

Figure 2. TPD profiles of the bases on γ -alumina(a) and γ -alumina modified with 5 wt% F(b). Temperature programming rate was 8 K/min and adsorbed amount of the bases were about 5×10^{-6} mole/0.5 g sample.

212213, 212221, 212223, 212311, 212313, 212321, and 212323, where site 111112 represents the site corresponding to peak 1 of pyridine, peak 1 of triethylamine, peak 1 of 1,4-dioxane, peak 1 of 2-propanone, peak 1 of tetrahydrothiophene, and peak 2 of thiobismethane. The values of the parameters, and the coefficient of determination R^2 ($R^2 = \text{SSR}/\text{SST}$) with respect to the groups of bases for typical sites are listed in Table 1.

In some cases, the estimated parameters are negative or R^2 's are much less than 1. The results can be explained as the peaks are mismatched or the encountering bases are not suitable for the model equation. We found that the set of cyclic bases showed reasonable values for the parameters and a good statistical reliability. It is also expected that the cyclic bases show an excellent measuring power for the parameters since they have the similar structure, different donor atoms and a wide range of the values of the parameters, i.e., pyridine ($C/E = 6.40/1.17$), 1,4-dioxane ($C/E = 2.38/1.09$) and tetrahydrothiophene ($C/E = 7.90/0.341$). Comparing TPD peaks of the bases adsorbed on the alumina and alumina modified with ammonium fluoride (Figure 2), it can be concluded that the alumina has two acid sites corresponding to the $E-C$ parameters, 19.0, 2.5 (Site $1 \times 1 \times 1 \times$); 23.8, 4.2 (Site $2 \times 2 \times 2 \times$) with standard errors, 3.5, 0.6; 4.5, 0.7, respectively.

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2. V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions", Plenum Press, New York/London, p. 4, 1978.
3. A good catalyst is thought to be able to form chemical bonds of appropriate strength with reactant(s). W. M. H. Sachtler and J. Fahrenfort, J. Actes du Deuxieme Congres International de Catalyse, p. 831, 1960.
4. By the relation, enthalpies of adduct formation, ΔH , have been described in the form, $-\Delta H = E_A E_B + C_A C_B$ where E_A and E_B crudely relate to tendencies of acids and bases, respectively, to undergo electrostatic bonding and C_A and C_B are similar tendencies to undergo covalent bonding. R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).
5. γ -Alumina was obtained from $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ (Aldrich, 99.999%) and calcined at 873 K. Its surface area was 50 m^2/g . γ -Alumina modified with chlorine or fluorine was prepared by treatment the alumina with NH_4Cl or NH_4F solution and calcination at 873 K.
6. In fact, the peak position of TPD profiles may depend on the adsorbed amount of bases and the experiment was performed with small amounts of adsorbed bases where the peak temperatures do not change with a further reduction of the amount of adsorbed bases.
7. P. A. Redhead, *Vacuum* **12**, 203 (1962). R. J. Cvetanovic and Y. Amenomiya, *Advan. Catal.* **17**, 103 (1967).
8. The activation energy of desorption for a chemisorbed state is generally greater than 20 kcal/mole. J. M. Thomas and W. J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis", p. 15, Academic Press, New York/London, 1967. 50 kcal/mole is the maximum activation energy of desorption which can be measured in the system since γ -alumina transforms to α -alumina from 873 K. The desorbed gas was checked with a coupled FTIR during the desorption and the decomposition was negligible below 720 K for the aluminas.

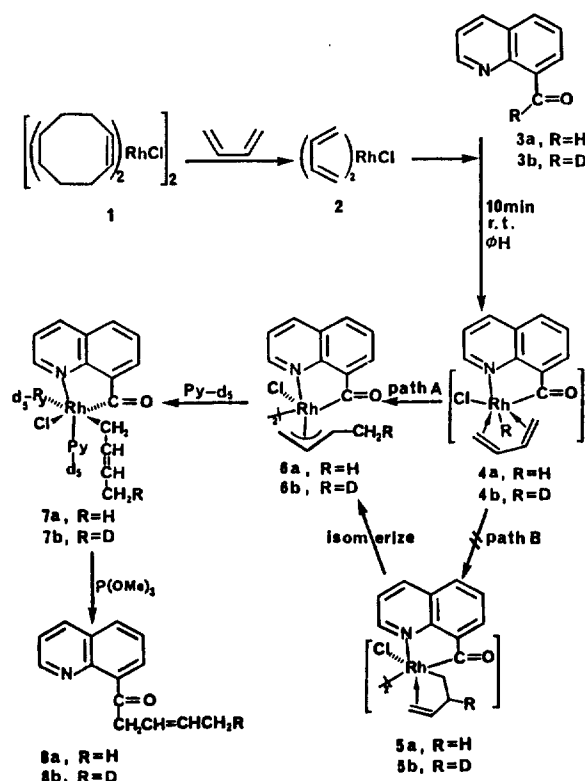
C-H Bond Activation and the Hydride-Mediated Ring-Cleavage of Methylene-cyclopropane by Rh(I)

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The activation of C-H bond¹ and C-C bond² by transition metal complexes has been one of the recent interests in organometallic chemistry. The C-H bond of aromatic aldehyde can be activated by transition metals to give cyclometallated complexes without producing any decarbonylated product³.

This C-H bond activation was applied to the synthesis of β, γ -unsaturated ketones through the η^1 - or η^3 -allylrhodium (III) complexes⁴. Recently we have studied the metal-hydride mediated C-C bond cleavage of the medium-strained ring compound having cyclobutyl group⁵. Although it is

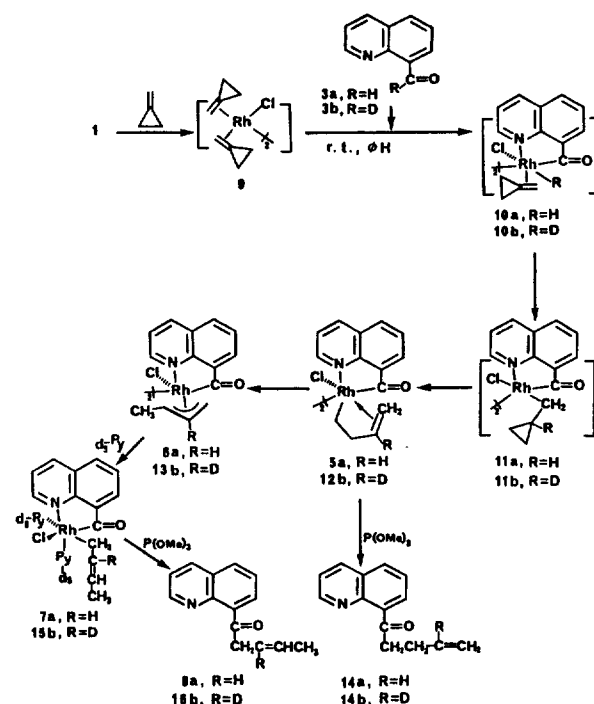


Scheme 1. Hydride (Deuteride) Insertion into Coordinated Butadiene

facile to incorporate deuteriums into the α -methylene group of alkyl ketones by deuterium-exchange reaction under acidic or basic conditions⁶, it is not easy to incorporate a deuterium into the other positions of the alkenyl group. Herein we report the selective deuteration on the alkenyl group and the possible isomerization mechanism of the metal bound alkenyl group.

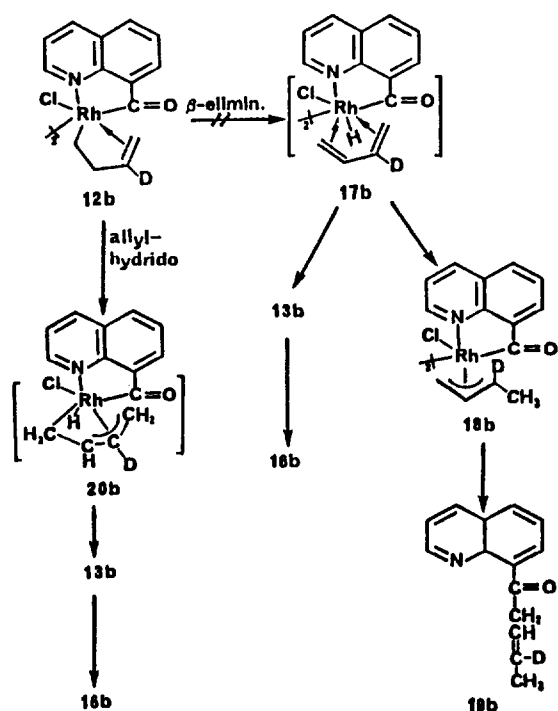
It has been reported that β,γ -unsaturated ketones **8a** was synthesized through acylrhodium(III)- η^3 -1-methylallyl complex **6a** formed by C-H bond activation (Scheme 1)⁴. There are two possible routes (path A and path B) to form **6a**. A direct hydride-insertion into a 1-position of the coordinated butadiene leads to **6a** (path A) while a hydride attack into a 2-position of butadiene forms **5a**, followed by the olefin-isomerization to give **6a** (path B). When **3b** was used as a substrate instead of **3a**, the deuterium was incorporated into the methyl group in **6b**. Ligand-promoted reductive-elimination⁷ of η^5 -alkenyl complex **7b** formed by treatment of **6b** with excess pyridine- d_5 (20 equivalents) gave **8b** exclusively in 93% yield. **8b**; ¹H NMR (80 MHz, CDCl₃) δ (ppm) 1.65 (br s, 2H, CH₂D), 4.1 (d, 2H, CH₂), 5.65 (m, 2H, -CH=CH-), 7.3-8.3 (m, 5H, quinoline ring protons), 8.95 (dd, 1H, quinoline C-2 proton); IR (neat) 3020, 2910, 1675, 1565, 1490, 1275, 960, 830, 790 cm⁻¹; Mass Spectrum: m/e (assignment, relative intensity) 212 (M⁺, 12), 211 (M⁺-1, 8), 156 (quinolinylCO⁺, 100), 128 (quinolinyl⁺, 42). The deuterium resides in the methyl group without scrambling the olefinic positions in **8b**. This result supports the mechanism of path A. Path B should have led to scrambling the deuterium of the methyl group with the allylic protons in **6b** and olefinic ones in **8b**.

Methylenecyclopropane⁸ is a good candidate as a synthon for butadiene since both have the identical molecular for-



Scheme 2. Hydride (Deuteride) Mediated Ring-Cleavage of Methylenecyclopropane

mula, C₄H₆, and the reaction of methylenecyclopropane derivatives and certain metals undergoes ring-opening to give butadiene derivatives⁹. Complex **9** was prepared *in situ* by the reaction of **1** and methylenecyclopropane in ether at room temperature for 5 min (Scheme 2). Strained olefins have a tendency to form rather stable metal complexes due to partial strain relief upon complexation¹⁰. The synthesis of a number of η^2 -methylenecyclopropane derivatives of Ir(I), Rh(I), Pt(0) and Pt(II) have been reported¹¹. Compound **3a** reacted with a solution of **9** in ether at room temperature for 1.5 min to give a chlorine-bridged dimer which is supposed to be **5a**. Treatment of **5a** with trimethylphosphite underwent reductive-elimination to give **14a** in 51% yield: ¹NMR (80 MHz, CDCl₃) δ (ppm) 2.55 (br q, 2H, -CH₂-), 3.35 (t, 2H, COCH₂), 5.0 (tm, 2H, CH₂=CH-), 5.7 (m, 1H, -CH=), 7.3-8.3 (m, 5H, quinoline ring protons), 8.9 (dd, 1H, quinoline C-2 proton); IR (neat) 3070, 2905, 1680, 1590, 1565, 1270, 990, 910, 830, 790 cm⁻¹; Mass Spectrum: m/e (assignment, relative intensity) 211 (M⁺, 9), 210 (M⁺-1, 13), 183 (36), 170 (quinolinyl COCH₂⁺, 43), 156 (quinolinyl CO⁺, 100), 129 (quinoline⁺, 79), 128 (quinolinyl⁺, 67). The reaction was carried out by using **3b** as a substrate, the deuterium resided only in the C-3 carbon of the but-3-enyl group in **14b**: ¹H NMR (80 MHz, CDCl₃) δ (ppm) 2.55 (br t, 2H, -CH₂-CH=), 3.46 (t, 2H, COCH₂), 5.0 (br s, 2H, CH₂=), 7.3-8.3 (m, quinoline ring protons), 8.9 (dd, 1H, quinoline C-2 proton); IR (neat) 3070, 2910, 1680, 1590, 1565, 1270, 960, 910, 830, 790 cm⁻¹; Mass Spectrum: m/e (assignment, relative intensity) 212 (M⁺, 8), 211 (M⁺-1, 10), 184 (32), 170 (quinolinyl COCH₂⁺, 40), 156 (quinolinyl CO⁺, 100), 129 (quinoline⁺, 66), 128 (quinolinyl⁺, 60). Complex **11a** is postulated as an intermediate in this ring opening reaction¹². Addition of methylenecyclopropane to the Rh-H bond of **10a** formed by C-H bond activation of **3a** followed by intramolecular olefin insertion affords the cyclo-



Scheme 3. Possible Isomerization Mechanism of the Alkenyl Group to the Allyl Group

propylcarbonylrhodium(III) intermediate 11a. Since a vacant coordination site in addition to ring strain of cyclopropyl group is generated in 11a which is a 16-electron Rh(III) species, β -alkyl elimination becomes very facile to form 5a, a stable 18-electron species¹³.

On a longer reaction time (1 hr), complex 5a initially formed isomerized to complex 6a. This is also supported by the observation that only 8a was isolated in 71% yield by trimethylphosphite after 1 hr reaction. In the isomerization of 12b to 13b, the deuterium resides only in the C-2 carbon of the allylic group in 13b. Addition of excess pyridine- d_5 to 13b gave 15b in which two diastereotopic protons of α -methylene group appear at 2.4 and 3.1 ppm as broad doublet. None has been incorporated in the other positions. Reductive-elimination of 15b with trimethylphosphite gave 16b: ^1H NMR (80 MHz, CDCl_3) δ (ppm) 1.7(d, 3H, CH_3), 4.1(s, 2H, COCH_2), 5.6(br m, 1H, $-\text{CH}=\text{CD}-$), 7.3–8.3(m, 5H, quinoline ring protons), 8.9 (dd, 1H, quinoline C-2 proton); Mass Spectrum; m/e (assignment, relative intensity) 212(M^+ , 10), 211($m^+ - 1.7$), 156(quinolinyl CO^+ , 100), 128(quinolinyl $^+$, 40). There are two major possible mechanisms to explain the isomerization of 12b to 13b (Scheme 3). The first one is the hydride addition-elimination mechanism. The β -hydride elimination (the hydride addition-elimination) is the most important mechanism for the metal catalyzed olefin isomerization. However it seems not likely involved since two η^3 -allylrhodium(III) complexes, 13b and 18b, should have been formed simultaneously *via* an intermediate 17b formed by β -hydride elimination of 12b. Neither 18b nor 19b was observed in the whole reaction process. The second possible mechanism involves π -allyl hydrido intermediate. Transfer of a hydrogen of C-2 to the metal gives a π -allylrhodium

hydride, 20b. The metal-bound hydrogen and C-1 carbon may be reductive-eliminated to give 13b. This kind of π -allyl metal hydrido mechanism has been observed in diene isomerization by $\text{Rh}^{14b,c}$ and double bond migration by $\text{Fe}_3(\text{CO})_{12}$ or $\text{PdCl}_2(\text{NCPH})_2$ ^{14d}. Although it is not clear how much hydride character is involved in the transition state, this seems to be the most probable mechanism. Also there is a possibility to form π -allyl complex *via* 1,2-hydride shift without generating a hydride. Agostic bond interaction in organometallic complexes has been observed in the transition state in C-H bond activation of β -elimination^{15a}. There is much evidence for three center interaction between metal and a β -C-H^{15b}. Therefore we cannot exclude this mechanism either. More detailed isomerization mechanism for the alkenyl complexes is under investigation.

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