C-H Bond Activation of Aldimine by Rh(I): New Synthesis of β,γ-Unsaturated Ketone from Aldehyde through Iminoacylrhodium(III)-η^3-allyl Complexes

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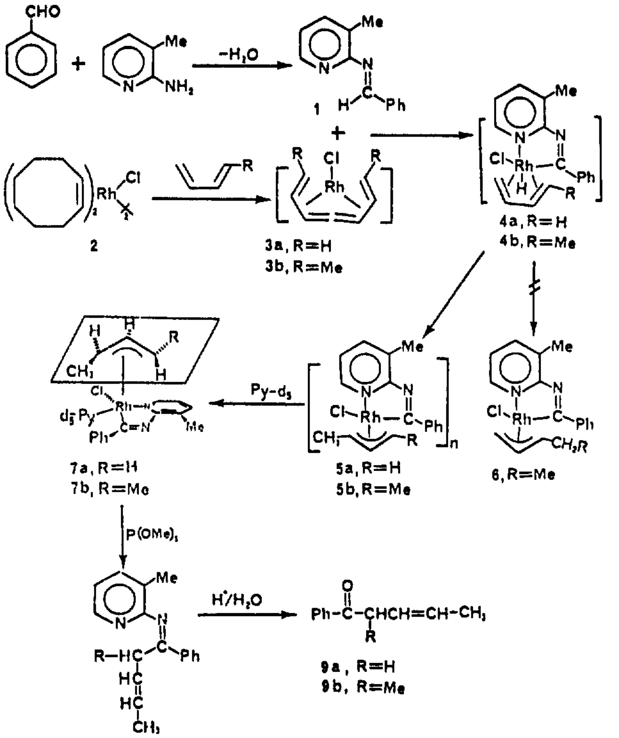
C-H bond activation by transition metals has been one of the recent interests in organometallic chemistry[1]. The hydride generated by C-H bond activation of 8-quinolinecarboxaldehyde by Rh(I) inserts into the coordinated olefin or diolefin to form acylrhodium(III) alkyl[2] or acylrhodium(III) η^1-, η^3- allyl complexes[3], which are reductive-eliminated to give alkyl ketones or β,γ-unsaturated ketones respectively. It has been reported that C-H bond activation of the aldimine by Wilkinson's catalyst generated iminoacylrhodium(III) hydride complex[4]. This Rh-hydride hydrometallates the olefins to form iminoacylrhodium(III) alkyl complex as an intermediate, which was easily reductive-eliminated to give ketimine. The ketimine is a potential precursor for ketone since hydrolysis of ketimine produces ketone. One of the advantages on the synthesis of ketones by C-H bond activation of aldimate is that 2-amino pyridine group used as a cyclometallation tool can be easily eliminated by hydrolysis. This report describes new synthesis of β,γ-unsaturated ketimine from aldimine by C-H bond activation through iminoacylrhodium(III) η^3-alkyl substituted allyl complexes: synthesis of β,γ-unsaturated ketones from aldehyde.



Scheme 1. Synthesis of β,γ-unsaturated ketones from benzaldehyde through iminoacylrhodium(III)-η^3-allyl complexes.

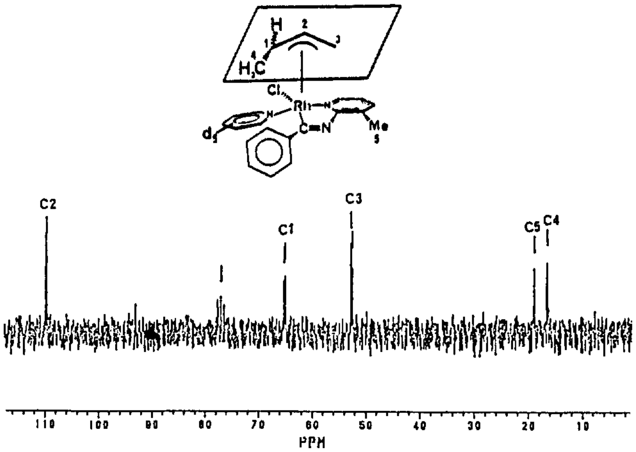


Figure 1. ^{13}C NMR spectra of η^3-*anti*-1-methylallyl group in 7a.

The compound **1**, 3-methyl-2-aminopyridyl aldimine was prepared by the reaction of benzaldehyde and 3-methyl-2-aminopyridine in THF at reflux in the presence of 3 Å molecular sieves (Scheme 1). Also **3a** was prepared *in situ* by the reaction of bis(cyclooctene)rhodium(I) chloride, **2** and 1,3-butadiene at 0 °C for 5 min during which time reddish yellow solution turned into yellow[5]. To a solution of **3a** in THF was added the aldimine, **1** and the resulting solution was heated at 55 °C for 10 min to give a yellow solution. After cooling the reaction mixture and addition of pentane, a yellow precipitate was filtered, and dried in vacuo. This solid complex was hard to be characterized due to insolubility of its dimeric (or polymeric) species since its monomeric complex of **5a** seems to dimerize (or polymerize) to make an 18-electron complex[3a]. It is not clear whether **5a** is dimeric or polymeric species. Addition of Br_2 to **5a** in $CDCl_3$ gave 1,2,3-tribromobutane identified by ^1H NMR spectra[3a]. The product, **5a** was solubilized in $CDCl_3$ by addition of a few drops of pyridine-d_5, giving the monomeric 5-coordinate iminoacylrhodium(III)-η^3-*anti*-1-methylallyl complex, **7a**: ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.4 (d, J = 5.18 Hz, 1H, H of C-2 in picoline), 7.6-7.0 (m, 7H, Hs of picoline and phenyl group), 4.2 (m, 1H, H of C-2 in η^3-allyl group), 3.7(m, 1H, H of *syn*-H of C-1 in η^3-allyl group), 3.45 (d, J = 3.04 Hz, 1H, *syn*-H of C-3 in η^3-allyl group), 3.50 (d, J = 10.1 Hz, *anti*-H of C-3 in η^3-allyl group), 2.6 (s, 3H, CH_3 in picoline), 0.5 (d, J = 6.20 Hz, 3H, *anti*-CH_3 to C-1 in η^3-allyl group); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 147-120 (m, carbons of picoline and phenyl group), 109 (d, J_{Rh-C_2} = 6.3 Hz, C-2 of η^3-allyl group), 85 (d, J_{Rh-C_1} = 10.12 Hz, C-1 of η^3-allyl group), 52 (d, J_{Rh-C_3} = 10.7 Hz, C-3 of η^3-allyl group), 18.67 (s, CH_3 of picoline), 16.46 (s, C of *anti*-CH_3 in η^3-1-methylallyl group). The ^1H NMR chemical shift of *anti*-methyl group in **7a** appears at 0.5 ppm as doublet[6]. Any η^3-*syn*-1-methylallyic rhodium(III) complex was not observed in the reaction mixture differently from 8-quinolinyl acylrhodium (III)-η^3-1-methylallyl complexes consisted of *syn*- and *anti*-isomers[3a]. ^{13}C NMR spectra of η^3-1-methylallyl group in **7a** is shown in Figure 1. The chemical shift of ^{13}C NMR spectra of the allylic carbons appears at 109, 85, 52 ppm as doublet respectively. The position of the resonances for the meso carbon atom of the η^3-allyl transition metal complexes generally falls in the range 128-102 ppm, while those for the terminal carbon atoms are found at 86–42 ppm[7]. The three carbons in η^3-allyl group interact with the Rh metal having a nuclear spin $I = 1/2$, which splits each of allyic carbons as doublet. Complex **5a** is supposed to be formed from the C–H bond activation of **1** by **3a** through an transient intermediate, **4a**. The hydride in **4a** must be inserted into the coordinated 1,3-butadiene to form **5a**. There are some reports about the characterizations of the hydrides in **4** prepared from C–H bond activation of aldimine by Rh(I) or Ir(I) complexes[4]. It is also reported that the hydride, generated from C–H bond activation of aldimine[4a] or 8-quinolinecarboxaldehyde[2a], must be inserted into ethylene to form the ethylrhodium(III) complexes when ethylene instead of triphenylphosphine in $(PPh_3)_3RhCl$ is used. Reductive-elimination of **7a** by trimethylphosphite at room temperature for 30 min gave β,γ-unsaturated ketimine **8a** in 36% yield after chromatographic isolation. **8a**: ^1H NMR (80 MHz, $CDCl_3$) δ (ppm) 8.25 (d, 1H, H of C-2 in picoline), 7.4–6.6 (brm, 7H, aromatic Hs of picoline and phenyl), 5.3 (brs, 2H, $-CH=CH-$), 3.4 (brs, 2H, α-methylene to C=N group), 2.1 (s, 3H, CH_3 of C-3 in picoline), 1.5 (brd, 3H, CH_3 to $-CH=CH-$); IR(neat) 3020, 2920, 1635, 1585, 1445, 1410, 1230, 1110, 965, 785, 690 cm^{-1}; TLC Rf = 0.4, hexane:ethylacetate = 5:2, SiO_2.

Compound **8a** was hydrolyzed by washing with a mixture of 0.1N HCl and CH_2Cl_2, and purified by column chromatography to give β,γ-unsaturated ketone **9a** in 82% yield. **9a**: ^1H NMR (80 MHz, $CDCl_3$) δ (ppm) 7.9–7.1 (m, 5H, phenyl group), 5.5 (m, 2H, $-CH=CH-$), 3.6 (brd, 2H, α-methylene to CO), 1.7 (brd, 3H, CH_3 to $-CH=CH-$); IR (neat) 3030, 2920, 1680, 1450, 1275, 1210, 965, 760, 690 cm^{-1}; TLC Rf = 0.69, hexane:ethylacetate = 5:2, SiO_2.

Same reaction was applied with piperylene (1,3-pentadiene)[5b] instead of 1,3-butadiene. Reaction of aldimine **1** and **3b**, prepared from olefin exchange reaction of **2** with piperylene (1,3-pentadiene), afforded **5b** through an intermediate **4b**. With addition of pentane, the complex **5b** was isolated, and characterized by ^1H NMR spectra after dissolving in $CDCl_3$ containing a few drops of pyridine-d_5, giving the iminoacylrhodium(III)-η^3-*anti, syn*-1,3-dimethylallyl complex, **7b**: ^1H NMR (200 MHz, $CDCl_3$) (ppm) 9.6 (d, J = 5.5 Hz, 1H, H of C-2 in picoline), 7.7–6.8 (m, Hs of picoline and phenyl group), 4.5 (m, 1H, *syn*-H in η^3-allyl group), 4.3 (m, 1H, H of C-2 in η^3-allyl group), 3.5 (m, 1H, *anti*-H in η^3-allyl group), 2.7 (s, 3H, CH_3 in picoline), 1.2 (d, J = 6.27 Hz, 3H, *syn*-CH_3 to n^3-allyl group), 0.6 (d, J = 6.23 Hz, 3H, *anti*-CH_3 to η^3-allyl group). The ^1H NMR chemical shift of *anti*- and *syn*-methyl groups in **7b** appears at 0.6 and 1.2 ppm as doublet respectively[6]. Complex **5b** must be formed by a hydride addition into a 1-position of the coordinated 1,3-pentadiene in **4b**. There are two possible positions of hydride additions into unsymmetrical conjugate dienes, a 1- and a 4-position in coordinated 1,3-pentadiene, which supposed to give **5b** and **6** respectively. Only **5b** was determined from the reaction of **1** and **3b**. There are some reports that a hydride adds into the unsubstituted terminal olefin rather than the internal olefin in conjugate dienes[8]. Reductive-elimination of **7b** by trimethylphosphite gave **8b** in 62% yield: ^1H NMR (80 MHz, $CDCl_3$) (ppm) 8.2 (d, 1H, H of C-2 in picoline), 7.8–6.6 (m, 7H, Hs of picoline and phenyl group), 5.6 (m, 2H, $-CH=CH-$), 3.6 (m, 7H, Hs of picoline and phenyl group), 5.6 (m, 2H, $-CH=CH-$), 3.6 (m, 1H, $-CH$ to CO), 2.0 (s, 3H, CH_3 in picoline), 1.65 (brs, J = 4.87 Hz, 3H, CH_3 to vinyl CH), 1.35 (d, J = 6.9 Hz, CH_3 to α-CH); IR(neat) 3.20, 2960, 2930, 1730(w), 1640, 1580, 1440, 1420, 1110, 970, 790, 700 cm^{-1}; TLC Rf = 0.28, hexane:ethylacetate = 5:2, SiO_2.

Hyrolysis of **8b** with a mixture of 0.1N HCl solution and CH_2Cl_2, and chromatographic isolation of the organic layer gave **9b** in 74% yield: ^1H NMR (80 MHz, $CDCl_3$) δ (ppm) 7.9 (m, 2H, *o*-protons of phenyl group), 7.5 (m, 3H, *m,p*-protons of phenyl group), 5.6 (m, 2H, $-CH=CH-$), 4.1 (m, 1H, α-CH to CO), 1.6 (brd, J = 4.1 Hz, 3H, CH_3 to vinyl CH), 1.3 (d, J = 6.7 Hz, 3H, CH_3 to α-CH); IR(neat) 2930, 2860, 1730, 1685, 1600, 1450, 1205, 975, 700 cm^{-1}; TLC Rf = 0.73, hexane:ethylacetate = 5:1, SiO_2.

From the above results it is possible to synthesize the β,γ-unsaturated ketone from the aldehyde by C–H bond activation of aldimine, a subsequent hydride addition into coordinated diolefins, and hydrolysis of the resulting β,γ-unsaturated ketimine formed from the reductive-elimination of iminoacylrhodium(III)-η^3-allyl complexes. The hydride addition into 1,3-pentadiene, conjugated diene, occurs at 1-position, a least hindered side, rather than 4-position. Also it is convenient to use 2-aminopyridine group as a tool for cyclometallation with ease of removing by hydrolysis. Applications of C–H bond activations for other substrates have been under investigation.

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