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14. All compounds were isolated and fully characterized by spectroscopic methods. For example: Compound **13** ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67 (d, 2H, *J*=8.06), 7.35 (d, 2H, *J*=8.06), 6.05 (s, 2H), 5.05 (t, 1H), 3.90 (dd, 1H, *J*=11.6, 4.2), 2.98 (ABq, 1H, *J*=15.5, 11.6), 2.75 (ABq, 1H, *J*=15.5, 4.2), 2.66 (m, 1H), 2.45 (s, 3H), 2.10 (s, 3H), 1.62 (s, 3H), 1.55 (m, 4H), 1.28 (s, 3H), 1.18 (s, 3H); exact mass calcd for $C_{24}H_{30}SO_5$ (M+1) 430.562, Obsd 430.560.

Chelation-Assisted Olefin-Isomerization and C-N Bond Cleavage by Rh(I)

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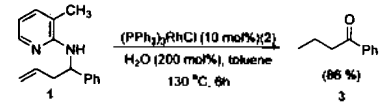
Double bond migration is one of the most extensively studied transition metal catalytic reactions. While many examples are focused on the conversion of 1-alkene into the more stable *trans*-2-alkene by a transition metal catalyst with a single movement of the double bond,[1] multiple double bond migration has been less explored in spite of its usefulness. Facile olefin-isomerization has been achieved with functionalized olefins including allylamine,[2] allyl alcohol[3] and allyl ether[4] by transition metal catalysts. Transition-metal can activate the allylic C-H bonds through coordination of an adjacent heteroatom, and a subsequent hydride transfer to the olefin completes the double bond migration. Therefore, studies of the useful double bond migrations have centered on the allylic olefin, not on the homoallylic olefin. The introduction of a pertinent auxiliary may provide an effective method for the multiple double-bond migration. The silyl group was used for this purpose, but not successful.[5] The pyridyl group should be a promising candidate since it is used as a good directing group in many C-H bond activation reactions.[6] In the present study, we explain the development of a model system that would undergo multiple double bond migrations into imine, which could be hydrolyzed to produce ketones.

(3-Methyl-2-pyridyl)-N-(1-phenyl-3-butenyl)amine (**1**)[7] reacted with H_2O at 130 °C for 6 h under a catalytic amount (10 mol%) of tris(triphenylphosphine)rhodium(I) chloride (**2**) to give butanophenone (**3**) in 86% isolated



(1)

yield after chromatographic isolation.

The reaction mechanism is believed to be that **1** is isomerized to imine **4**, which is hydrolyzed by adding H_2O to produce **3**. In this double bond migration, the pyridyl group in **1** was the important auxiliary, since **3** was not isolated when **5**[8] with no coordination site was used in place of **1**. The first step of this double bond migration must be precoordination of the rhodium catalyst to the nitrogen atom in the pyridyl group. Then, multiple double-bond migration continues until imine is formed. The generated imine might form metal complex **6**.

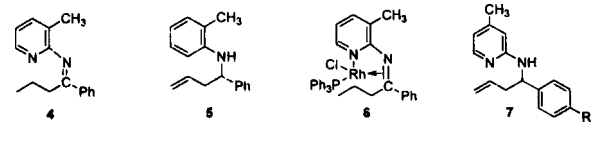


Table 1. Catalytic Reaction of **7** and H_2O by 5 mol% of Complex **2**[a]

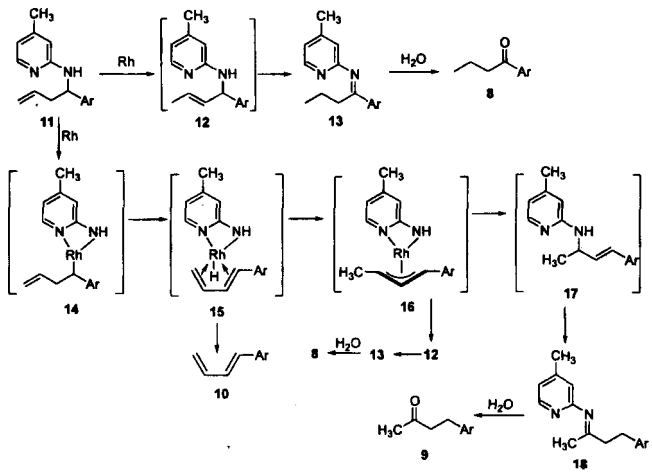
Entry	Reactant 7 (R)	Product (Isolated yield)
1	—H (7a)	3 (76 %)[b]
2	—CH_3 (7b)	8b (87 %)
3	—Ph (7c)	8c (90 %)
4	—CF_3 (7d)	8d (67 %)[c]
5	—OCH_3 (7e)	8e (64 %), 9e (8 %), 10e (4 %)
6	—$N(CH_3)_2$ (7f)	8f (13 %), 9f (34 %), 10f (32 %)

[a] The reaction was carried out with **7** and 200 mol% of H_2O by 5 mol% of **2** at 130 °C for 6h. [b] 9% of ketimine is included. An additional 6% of the single double-bond migration product of **7a** was detected by GC-MSD. [c] An additional 10% of the single double-bond migrated product of **7d** was detected by GC-MSD.

Generating the stable metal complex **6** must be a driving force for this multiple double bond migration. The multiple double bond migration of methyl oleate by a stoichiometric amount of iron carbonyl complex has been reported. The driving force for the double bond migration in this reaction can be explained as the formation of the stable α,β-unsaturated ketone-iron carbonyl complex.[9] Complex **6** could be hydrolyzed by H_2O to give ketone **3** with the regeneration of the rhodium complex, making the catalytic reaction. The reaction was carried out with a modified model system **7** with various substituents (R) under 5 mol% of **2** at 130 °C for 6 h (Table 1).[10]

Amines bearing electron-donating substituents in phenyl group such as a methyl and a phenyl group (entry 2 and 3) underwent more facile double bond migration compared with ones with electron-withdrawing substituents such as trifluoromethyl group (entry 4). When the reaction was carried out with **7e**, a mixture of **8e**, **9e** and **10e** was isolated in 64%, 8%, and 4% yield, respectively (entry 5). For **7f** bearing dimethylamino group, the strong electron-donating substituent, 34% yield of **9f** and 32% yield of **10f** were also isolated along with 13% yield of **8f**. The formation mechanism of **9** and **10** can be explained in Scheme 1.

The initial step of the formation of **9** and **10** must be C-N bond cleavage in **11** by Rh(I) to generate **14**. Intermediate **14** must be isomerized to π-allyl rhodium(III) complex **16** through **15** formed from β-elimination of **14**. Two possible reductive elimination processes are available from complex **16**. One produces **12**, which is further isomerized and hydrolyzed into **8**, the identical process of the direct isomerization of **11** to **13**. The other one forms **17**, which is also olefin-isomerized further into **18**. Hydrolysis of **18** produces **9** as a final product. The key process for this isomerization is β-elimination in **14** to generate **15**, which is confirmed by the formation of **10** (**10e** for **7e** and **10f** for **7f**). Some of **10** may be liberated from **15**. Formation of π-allyl metal complexes from a hydride addition



Scheme 1.

into the conjugate diene and a ligand-promoted reductive-elimination of the resulting π-allyl complexes to β,γ-unsaturated ketone have been reported with a model compound.[11] Compound **11** carried out two competing processes by **2**: a multiple double bond migration and a C-N bond cleavage by Rh(I). The major catalytic process is a olefin-isomerization process to produce **8** (Table 1, entry 1-4). The strong electron-donating substituents in phenyl group may accelerate the C-N bond cleavage to produce a mixture of **9** and **10** (entry 5 and 6). At this moment, it is not clear whether **8** is formed through the intermediate **16** or through direct isomerization of **11** into **13**.

In conclusion, this report deals with double-bond migration catalyzed by a transition metal with suitably designed model compounds. Depending on the substrates bearing electron-donating substituent or electron-withdrawing substituent, a double bond migration and a C-N bond cleavage compete each other. More detailed mechanistic studies are underway.

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7. **1**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*=3.8 Hz, 1H), 7.4-6.4 (m, 7H), 5.7 (m, 1H), 5.3 (q, *J*=6.8 Hz, 1H), 5.1 (m, 2H), 4.5 (d, *J*=6.8 Hz, 1H), 2.7 (m, 2H), 2.1 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 155.8-133.0 (Cs in pyridyl and phenyl), 134.7, 117.7, 53.2, 41.5, 16.7; IR (neat) 3452 (NH), 3082, 3050, 2929, 2373, 1600, 1495, 1423, 1334, 1004, 932; Mass (70 eV) m/z 238 (3) [M$^+$], 197 (100), 108 (6), 92 (23); HRMS calcd for $C_{16}H_{18}N_2$ 238.146999, found 238.147025.
8. **5**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.4-6.3 (m, 9H), 5.8 (m, 1H), 5.2 (m, 2H), 4.4 (q, *J*=4.9 Hz, 1H), 4.1 (d, *J*=6.8 Hz, 1H), 2.6 (m, 2H), 2.2 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 145.0-111.0 (Cs in phenyls), 134.7, 118.1, 56.7, 43.4, 17.3; IR (neat) 3435 (NH), 3076, 3032, 2981, 2856, 1600, 1514, 1455, 1323, 1055, 914; Mass (70 eV) m/z 237 (4) [M$^+$], 196 (100), 118 (14), 91 (32); HRMS calcd for $C_{17}H_{19}N$ 237.151750, found 237.151680.
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10. **7a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*=5.0 Hz, 1H), 7.3-6.0 (m, 7H), 5.7 (m, 1H), 5.1 (m, 3H), 4.6 (q, *J*=5.0 Hz, 1H) 2.6 (m, 2H), 2.1 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 158.2-106.8 (Cs in pyridyl and phenyl), 134.0, 118.2, 55.4, 42.5, 21.0; IR (neat) 3411 (NH), 3247, 3077, 3029, 2920, 1611, 1568, 1502, 1447, 1356, 1181, 1095, 926; Mass (70 eV) m/z 238 (1) [M$^+$], 197 (100), 108 (2), 92 (19); HRMS calcd for $C_{16}H_{18}N_2$ 238.146999, found 238.147430. **7b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*=5.0 Hz, 1H), 7.3-6.0 (m, 6H), 5.7 (m, 1H), 5.1 (m, 2H), 5.0 (d, *J*=6.0 Hz, 1H), 4.6 (q, *J*=6.3 Hz, 1H), 2.6 (m, 2H), 2.3 (s, 3H), 2.1 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 158.2-106.7 (Cs in pyridyl and phenyl), 134.1, 117.8, 55.0, 42.4, 20.9, 21.0; IR (neat) 3411 (NH), 3253, 3078, 3011, 2926, 1611, 1520, 1489, 1314, 1181, 920; Mass (70 eV) m/z 252 (1) [M$^+$], 211 (100), 105 (4), 92 (21); HRMS calcd for $C_{17}H_{20}N_2$ 252.162649, found 252.162624. **7c**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*=5.0 Hz, 1H), 7.6-6.0 (m, 11H), 5.7 (m, 1H), 5.1 (m, 3H), 4.7 (q, *J*=6.5 Hz, 1H), 2.6 (m, 2H), 2.1 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm)158.2-107.0 (Cs in pyridyl and biphenyl), 134.1, 118.6, 55.1, 42.6, 21.2; IR (neat) 3405 (NH), 3265, 3076, 2917, 1620, 1570, 1487, 1449, 1317, 1190, 1095, 917; Mass (70 eV) m/z 314 (1) [M$^+$], 273 (100), 136 (8), 92 (30); HRMS calcd for $C_{28}H_{26}N_2$ 314.178299, found 314.178064. **7d**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*=5.0 Hz, 1H), 7.6-6.0 (m, 6H), 5.7 (m, 1H), 5.1 (m, 2H), 5.0 (d, *J*=5.8 Hz, 1H), 4.7 (q, *J*=6.3 Hz, 1H), 2.6 (m, 2H), 2.1 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 157.9-107.0 (Cs in pyridyl and phenyl), 133.4, 129.0 (q, CF_3), 118.7, 55.0, 42.2, 20.9; IR (neat) 3414 (NH), 3256, 3079, 2927, 1611, 1571, 1485, 1335, 1130, 920; Mass (70 eV) m/z 306 (3) [M$^+$], 265 (100), 108 (4), 92 (21); HRMS calcd for $C_{17}H_{17}N_2F_3$ 306.134383, found 306.134155. **7e**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*=5.1 Hz, 1H), 7.3-6.0 (m, 6H), 5.7 (m, 1H), 5.1 (m, 2H), 5.0 (d, *J*=5.9 Hz, 1H), 4.6 (q, *J*=6.4 Hz, 1H), 3.8 (s, 3H), 2.5 (m, 2H), 2.1 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 158.3-106.8 (Cs in pyridyl and phenyl), 134.1, 118.0, 54.9, 54.8, 42.5, 21.0; IR (neat) 3414 (NH), 3263, 3079, 2940, 1616, 1511, 1456, 1304, 1178, 1038, 924; Mass (70 eV) m/z 268 (1) [M$^+$], 227 (100), 119 (14), 92 (45); HRMS calcd for $C_{17}H_{20}N_2O$ 268.157563, found 268.157661. **7f**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*=5.2 Hz, 1H), 7.2-6.0 (m, 6H), 5.7 (m, 1H), 5.1 (m, 3H), 4.6 (q, *J*=6.4 Hz, 1H), 2.9 (s, 6H), 2.5 (m, 2H), 2.1 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm) 158.4-106.8 (Cs in pyridyl and phenyl), 134.5, 117.9, 54.9, 42.6, 40.5, 21.1; IR (neat) 3409 (NH), 3253, 3078, 2980, 1617, 1448, 1227, 1182, 955; Mass (70 eV) m/z 281 (1) [M$^+$], 240 (40), 173 (100), 108 (58); HRMS calcd for $C_{18}H_{23}N_3$ 281.189198, found 281.189286.
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