Hz, C of the allyl group adjacent to the *syn*-methyl group) and 59.4 ppm (d, J(Rh–C) 11.13 Hz, C of the allyl group adjacent to the *anti*-methyl group) as doublets indicating that all three carbons in the allyl group are coupled with the Rh while those of the *syn*- and the *anti*-methyl groups appear at 18 and 15.7 ppm as singlets, respectively.

A twenty-fold excess of pyridine-d_5 added to a $CDCl_3$ solution of **17** and a mixture of **8a** and **8b**, transforms only **8a** and **8b** into **11a**, **17** remains unchanged. This is probably because of the difficult coordination to Rh of the second pyridine-d_5 owing to steric hindrance by the η^3-1,3-dimethylallyl group in **17** or to the formation from **17** of an unstable complex having a secondary alkenyl C–Rh bond. Treatment of a mixture of **17** and **11a** with Br_2 gives 2,3,4-tribromopentane and a trace of 1,2,3-tribromopentane. Trimethylphosphite causes facile ligand-promoted reductive-elimination of **17** and **11a** to give two β,γ-unsaturated ketones, **18** and **9** in an 8 : 2 ratio, as expected, in 95% yield. A charateristic strong band at 970 cm^{-1} confirms the trans-olefin isomer of **18**. Compound **13** is regarded as an intermediate in the reaction of **3** and **16** via C–H bond activation. The hydride addition to the 1,3-pentadiene in **13** takes place at the 1- and the 4-positions in an 8 : 2 ratio, to give **7** and **14** respectively. The major hydride addition to 1,3-pentadiene is at the 1-position. This result contradicts the hydride addition–elimination mechanism for the isomerization of **5** to **7** shown in Scheme 1, since **14** should have been the major product in the isomerization of **5** via **13** (Scheme 3). Thus the hydride addition–elimination mechanism is scarcely operating in the isomerization of **5** to **7**; an alternative is the π-allyl hydrido mechanism [15]. This type of π-allyl hydrido mechanism has been observed in diene isomerization by Rh [15a,b] and double bond migration by $Fe_3(CO)_{12}$ and $PdCl_2(NCPh)_2$ [15c]. Although Rh in the intermediate **15** is in the high oxidation state, as rhodium(V), it is the most probable. Some examples of high oxidation state for rhodium(V) metal complexes have recently been reported [17]. From this evidence and our results, we can conclude that the π-allyl hydrido mechanism is operating in the isomerization of the alkenyl rhodium complex to the η^3-1-alkylallyl rhodium complex via the rhodium(V) intermediate. More detailed examination of the isomerization mechanism for the alkenyl metal complexes is in progress.

Experimental

All reactions were carried out under nitrogen, in Schlenk-type glassware. Chlorobis(cyclooctene)rhodium(I) (**1**) and 8-quinolinecarboxaldehyde (**3**) were prepared by published procedures [18,10]. Piperylene(1,3-pentadiene) and 1,4-pentadiene were purchased from Aldrich Chemical Co. and used without further purification. All solvents were distilled and stored over molecular sieves (4 Å). NMR spectra were recorded with either a Bruker AC-200 (200 MHz) or a Varian FT-80A (80 MHz) spectrometer. The chemical shifts (δ) of the ^1H and ^{13}C resonances are in ppm relative to internal Me_4Si. Infrared spectra were recorded with a Perkin–Elmer 683 spectrometer. Microanalyses were conducted by ADD Analytical Laboratory. GC/MS and HRMS were performed by Analytical Laboratory at the Korean Research Institute of Chemical Technology (KRICT).

8-Quinolinyl pent-4'-enyl ketone (6)

To 0.1 g (0.28 mmol) of chlorobis(cyclooctene)rhodium(I), **1**, $[RhCl(C_8H_{14})_2]_n$, in a Schlenk flask was added 1 ml of 1,4-pentadiene at 0 °C under nitrogen. The mixture was stirred at room temperature for 10 min during which the color of the suspension turned from brown to yellow. To this suspension was rapidly added

0.046 g (0.29 mmol) of **3** in 3 ml of ethyl ether. A white-yellow precipitate formed simultaneously on addition of the aldehyde solution. The reaction was allowed to proceed for 10 min. The white-yellow precipitate dissolved completely on addition of 2 ml of trimethylphosphite, to give a clear yellow solution which was evaporated to dryness at 80 °C under reduced pressure. The crude residue was purified by column chromatography to give 0.026 g (42% yield) of 8-quinolinyl pent-4′-enyl ketone, **6**: IR(neat) 3070 (w), 2930 (m), 1685 (s), 1640, 1595, 1570 (s), 1495 (m), 1250 (m), 1050 (w), 970 (m), 910 (m), 827, 740, 720, 695 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ (ppm) 8.9 (dd, J 4.2, 1.9 Hz, 1H, H of C-2 in quinoline), 8.3–7.2 (m, 5H, H's of quinoline), 5.6 (m, 1H, –CH=), 5.0 (ABX pattern, 2H, CH_2=), 3.3 (t, J 7.4 Hz, 2H, CH_2CO), 2.3–1.7 (m, 4H, $-CH_2CH_2-$); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ (ppm) 150–121 (m, C of quinoline), 138.3 (C of –CH=), 114.9 (C of CH_2=), 41.1 (α-carbon to ketone), 33.2 (C-3′ in pent-4′-enyl group), 23.5 (C-2′ in pent-4′-enyl group); HRMS calcd for $C_{15}H_{15}NO$ (M^+): 225.1153. Found: 225.1148; m/e (relative intensity), 225 (M^+, 16), 224 ($M^+ - 1$, 16), 197 (8.4), 196 (8.1), 184 (46), 171 (15), 156 (100), 128 (40); TLC $R_f = 0.49$, hexane : ethyl acetate = 5 : 2, SiO_2.

*Chloro-η^3-1-*anti*-1-ethylallyl(8-quinolinecarbonyl-*C,N*)(pyridine-*d$_5$*)rhodium (**8a**) and* syn*-isomer (**8b**)*

To 0.2 g (0.56 mmol) of chlorobis(cyclooctene)rhodium(I) (**1**) was added 1 ml of 1,4-pentadiene at 0 °C under nitrogen. The mixture was stirred at room temperature for 10 min. To the resulting suspension was added 0.092 g (0.58 mmol) of **3** in 3 ml of $CHCl_3$. The reaction was allowed to proceed for 24 h at room temperature, and the yellow precipitate that separated on addition of pentane, was filtered, and dried in vacuo to give 0.172 g (85% yield) of **7**: decomp. > 300 °C; Anal. calcd. for $C_{30}H_{30}Cl_2N_2O_2$: C, 49.52; H, 4.13; N, 3.85. Found: C, 50.00; H, 4.07; N, 4.16%; IR (nujol) 1725 (w), 1678 (s), 1645 (s), 1588, 1570, 1500, 1375 (s), 1236, 1160, 1050 (m), 895, 835, 790 cm^{-1}.

To a suspension of 0.020g of **7** in 1.5 ml of $CDCl_3$ was added 0.1 ml of Br_2 to give a reddish yellow precipitate. The precipitate was filtered off through a $MgSO_4$ column giving 1,2,3-bromopentane in $CDCl_3$ solution, identified by ^1H NMR spectroscopy.

To a suspension of 0.086 g (0.24 mmol) of **7** in 2ml of $CDCl_3$ was added 0.040 g (0.48 mmol) of pyridine-d_5 giving a yellow solution of a mixture of acylrhodium(III)-η^3-*anti*-1-ethylallyl complex (**8a**) and *syn*-isomer (**8b**) in a 2 : 1 ratio, as determined from the ^1H NMR spectrum. **8a**: ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 10.7 (d, J 4.16 Hz, 1H, H of C-2 in quinoline), 8.4–7.4 (m, 5H, H's of quinoline), 4.8 (m, 1H, H of C-2 in allylic group), 3.9 (d, J(*syn*-H in C-3,*meso*-H) 7.4 Hz, 1H, *syn*-H of C-3 in allyl group), 3.3 (d, J(*anti*-H in C-3,*meso*-H) 11.7 Hz, 1H, *anti*-H of C-3 in allyl group), 0.9 (m, 2H, CH_2 of *anti*-ethyl group), 0.6 (t, J 7 Hz, 3H, CH_3 of *anti*-ethyl group); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ(ppm) 153–122 (m, C of quinoline), 112 (d, J(Rh–C) 6.65 Hz, C-2 of allyl group), 70.8 (d, J(Rh–C) 9.40 Hz, C-1 of allyl group), 54.0 (d, J(Rh–C) 12.05 Hz, C-3of allyl group), 24.4 (C of CH_2 in *anti*-ethyl group), 14.1 (C of CH_3 in *anti*-ethyl group). **8b**: ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 10.7 (d, J 4.16 Hz, 1H, H of C-2 in quinoline), 8.4–7.4 (m, 5H, H's of quinoline), 4.8(m, 1H, H of C-2 in allyl group), 4.4(m, 1H, *anti*-H of C-1 in allyl group), 3.0(d, J(*anti*-H in C-3,*meso*-H) (11.4 Hz, *anti*-H of C-3 in allyl group), 2.9 (d, J(*syn*-H in C-3,*meso*-H) 7.2 Hz, 1H, *syn*-H of C-3 in allyl group), 2.3

(m, 2H, CH_2 of *syn*-ethyl group), 1.20 (t, J 7.02 Hz, 3H, CH_3 of *syn*-ethyl group); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ (ppm) 153–122 (m, C's of quinoline), 111 (d, J(Rh–C) 6.75 Hz, C-2 of allyl group), 70.8 (d, J(Rh–C) 9.40 Hz, C-1 of allyl group), 54.0 (d, J(Rh–C) 12.05 Hz, C-3 of allyl group), 26.5 (s, C of CH_2 in *syn*-ethyl group), 15.4 (s, C of CH_3 in *syn*-ethyl group); IR spectra of a mixture of **8a** and **8b**: ($CHCl_3$) 2976 (s), 1640(s), 1600, 1579 (m), 1500 (m), 1444 (m), 1065, 1040 (w), 900 (s), 832 cm^{-1}.

Reductive-elimination of a mixture of 8a and 8b

To a solution of a mixture (0.24 mmol) of **8a** and **8b** was added 2 ml of trimethylphosphite upon which the color changed from yellow to red. After 15 min stirring, the mixture was concentrated at 80°C under reduced pressure leaving a dark brown residue. The residue was purified by column chromatography on silica gel (hexane : ethyl acetate 5 : 2) to give a mixture of 8-quinolinyl pent-2′-enyl ketone (**9**) and 8-quinolinyl pent-1′-en-3′-yl ketone (**10**) in 78% yield in a 10 : 3 ratio as determined from the ^1H NMR spectrum. The mixture was separated by column chromatography by use of a different solvent ratio system (hexane : ethyl acetate = 5 : 1). **9**: IR(neat) 3040 (w), 2960 (s), 2870, 1685 (s), 1595, 1570, 1500, 1460, 1270 (w), 1110, 970 (s), 830, 795, 760 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ (ppm) 8.9 (dd, J 4.18, 1.81 Hz, 1H, H of C-2 in quinoline), 8.3–7.3 (m, 5H, H's of quinoline), 5.6 (m, 2H, –CH=CH–), 4.1 (brd, J 5.2 Hz, 2H, α-CH_2 to CO), 2.1 (m, 2H, CH_2 of ethyl group), 0.9 (t, J 7.6 Hz, 3H, CH_3 of ethyl group); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ (ppm) 150–121 (m, quinoline, C-2 and C-3 of pent-2′-enyl group), 48.5 (C of α-CH_2 to CO), 25.87 (C of CH_2 in ethyl group), 13.6 (C of CH_3 group); mass spectrum; HRMS calcd for $C_{15}H_{15}NO$ (M^+) 225.115364. found: 225.1162; m/e (relative intensity) 225 (M^+, 10), 224 ($M^+ - 1$, 18), 196 (15), 182 (80), 156 (100), 128 (46); TLC $R_f = 0.41$, hexane : ethylacetate = 5 : 1. **10**: IR (neat) 3030 (w), 2960 (m), 2930 (w), 1690 (s), 1590 (w), 1570 (m), 1492 (m), 1170 (w), 1050 (w), 970 (w), 920 (w), 830 (w), 790 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ (ppm) 8.95 (dd, J 4.2 Hz, J 1.7 Hz, 1H, H of C − 2 in quinoline), 8.3–7.2 (m, 5H, quinoline), 5.8 (m, 1H, –CH=), 5.08 (ABX pattern, 2H, =CH_2), 4.0 (td, J 8.1 Hz, J 2.7 Hz, 1H, α-CH to CO), 1.6–2.1 (m, 2H, –CH_2–), 0.9 (t, J 7.3 Hz, 3H, CH_3); mass spectrum; m/e (relative intensity), 225 (M^+, 9), 210 (25), 196 (9), 156(100), 128 (35); TLC $R_f = 0.38$, hexane : ethyl acetate = 5 : 1, SiO_2.

*Chloro-pent-2′-enyl(8-quinolinecarbonyl-*C,N*)bis(pyridine-*d$_5$*)rhodium (11a)*

To a solution of a mixture (0.24 mmol) of **8a** and **8b** in 1 ml of $CDCl_3$ was added 0.80 g (9.5 mmol) of pyridine-d_5 giving a yellow solution of **11a**: IR ($CDCl_3$ + Py-d_5) 2900 (w), 1630 (s), 1590 (w), 1535, 1320, 1230, 975, 835 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$)δ (ppm) 10.7 (d, J 4.8 Hz, 1H, H of C-2 in quinoline), 8.3–7.3 (m, 5H, quinoline), 5.2 (m, 1H, –CH= of C-3 in pent-2′-enyl group), 4.6 (m, 1H, =CH– of C-2 in pent-2′-enyl group), 3.2(td, J 8.24, 3.28 Hz, 1H, one of diastereotopic protons of α-CH_2 to Rh), 2.6 (td, J 8.27, 2.86 Hz, 1H, one of diastereotopic protons of α-CH_2 to Rh), 1.0 (m, 2H, CH_2 in ethyl group), 0.35 (t, J 7.7 Hz, 3H, CH_3 in ethyl group); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ (ppm) 155–122 (m, quinoline, C-2 and C − 3 of pent-2′-enyl group), 24.8 (C of CH_2 in ethyl group), 12.3 (C of CH_3), 19.3 (d, J(Rh–C) 23.4 Hz, α-CH_2 to Rh).

*Reductive-elimination of **11a***

To a solution of **11a** in $CDCl_3$ was added 2 ml of trimethylphosphite upon which the color changed from yellow to red. After 15 min of stirring, the mixture was concentrated at 80 °C under reduced pressure leaving a dark brown residue. The residue was purified by column-chromatography on silica gel to give 0.053 g (86% yield) of **9**.

*A mixture of chloro-η^3-*anti,syn*-1,3-dimethylallyl(8-quinolinecarbonyl-*C,N*)(pyridine-*d$_5$*)rhodium (17), **8a** and **8b***

To 0.1 g (0.28 mmol) of chlorobis(cyclooctene)rhodium(I) **1**, in a Schlenk flask, was added 1 ml of piperylene (1,3-pentadiene) at −10 °C under nitrogen. The mixture was stirred for 10 min during which the brown suspension became a yellow solution, that of **16**. To this solution was added 0.046 g (0.29 mmol) of **3** in 3 ml of $CHCl_3$. Reaction was allowed to proceed for 3 h at room temperature. The yellow precipitate that formed on addition of pentane, was filtered, washed with pentane, and dried in vacuo to give 0.085 g (84% yield) of yellow solid of **14** and **7**; decomp. > 300 °C; Anal calcd for $C_{30}H_{30}Cl_2N_2O_2$: C, 49.52; H, 4.13; N, 3.85. Found: C, 49.1; H, 4.46; N, 3.84%. IR (nujol) 1723 (w), 1670 (s), 1645 (w), 1575 (w), 1500, 1230, 1046, 895 (m), 830 (m), 790, cm^{-1}.

To a suspension of 0.085 g (0.234 mmol) of yellow solid in 2ml of $CDCl_3$ was added 0.020 g (0.24 mmol) of pyridine-d_5 giving a yellow solution of a mixture of **17** and **8a,8b** in a 8 : 2 ratio as determined from the ^1H NMR spectrum. **17**: ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 10.7 (d, J 4.86 Hz, 1H, H of C-2 in quinoline), 8.4–7.5 (m, 5H, quinolne), 4.6 (m, 1H, H of C-2 in allyl group), 4.2 (m, 1H, *syn*-H of allyl group), 3.8 (m, 1H, *anti*-H of allyl group), 1.7 (d, J 6.1 Hz, 3H, *syn*-CH_3), 0.6 (d, J 6.2 Hz, 3H, *anti*-CH_3); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ (ppm) 153–123 (m, quinoline), 114(d, J(Rh–C) 6.61 Hz, C-2 of allyl group), 66.8 (d, J(Rh–C) 9.96 Hz, C of allyl group attached to *syn*-CH_3 group), 59.4(d, J(Rh–C) 11.13 Hz, C of allyl group attached to *anti*-CH_3 group), 18.0 (C of *syn*-CH_3 group), 15.7 (C of *anti*-CH_3 group); IR ($CDCl_3$) 2960, 1630, 1495, 1260, 1040, 910, 780 cm^{-1}.

To a suspension of 0.02 g of **17** and **8a,8b** in 1.5 ml of $CDCl_3$ was added 0.5 ml of Br_2 to give a red-yellow precipitate. This precipitate was filtered off through a $MgSO_4$ column, giving 2,3,4-tribromopentane with trace of 1,2,3-tribromopentane, and was identified from its ^1H NMR spectrum.

*Reductive-elimination of a mixture of 17 and **8a, 8b***

To a solution of a mixture (0.234 mmol) of **17** and **8a,8b** was added 0.80 g (9.5 mmol) of pyridine at room temperature. After 5 min of stirring, the mixture was treated with 2 ml of trimethylphosphite, and concentrated at 80 °C under reduced pressure. The residue was purified by column chromatography on silica gel to give 0.050 g (95% yield) of a mixture of 8-quinolinyl pent-3′-en-2′-yl ketone (**18**) and **9** in an 8 : 2 ratio. **18**: IR (neat) 2960 (s), 2940 (s), 1680 (s), 1565 (m), 1490 (m), 1250(s), 1050, 963 (s), 830, 795 cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ (ppm) 8.9 (dd, J 4.18, 1.8 Hz, 1H, H of C-2 in quinoline), 8.3–7.3 (m, 5H, quinoline), 5.5 (m, 2H, –CH=CH–), 4.5 (quintet, J 6.2 Hz, 1H, α-CH to CO), 1.6 (dd, J 4.8, 0.8 Hz, 3H, CH_3 to vinyl group), 1.35 (d, J 6.9 Hz, 3H, CH_3 to α-CH group); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ (ppm) 150–121 (m, quinoline, and C's of (CH=CH–), 50.3 (C of α-CH to CO), 17.9 (C of CH_3 to α-methine group), 16.4 (C of CH_3 to vinyl group);

HRMS (M^+) calcd for $C_{15}H_{15}NO$ 225.1153. Found 225.1134; m/e (relative intensity) 225 (M^+, 5), 224 (M^+-1, 4), 210 (2), 196 (37), 156 (100), 128 (37); TLC $R_f = 0.50$, hexane : ethylacetate = 5 : 2, SiO_2.

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