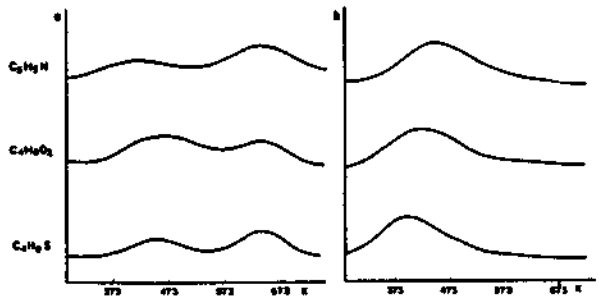

Figure 2. TPD profiles of the bases on γ-alumina(a) and γ-alumina modified with 5 wt% F(b). Temperature programming rate was 8 K/min and adsorbed amount of the bases were about 5×10^{-6} mole/0.5 g sample.

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 = SSR/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 encounting 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 1×1×1×); 23.8, 4.2 (Site 2×2×2×) with standard errors, 3.5, 0.6; 4.5, 0.7, respectively.

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5. γ-Alumina was obtained from $Al(NO_3)_3 \cdot 9\ H_2O$ (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.
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C-H Bond Activation and the Hydride-Mediated Ring-Cleavage of Methylenecyclopropane by Rh(I)

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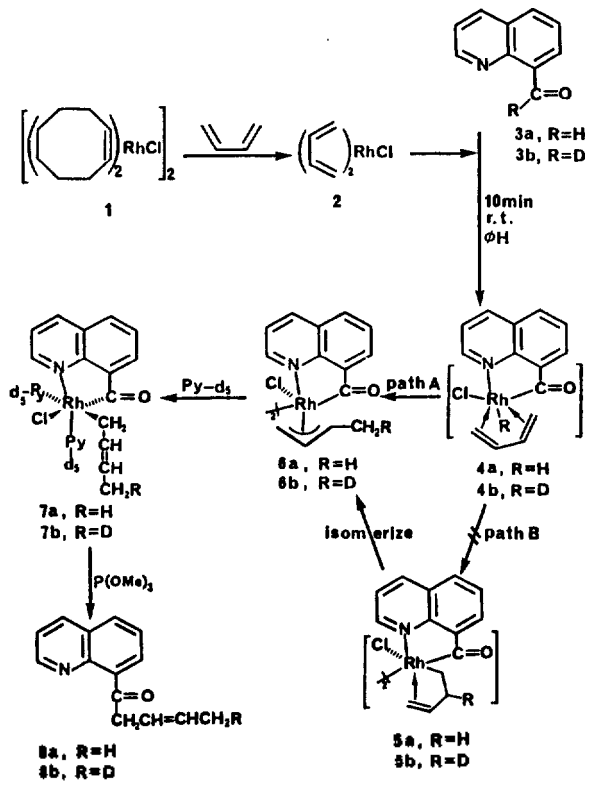
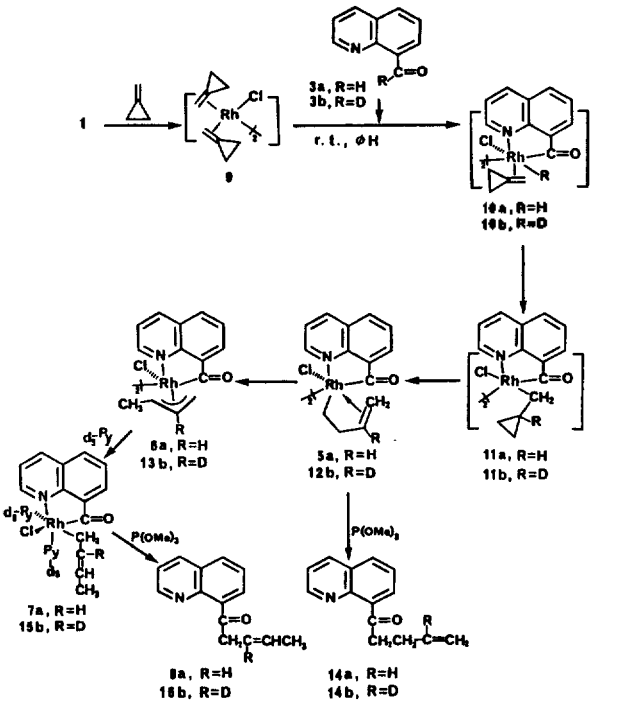
The activation of C-H bond[1] and C-C bond[2] by transition metal complexes has been one of the recent interests in organometallic chemistry. The C-H bond of aromatic aldehyde can be activated by transition metals to give cyclometallated complexes without producing any decarbonylated product[3]. This C-H bond activation was applied to the synthesis of β,γ-unsaturated ketones through the η^1- or η^3-allylrhodium (III) complexes[4]. Recently we have studied the metal-hydride mediated C-C bond cleavage of the medium-strained ring compound having cyclobutyl group[5]. Although it is



Scheme 1. Hydride (Deuteride) Insertion into Coordinated Butadiene

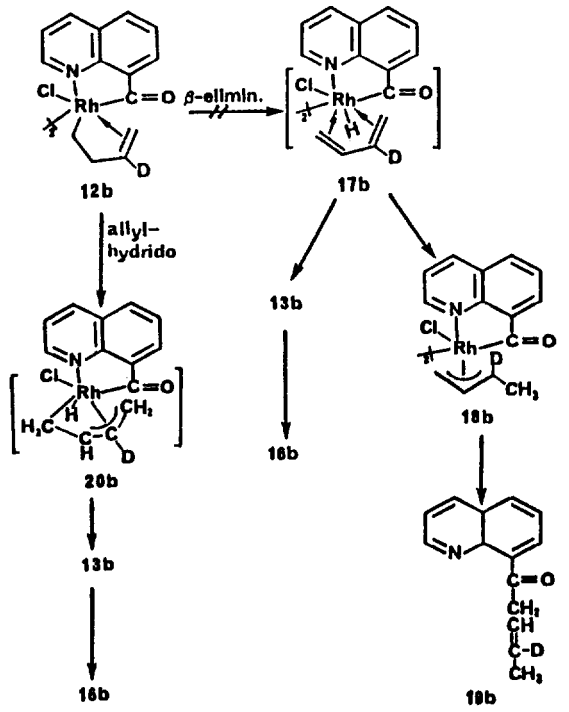


Scheme 2. Hydride (Deuteride) Mediated Ring-Cleavage of Methylenecyclopropane

facile to incorporate deuteriums into the α-methylene group of alkyl ketones by deuterium-exchange reaction under acidic or basic conditions[6], 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-methylally 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-elimination[7] of η'-alkenyl complex 7b formed by treatment of 6b with excess pyridine-d_5 (20 equivalents) gave 8b exclusively in 93% yield. 8b; ^{1}H NMR (80 MHz, $CDCl_3$) δ(ppm) 1.65 (br, s, 2H, CH_2D), 4.1 (d, 2H, CH_2), 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.

Methylenecycloprpane[8] is a good candidate as a synthon for butadiene since both have the identical molecular formula, C_4H_6, and the reaction of methylenecyclopropane derivatives and certain metals undergoes ring-opening to give butadiene derivatives[9]. 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 complexation[10]. The synthesis of a number of η^2-methylenecyclopropane derivatives of Ir(I), Rh(I), Pt(O) and Pt(II) have been reported[11]. 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: ^{1}NMR (80 MHz. $CDCl_3$) δ(ppm) 2.55 (br q, 2H,-CH_2-), 3.35 (t, 2H, $COCH_2$), 5.0 (tm, 2H, CH_2=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 $COCH_2^+$, 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: ^{1}H NMR (80 MHz, $CDCl_3$) δ(ppm) 2.55 (br t, 2H, -CH_2-CH=), 3.46 (t, 2H, $COCH_2$), 5.0 (br s, 2H, CH_2=), 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 $COCH_2^+$, 40), 156 (quinolinyl CO^+, 100), 129 (quinoline$^+$, 66), 128 (quinolinyl$^+$, 60). Complex 11a is postulated as an intermediate in this ring opening reaction[12]. 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

propylcarbinylrhodium(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-electrion species[13].

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 resisdes 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: ^{1}H NMR (80 MHz, $CDCl_3$) δ (ppm) 1.7(d, 3H, CH_3-). 4.1(s, 2H, $COCH_2$-), 5.6(br m, 1H, -CH=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 catalized olefin isomerization. However it seems not likely involved since tw 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. Tiis kine of π-allylmetal hydrido mechanism has been observed in diene isomerization by Rh[14b,c] and double bond migration by $Fe_3(CO)_{12}$ or $PdCl_2(NCPh)_2$[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. Agosic 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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