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Stepwise Skeletal Rearrangement: Four-Membered-Ring Cyclization *via* C−H Bond Cleavage and C−C Bond Cleavage of a Four-Membered Ring by Rhodium(I)

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Summary: Four-membered-ring cyclization from 8-quinolinecarboxaldehyde and chloro(1,5-hexadiene)rhodium(I) and C−C bond cleavage of the generated four-membered ring by dichlorotetrakis(ethylene)dirhodium(I) have been studied.

The activation of C−C bonds by soluble transition-metal complexes[1] has been of special interest, due to its application to important industrial processes such as alkane skeletal rearrangements and cracking. For example, transition-metal hydrides can effect C−C bond-forming or -breaking processes for simple dienes to afford branched dienes.[2] Although four-membered-ring cyclization is an uncommon cyclization reaction, a cyclobutylmethyl metal complex, generated from the reaction of metal hydride and diene, is postulated as one of the important intermediates in some skeletal rearrangements.[3] However, any direct evidence for formation of a cyclobutylmethyl metal complex from hydride insertion into dienes has not been observed. Herein the stepwise skeletal rearrangement mechanism of 1,5-hexadiene through four-membered-ring cyclization and its ring opening on rhodium is described.

8-Quinolinecarboxaldehyde (**1**) reacted with a suspension of chloro(1,5-hexadiene)rhodium(I) dimer (**2b**) in $CHCl_3$ at room temperature for 1 h to give a yellow chlorine-bridged acylrhodium(III) η^3-1-propylallyl complex, **3b** (Scheme 1).

Ligand-promoted reductive elimination of **3b** with $P(OMe)_3$ produced β,γ-unsaturated ketone **4b**[4] in 76% yield after chromatographic isolation. Previously, chloro(1,4-pentadiene)rhodium(I) dimer (**2a**) was used to make β,γ-unsaturated ketone **4a** *via* (η^3-1-ethylallyl)rhodium(III) complex **3a**.[5] When the reaction of **1** and **2b** proceeded in ether at ambient temperature for 5 min,

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(1) (a) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241. (b) Suzuki, H.; Takaya, T.; Takemori, T.; Tanaka, M. *J. Am. Chem. Soc.* **1994**, *116*, 10779. (c) Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540. (d) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (e) Hughes, R. P.; Robinson, D. J. *Organometallics* **1989**, *8*, 1015. (f) Hemond, R. C.; Hughes, R. P.; Robinson, D. J.; Rheingold, A. L. *Organometallics* **1988**, *7*, 2239. (g) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (h) Hemond, R. C.; Hughes, R. P.; Locker, H. B. *Organometallics* **1986**, *5*, 2391. (i) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (j) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3773. (k) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(2) (a) Golden, H. J.; Baker, D. J.; Miller, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4235. (b) Pinke, P. A.; Stauffer, R. D.; Miller, R. G. *J. Am .Chem. Soc.* **1974**, *96*, 4229. (c) Pinke, P. A.; Miller, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 4221. (d) Miller, R. G.; Pinke, P. A.; Stauffer, R. D.; Golden, H. J.; Baker, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 4211.

(3) (a) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976. (b) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076.

(4) **4b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.0 (dd, J = 1.9 Hz & J = 4.2 Hz, 1H, H of C-2 in quinoline group), 8.2−7.4 (m, 5H, H of quinoline group), 5.68−5.54 (m, 2H, −CH═CH−), 4.1 (d, J = 5.8 Hz, 2H, α-CH_2 to CO), 2.0 (q, J = 7.1 Hz, 2H, H-4 in 2-hexenyl group), 1.3 (m, 2H, H-5 in 2-hexenyl group), 0.82 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 150.0−121.0 (C of quinoline & C═C), 48.5 (α-C to CO), 34.7, (C-4 in 2-hexenyl group), 22.3 (C-5 in 2-hexenyl group), 13.5 (C of CH_3); IR (neat) 1675 cm^{-1} (CO); mass spectrum *m/e* (assignment, relative intensity) 239 (M^+, 9), 184 (48), 171 (quinolinylC(OH)═CH_2^+, 21), 157 ($M^+ - C_6H_{10}$, 100), 129 (quinoline$^+$, 60). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.86. Found: C, 80.80; H, 7.40; N, 5.84.

(5) Jun, C.-H. *J. Organomet. Chem.* **1990**, *390*, 361.

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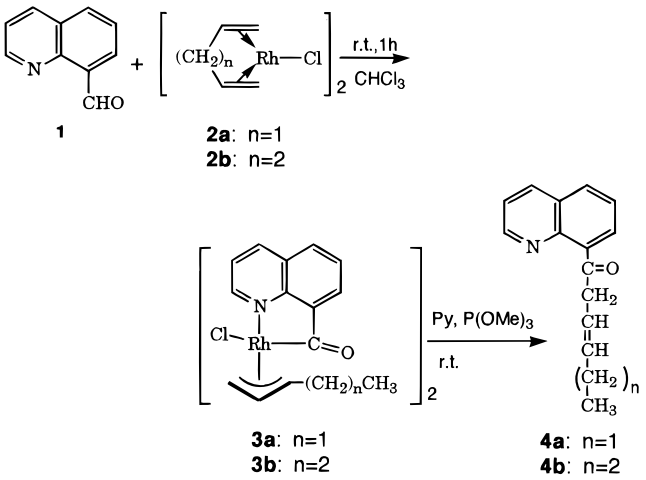
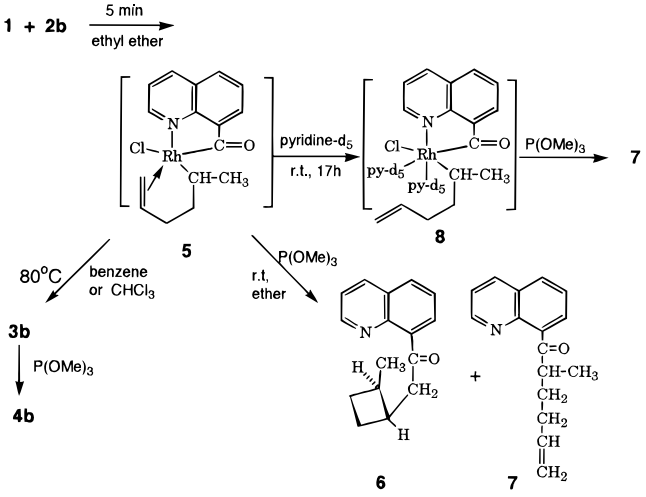
Scheme 1

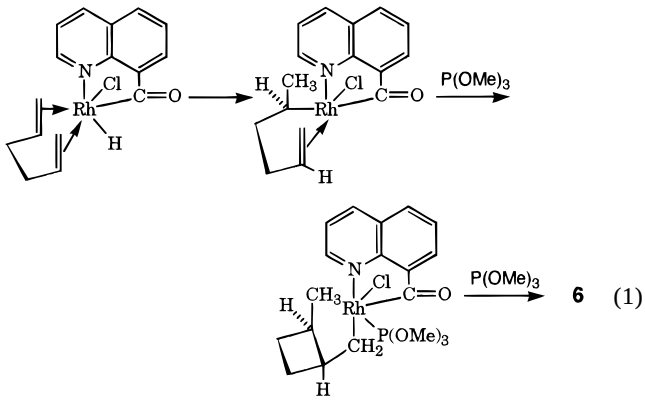


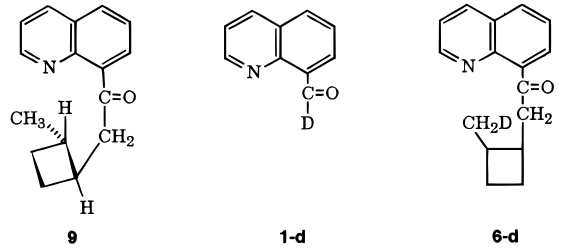
Scheme 2



an initial hydrometalated intermediate complex, an insoluble white-yellow precipitate, was formed (Scheme 2).[6]

Attempts to characterize this intermediate complex failed due to facile isomerization in a solubilizing solvent. Dissolving the complex in $CHCl_3$ for 1 h or heating it in benzene at 80 °C for 1 h allowed complete isomerization to give **3b**, which was identified as **4b** after ligand-promoted reductive elimination with P(OMe)$_3$.[7] When P(OMe)$_3$ was added to the suspension of the former insoluble complex generated *in situ* in ether, a clear solution was generated in a few seconds at room temperature. Purification by column chromatography gave a mixture of **6**[8] and **7** in 82% yield in a 83:17 ratio. From the partial formation of **7**, the former yellow complex can be inferred to be **5**. Exclusive synthesis of **7** was as follows.[9] After complex **5** was dissolved in pyridine-d_5 and the resulting solution was stirred at room temperature for 17 h in order to liberate the coordinated terminal olefin group completely from Rh, **8** was formed, determined by ^{1}H NMR and ^{13}C NMR spectroscopy.[10] Treatment of **8** with P(OMe)$_3$ produced **7** in 95% yield after chromatographic isolation. Formation of **6** from **5** and P(OMe)$_3$ can be explained by cyclization of the 5-hexen-2-yl group in **5**. The stereochemistry of the (2-methylcyclobutyl)carbinyl group in **6** is exclusively cis, identified by NOESY NMR spectra (compared with COSY NMR spectra). No trans isomer (**9**) was detected. The four-membered-ring cyclization mechanism is shown in eq 1.





When **1-d** was used as a substrate under identical reaction conditions to trace an aldehydic hydrogen in **1**, compound **6-d** was isolated.

C−C bond cleavages in 8-quinolinyl alkyl ketone by Rh(I) *via* cyclometalation to yield the corresponding acylrhodium(III) alkyls have already been reported.[11] Compound **6** was subjected to C−C bond cleavage by Rh(I). Compound **6** reacted with a suspension of dichlorotetrakis(ethylene)dirhodium(I) (**10**) in benzene at 100 °C for 4 h to give an insoluble yellow precipitate (Scheme 3). This yellow precipitate was supposed to be a mixture of **12** and **13**, since reductive elimination by pyridine and P(OMe)$_3$ gave a mixture of β,γ-unsaturated ketones

(6) As soon as the complex was formed in ether, it precipitated out without inducing isomerization of olefin, since the metal complex could not be dissolved in this solvent.

(7) Suggs, J. W.; Wovkulich, M. J.; Cox, S. D. *Organometallics* **1985**, *4*, 1101.

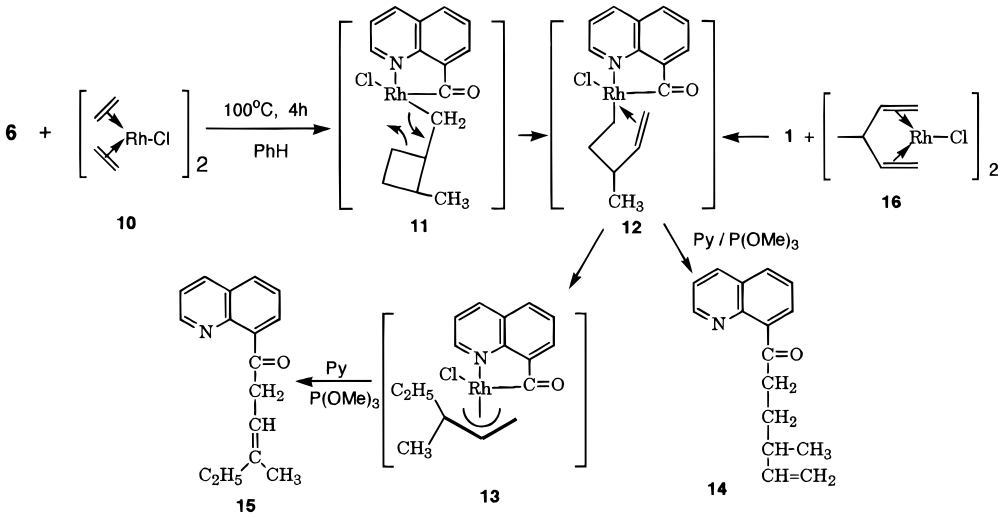
(8) **6**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.0 (dd, J = 1.9 Hz & J = 4.3 Hz, 1H, H of C-2 in quinoline group), 8.2−7.3 (m, 5H, H of quinoline group), 3.45 (ABX pattern, J_{AB} = 15.9 Hz, J_{AX} = 6.5 Hz, J_{BX} = 7.8 Hz, 2H, α-CH_2 to CO), 2.35 (m, 1H, β-CH to CO), 2.1−1.9 (m, 3H, cyclobutyl group), 1.6−1.4 (m, 2H, cyclobutyl group), 1.0 (d, J = 6.3 Hz, CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 150.2−121.3 (C of quinoline), 51.1 (α-C to CO), 39.7, (β-C to CO), 37.5 (C of CH attached to CH_3 in cyclobutyl group), 27.0 & 25.2 (two C of CH_2 in cyclobutyl group), 20.8 (C of CH_3); IR (neat) 1680 cm^{-1} (CO); mass spectrum *m/e* (assignment, relative intensity) 239 (M^+, 12), 211 (M^+ − CO, 9), 210 (M^+ − CHO, 9), 196 (M^+ − CH_2CO, 58), 171 (quinolinylC(OH)=CH_2^+, 21), 157 (M^+ − C_6H_{10}, 100), 129 (quinoline$^+$, 60). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.33; H, 7.11; N, 5.86. Found: C, 80.00; H, 7.33; N, 5.98.

(9) This was already reported: Jun, C.-H.; Kang, J.-B. *Bull. Korean Chem. Soc.* **1993**, *14*, 153.

(10) **8**: ^{1}H NMR (250 MHz, pyridine-d_5) δ (ppm) 11.1 (br, 1H, H of C-2 in quinoline group), 8.8−7.5 (m, 5H, H of quinoline group), 5.5 (m, 1H, =CH−), 4.8 (m, 2H, $=CH_2$), 2.9 (br, 1H, α-CH to Rh), 2.4 (m, 2H, γ-CH_2 to Rh), 1.2 (m, β-CH_2 to Rh), 0.8 (d, J = 5.9 Hz, 3H, CH_3); ^{13}C NMR (62.9 MHz, pyridine-d_5) δ (ppm) 232.6 (d, J = 39.9 Hz, C=O), 155.9−122.8 (C of quinoline & −CH=), 113.5 (=CH_2), 40.4 (γ-C to Rh), 33.3 (β-C to Rh), 26.9 (d, J = 25.8 Hz, α-CH to Rh), 24.1 (C of CH_3). Isolation of complex **8** failed due to the facile isomerization to pyridine-coordinated **3b** without pyridine solvent.

(11) (a) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054. (b) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92. (c) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679.

Scheme 3



15 and **14** in 65% yield in a 9:1 ratio after chromatographic isolation. The first step must be direct oxidative addition into the α-ketone C−C bond by Rh(I) in **6** to generate **11** as a transient intermediate. The cyclobutylcarbinyl group bonded to Rh without stabilizing ligands in **11** is unstable, leading to ring opening to **12**.[12] Recently this type of β-alkyl elimination has been directly observed.[13] Isomerization of **12** to **13** is facile, and this type of isomerization, 4-pentenyl group to η^3-1-ethylallyl group, has been previously studied.[5,12] Identical products, **14** and **15**, were also obtained in a 4:6 ratio in 71% yield from the reaction of **1** and **16** in chloroform at room temperature for 1 h and subsequent reductive elimination with pyridine and $P(OMe)_3$.[14] Longer reaction times allowed isomerization of **12** to **13** to give the higher ratio of **15**:**14** after ligand-promoted reductive elimination.

In conclusion, this report shows the possibility of the stepwise skeletal rearrangement mechanism of 1,5-hexadiene on a metal hydride through a four-membered-ring cyclization, in which each intermediate was trapped by ligand-promoted reductive elimination to form 8-quinolinyl alkyl ketone.

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Supporting Information Available: Figures giving H−H NOESY and H−H COSY NMR spectra for a mixture of 83% of **6** and 17% of **7** (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(12) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795.
(13) McNeill, K.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 3625.

(14) **14**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.95 (dd, J = 1.8 Hz & 4.2 Hz, 1H, H-2 in quinolinyl group), 8.20−7.40 (m, 5H, quinolinyl group), 5.70 (m, 1H, −CH═), 4.96 (ABX system, 2H, CH_2═), 3.30 (t, J = 7.7 Hz, 2H, α-CH_2 to CO), 2.2−1.3 (m, 5H, −CH_2CH_2CH−), 1.04 (d, J = 6.8 Hz, 3H, CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 207.0 (CO), 151.2−121.4 (C of quinoline), 113.1 (CH_2═), 42.7 (α-C to CO), 37.5 (γ-C to CO), 30.8 (β-C to CO), 20.2 (C of CH_3); IR (neat) 1685 cm^{-1} (CO); mass spectrum *m/e* (assignment, relative intensity) 239 (M^+, 1), 238 ($M^+ - 1$, 9), 184 ($M^+ - C_4H_7$, 100), 171 (quinolinyl−C(OH)═CH_2^+, 8), 156 (quinolinyl−CO^+, 77), 128 (quinolinyl$^+$, 53); HRMS calcd for $C_{16}H_{17}NO$ 239.131 014, found 239.131 035. **15**: ^{1}H NMR (80 MHz, $CDCl_3$) δ (ppm) 8.95 (dd, J = 1.8 Hz & 4.2 Hz, 1H, H-2 in quinolinyl group), 8.25−7.30 (m, 5H, quinolinyl group), 5.50 (m, 1H, −CH═), 4.08 (d, J = 6.9 Hz, 2H, α-CH_2 to CO), 2.3−1.8 (m, 2H, CH_2 in ethyl group), 1.72 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.00 (t, J = 6.7 Hz, 3H, CH_3 in ethyl group), 0.94 (t, J = 7.3 Hz, 3H, CH_3 in ethyl group); IR (neat) 1685 cm^{-1} (CO); mass spectrum *m/e* (assignment, relative intensity) 239 (M^+, 11), 238 ($M^+ - 1$, 8), 224 ($M^+ - CH_3$, 3), 210 ($M^+ - C_2H_5$, 21), 182 (43), 156 (quinolinyl−CO^+, 100), 128 (quinolinyl$^+$, 61); HRMS calcd for $C_{16}H_{17}NO$ 239.131 014, found 239.130 318.