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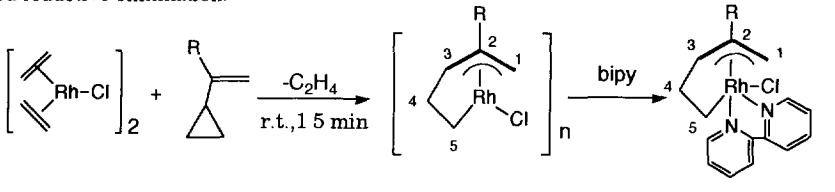
Ring Opening and Ring Closure of Vinylcyclopropanes on Rh and Application to Unstrained C-C Bond Cleavage

[a]Chul-Ho Jun,* [b]Jung-Bu Kang, and [b]Yeong-Gweon Lim

[a]Department of Chemistry, Yonsei University, Seoul 120-749,
[b]Agency for Defense Development, Yuseong 305-600, Korea

Abstract: Formation of σ,η^3-allyl rhodium complexes from vinylcyclopropanes by Rh, ligand promoted regeneration of vinylcyclopropanes, and its application of C-C bond cleavage are demonstrated.

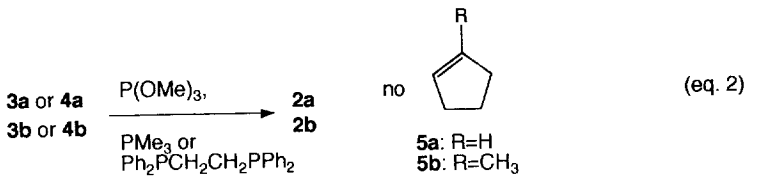
Transformations of vinylcyclopropanes into cyclopentenes[1], dienes[2], and vinylcyclopropane epimers[3] by transition metal catalyst have attracted considerable interest in synthetic procedures.[4] The σ,η^3-allyl metal complexes have been postulated as intermediates for those transformations. Especially, vinylcyclopropanes undergo an epimerization reaction in the presence of dicarbonylrhodium(I) chloride dimer as catalyst.[3] This transformation is accounted for by reversible formation of a σ,η^3-allyl rhodium(III) intermediate through oxidative addition of a strained C-C σ-bond of the three membered ring in vinylcyclopropane to rhodium(I). This kind of σ,η^3-allyl metal complexes have been prepared by many different methods and well characterized.[5] Even though there are a few examples of generating cyclopropane from metallacyclobutanes, prepared by nucleophilic addition of enolates to the central carbon of transition-metal η^3-allyl complex[6], very limited example of generating vinylcyclopropane from σ,η^3-allyl metal complexes has been reported.[7] In this report, we describe the formation of σ,η^3-allyl rhodium complexes from vinylcyclopropanes and regeneration of vinylcyclopropane by ligand promoted reductive elimination.



1 **2a**: R=H **2b**: R=CH_3 **3a**: R=H **3b**: R=CH_3 **4a**: R=H **4b**: R=CH_3

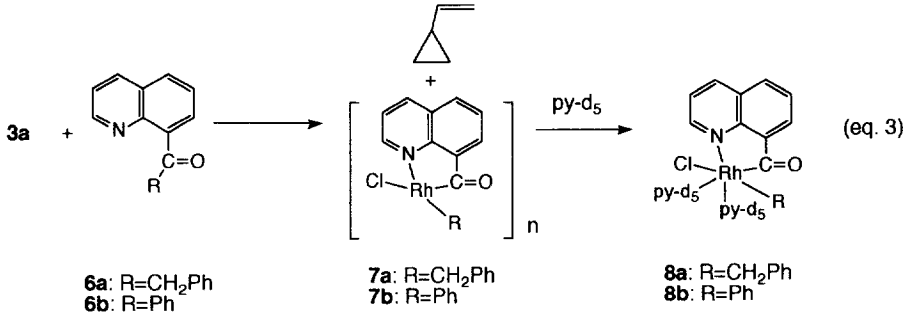
To 50 mg (0.13 mmol) of bis(ethylene)rhodium(I) chloride dimer (**1**) was added 0.18g (2.5 mmol) of vinylcyclopropane (**2a**) at ambient temperature under nitrogen with loss of ethylene (eq. 1). After the reaction mixture was stirred for additional 15 min, excess vinylcyclopropane was completely removed *in vacuo* to provide

a yellow precipitate, which was supposed to be σ,η^3-allyl rhodium complex (**3a**). Since **3a** decomposed slowly in chloroform to give 1,3-pentadiene, addition of 44 mg (0.26 mmol) of bipyridine in CH_2Cl_2 afforded an air stable complex **4a** with pentane (56 mg, 61 % yield, recrystallized from CH_2Cl_2-pentane).[8] The spectral data of **4a** closely match those reported for a variety of σ,η^3-allyl complexes.[5] The most characteristic spectral feature of **4a** is the strong shielding by the σ-bound C5 (-11.0 ppm) to Rh as doublet (J=15.2 Hz) in the ^{13}C NMR spectrum. The protons associated with C5 are also strongly shielded, appearing at δ 0.2 and -0.2 ppm, respectively, in the ^1H NMR spectrum. The ^1H NMR signals for *anti*- and *syn*-H on the allylic C1 of **4a** appear at 2.32 (J=9.6 Hz) and 3.68 ppm (J=7.6 Hz) as doublet. The ^{13}C NMR signals for the allylic three C1, C2, and C3 carbons in **4a** clearly show the characteristic η^3-allyl peaks at 39.4, 110.6 and 47.0 ppm, respectively. Although **3a** is unstable, it also shows the similar spectroscopic data to **4a**.[9] The ^1H NMR chemical shifts for *anti*- and *syn*-H in C1 of **3a** appear at 2.1 (J=10.0 Hz) and 3.7 ppm (J=5.5 Hz) as doublets while those in C-5 appear at 1.6 and 0.4 ppm, respectively. The ^{13}C NMR for **3a** also shows the signals of σ,η^3-allyl metal complex similar to those of **4a**: 102.0 (C2), 44.7 (C3), and 41.0 ppm (C1) for η^3-allyl group and -6.5 ppm as doublet (J=14.9 Hz) for σ-bound C5 to Rh.



(eq. 2)

Addition of strong π-acceptor ligand like trimethylphosphite, trimethylphosphine or 1,2-diphenylphosphinoethane to complex **4a** induced reductive-elimination to give **2a** quantitatively, not **5a** (eq. 2).[10] Common rearrangements of vinylcyclopropanes by transition metals should have given strain-free cyclopentene through the presumed σ,η^3-allyl intermediate[1], but any cyclopentene has not been found. When α-methyl vinylcyclopropane (**2b**) instead of **2a** was applied in this reaction,

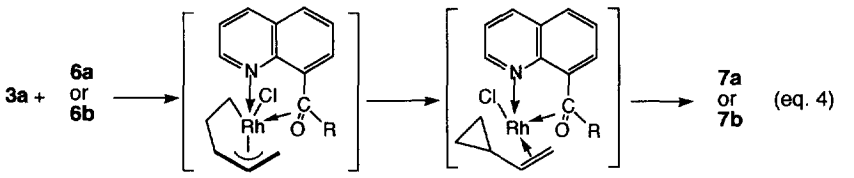


(eq. 3)

the σ,η^3-allyl rhodium complexes, **3b**[9] and **4b**[8], were obtained as expected, and the subsequent ligand-promoted

reductive-elimination of **3b** or **4b** also produced **2b**.

Another interesting feature was that even 8-quinolinyl benzyl ketone (**6a**) induced reductive-elimination of **3a** at 80°C for 1h to generate vinylcyclopropane and a yellow precipitate **7a**, which was solubilized by pyridine-d_5 to form **8a** (eq. 3). Complex **7a** has been already prepared by oxidative addition of C-C bond of **6a** with Rh(I) and characterized as **8a**.[11a] The mechanism of regenerating vinylcyclopropane and C-C bond cleavage of **6a** by **3a** can be explained in eq.4.



9 **10**

A plausible sequence would involve regeneration of vinylcyclopropane from the σ,η^3-allyl rhodium complex in **9**, followed by oxidative addition of the C-C bond of 8-quinolinyl alkyl ketone to the rhodium center.[11] Already we have seen that the strong bidentate coordinating ligand such as 1,2-diphenylphosphinoethane induced the reductive elimination to generate vinylcyclopropane as in eq.2. With reductive elimination of **9**, Rh(III) might be reduced to Rh(I) in **10**. At the intermediate **10**, Rh(I) might undergo oxidative addition to C-C bond of 8-quinolinyl alkyl ketone. The oxidative-addition mechanism of Rh(I) with 8-quinolinyl alkyl ketone has been studied[11] and η^2-carbonyl coordination to Rh is supposed to be the very important key step for the oxidative addition reaction.[12] **4a** was much less reactive for generating vinylcyclopropane than **3a**. With the reaction of **3a** and 8-quinolinyl phenyl ketone (**6b**), 50 % of vinylcyclopropane was formed in 10 min even at room temperature and a yellow complex **7b**, identified as **8b**.[13] However, the reaction of **4a** with **6b** did not generate vinylcyclopropane at room temperature. Instead, more vigorous condition such as 100°C for 1h fulfills the generation of vinylcyclopropane. The reason must be that the coordinated bipyridine in **4a** needed to be replaced by 8-quinolinyl alkyl ketone in order for the σ,η^3-allyl rhodium complexes to undergo reductive elimination.

In conclusion, our results demonstrate the stepwise nature of metal-promoted ring opening/ring closure reaction of vinylcyclopropanes and its application to unstrained C-C bond cleavage. Further studies on the application of σ,η^3-allyl metal complexes to the C-H bond cleavage in 8-quinolinecarboxaldehyde are in progress.

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8. Spectroscopic and elemental analysis data for **4a** and **4b** are as follows. **4a**: mp 207-209°C (decomp.); ^{1}H NMR (200 MHz, $CDCl_3$)δ(ppm) 9.6-7.3 (m, 8H, bipy), 5.1 (q, *J*=9.8 Hz, 1H, H3), 4.20 (m, 1H, H2), 3.7 (d, *J*=7.6 Hz, 1H, *syn*-H1), 2.3 (d, *J*=9.6 Hz, *anti*-H1), 2.2-1.9 (m, 2H, two H4s), 0.2 (br, 1H, one of two H5s), -0.2 (br, 1H, one of two H5s); ^{13}C NMR (50.5 MHz, $CDCl_3$)δ(ppm) 154.8-122.4 (Cs of bipy), 110.6 (d, *J*=6.9 Hz, C2), 47.0 (d, *J*=5.1 Hz, C3), 39.4 (d, *J*=15.2 Hz, C1), 27.6 (C4), -10.9 (d, *J*=15.2, C5); IR spectrum (KBr) 3050, 3030, 3010, 2945, 1590, 1460, 1435, 1305, 1145, 770, 730 cm^{-1}; Anal. Calcd for $C_{15}H_{16}N_2ClRh$: C, 49.68; H, 4.44; N, 7.72. Found: C, 49.20; H, 4.13; N, 7.60 %.
4b: ^{1}H NMR (200 MHz, $CDCl_3$)δ(ppm) 9.6-7.3 (m, 8H, bipy), 3.9 (d, *J*=5.3 Hz, 1H, H3), 3.5 (s, 1H, *syn*-H1), 2.4 (s, 1H, *anti*-H1), 2.3-2.1 (m, 2H, two H4s), 1.9 (s, 3H, CH_3), 0.3 (br, 1H, one of two H5s), -0.9 (br, 1H, one of two H5s); ^{13}C NMR (50.5 MHz, $CDCl_3$)δ(ppm) 154.8-122.2 (Cs of bipy), 46.2 (d, *J*=5.0 Hz, C3), 40.6 (d, *J*=14.6 Hz, C1), 28.6 (C4), 24.5 (s, CH_3), -9.6 (d, *J*=16.4 Hz, C-5); IR spectrum (KBr) 3025, 2894, 2834, 1598, 1467, 1445, 1309, 1245, 1159, 1032, 869, 770, 732 cm^{-1}; Anal. Calcd for $C_{16}H_{18}N_2ClRh$: C, 51.02; H, 4.82; N, 7.44. Found: C, 50.56; H, 4.91; N, 7.61 %.
9. The intermediate σ,η^3-allyl rhodium complexes, **3a** and **3b** in $CDCl_3$ decomposed slowly to 1,3-pentadiene within 24h. The ^{1}H and ^{13}C NMR data for **3a** and **3b** were closely matched to those reported in ref. 5. **3a**: ^{1}H NMR (200 MHz, $CDCl_3$)δ(ppm) 4.2 (br, 1H, H3), 4.2 (m, 1H, H2), 3.7 (d, *J*=5.5 Hz, 1H, *syn*-H1), 2.1 (d, *J*=10.0 Hz, *anti*-H1), 2.2 (br, 1H, one of two H-4s), 1.8 (br, 1H, one of two H4s), 1.6 (br, 1H, one of two H5s), 0.4 (br, 1H, one of two H5s); ^{13}C NMR (50.5 MHz, $CDCl_3$)δ(ppm) 102.6 (d, *J*=8.4 Hz, C2), 44.7 (br, C3), 41.0 (d, *J*=16.3 Hz, C1), 28.6 (C4), -6.6 (d, *J*=14.9, C5).
3b: ^{1}H NMR (200 MHz, $CDCl_3$)δ(ppm) 3.8 (br, 1H, H-3), 3.5 (s, 1H, *syn*-H1), 2.0 (s, 1H, *anti*-H1), 2.2 (br, 1H, one of two H4s), 1.9 (br, 1H, one of two H4s), 1.8 (s, 3H, CH_3), 1.7 (br, 1H, one of two H5s), 0.6 (br, 1H, one of two H5s); ^{13}C NMR (50.5 MHz, $CDCl_3$)δ(ppm) 114.5 (C2), 43.4 (C3), 41.4 (d, *J*=16.8 Hz, C1), 29.2 (C4), 23.4 (s, CH_3), -6.3 (d, *J*=15.3 Hz, C5);
10. Just after addition of more than 3 equivalents of $P(OCD_3)_3$ to **4a** or **3a** in $CDCl_3$ at room temperature, the ^{1}H NMR spectra show only the signals of vinylcyclopropane. When $P(OMe)_3$, PMe_3 or diphenylphosphinoethane were applied instead of $P(OCD_3)_3$, similar results were obtained in the ^{1}H NMR spectra.
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13. The reaction was continued for 24h for completion and complex **7b** was obtained with addition of pentane.
8b: ^{1}H NMR (200 MHz, $CDCl_3$)δ(ppm) 10.6 (d, 1H, quinoline C2), 8.4-7.3 (m, 5H, quinoline ring), 7.1-6.7 (m, 5H, Ph);
7b: IR spectrum (nujol) 1639, 1565, 1372, 1240, 1010, 900, 833, 778 cm^{-1}; Anal. Calcd for $C_{16}H_{11}ClNORh$: C, 51.68; H, 2.96; N, 3.77. Found: C, 51.58; H, 3.20; N, 3.82 %.

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