Catalytic Carbon-Nitrogen Bond Cleavage by Rh(I)

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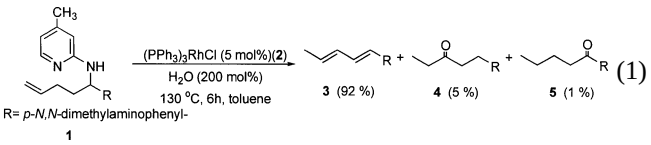
Carbon-nitrogen bond cleavage by transition metal complexes has been one of the recent developments in organometallic chemistry[1]. Recently we found the chelation-assisted olefin-isomerization in homoallylamine model systems.[2] In these homoallylamine model systems, the carbon-nitrogen bond cleavage as well as olefin-isomerization has been found depending on the substituent. It seems likely that an electron-donating substituent near the carbon-nitrogen bond facilitates the carbon-nitrogen bond cleavage before olefin-isomerization, while an electron-withdrawing substituent resists carbon-nitrogen bond cleavage. The homoallylamine bearing no electron-donating substituent undergoes olefin-isomerization to afford imine, which is readily hydrolyzed to give ketone. In the present study, we have found the limitation of the carbon-nitrogen bond cleavage in chelation-assisted model systems by changing the length of carbon tether between olefin and the amino group.

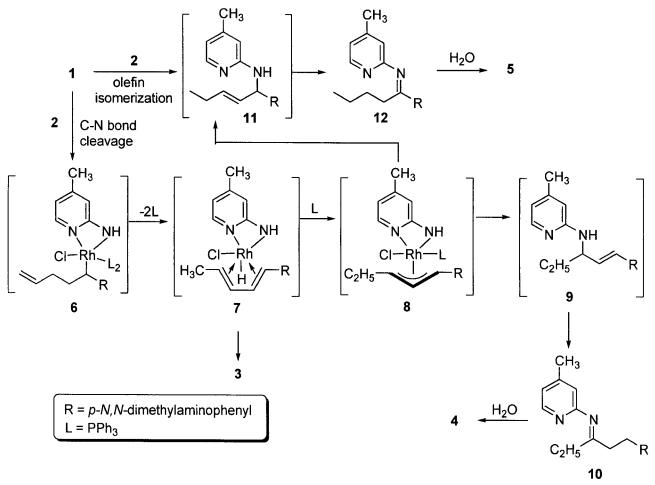
4-Pentenylamine, (4-Methyl-2-pyridyl)-*N*-{1-(4-*N*,*N*-dimethylaminophenyl)-4-pentenyl}amine (**1**)[3], reacted with H_2O (200 mol%) at 130 °C for 6 h under a catalytic amount (5 mol%) of tris(triphenylphosphine)rhodium(I)chloride (**2**) to give mixtures of 1-(4-*N*,*N*-dimethylaminophenyl)-1,3-pentadiene (**3**) and 1-(4-*N*,*N*-dimethylamino phenyl)-3-pentanone (**4**) in 92% and 5% yields along with a trace amount (1%) of 4-*N*,*N*-dimethylaminophenyl butyl ketone (**5**).



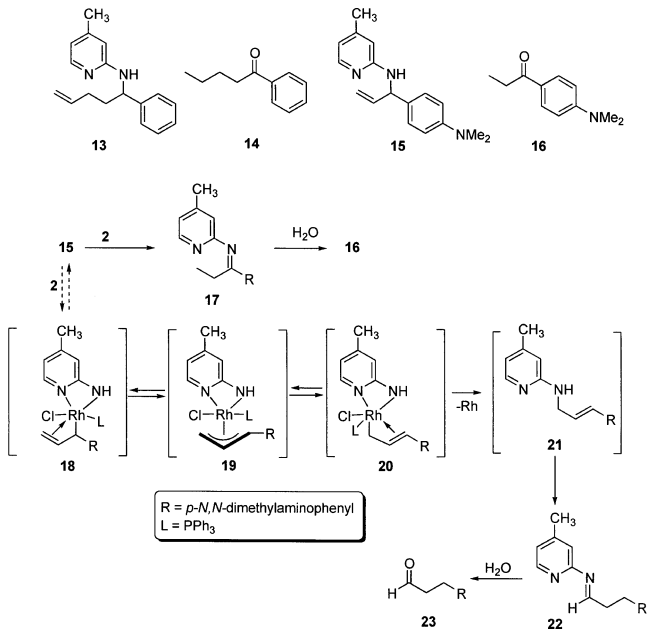
(1)

For the formation of the major product **3**, the first step must be the chelation-assisted cleavage of carbon-nitrogen bond of **1** by **2** to generate **6** (Scheme 1). The β-hydrogen elimination and olefin isomerization in **6** produce **7**. Diene **3** would be liberated from complex **7**, while the hydride addition into diene in **7** forms π-allyl complex **8**. The reductive elimination of **8** produces **9** and **11** as intermediates. Olefin isomerization of **9** and **11** affords ketimines **10** and **12**, followed by hydrolysis to give ketones **4** and **5**. In this process the formation of **4** is favored over that of **5** since the intermediate **9** is more stable than the intermediate **11** due to the better conjugation of olefin with the phenyl group in **9** than in **11**. Compound **5** could be also obtained by direct olefin isomerization of **1**.

Similarly, a carbon-nitrogen bond cleaved product was obtained with homoallylamine, (4-Methyl-2-pyridyl)-*N*-{1-(4-*N*,*N*-dimethylaminophenyl)-3-butenyl}amine, under identical reaction conditions.[2] When (4-Methyl-2-pyridyl)-*N*-(1-phenyl-4-pentenyl)amine (**13**)[4] bearing no electron-donating



Scheme 1. C-N bond Cleavage and Olefin Isomeization in Alkenylamine System.



Scheme 2. Expected Product and Mechanism for C-N Bond Cleavage Reaction.

substituent was applied to this reaction, only pentanophenone (**14**) was isolated in a 66% yield without giving a C-N bond cleaved product. From this result, it is clear that electron-donating substituent near a carbon-nitrogen bond facilitates carbon-nitrogen bond cleavage.

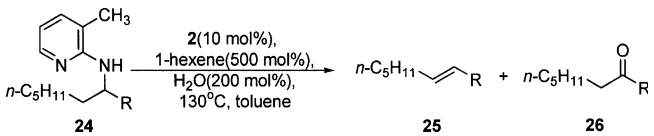
(4-Methyl-2-pyridyl)-*N*-{1-(4-*N*,*N*-dimethylaminophenyl)-2-propenyl}amine (**15**)[5] was applied to the catalytic carbon-nitrogen bond cleavage at 130 °C for 6 h with H_2O (200

mol%) under the catalytic amount (5 mol%) of **2**, which resulted in 4-*N*,*N*-dimethylaminophenyl ethyl ketone (**16**) in 87% isolated yield, exclusively. According to the previous mechanism of the alkenylamine bearing an electron-donating substituent, the expected product should have been **23**. The carbon-nitrogen bond cleavage in **15** by rhodium **2** should have given π-allyl complex **19**, in which its resonance forms are **18** and **20**. Reductive elimination of **20**, olefin isomerization of **21** and hydrolysis of the resulting ketimine **22** would produce **23**. Once the carbon-nitrogen bond is cleaved, it should give **20**, since **20** is more stable than **18**. In spite of this postulate, **23** was not isolated, but **16** was the only product isolated. Any carbon-nitrogen bond cleavage was not observed in this allylamine system. Facile olefin-isomerization by transition metal catalysts has been reported with functionalized olefins such as allylamine[6], allyl alcohol[7] and allylether[8]. Facile double bond isomerization in the allylamine system is explained as nitrogen-triggered mechanism by R. Noyori.[6] Exclusive formation of **16** can be explained by that olefin-isomerization is much faster than carbon-nitrogen bond cleavage in allylamine **15**.

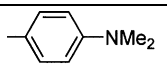
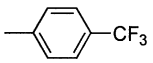
To eliminate the possible olefin isomerization, the alkylamine system such as **24** was applied to the cleavage of the carbon-nitrogen bond.[9] As expected, the electron-donating substituent such as *N*,*N*-dimethylaminophenyl group showed the carbon-nitrogen bond cleavage to give **25a** in 94% isolated yield, exclusively (Table 1, entry 1). The electron-rich ferrocenyl group also showed the similar result (entry 2). However, the electron-withdrawing substituent, such as 4-trifluoromethylphenyl group, did not show any formation of the C-N bond cleavage product, but that of a little amount of dehydrogenation-hydrolysis product **26d** (entry 4). Even **24c** bearing no substituent on the phenyl group gave a similar result (entry 3).

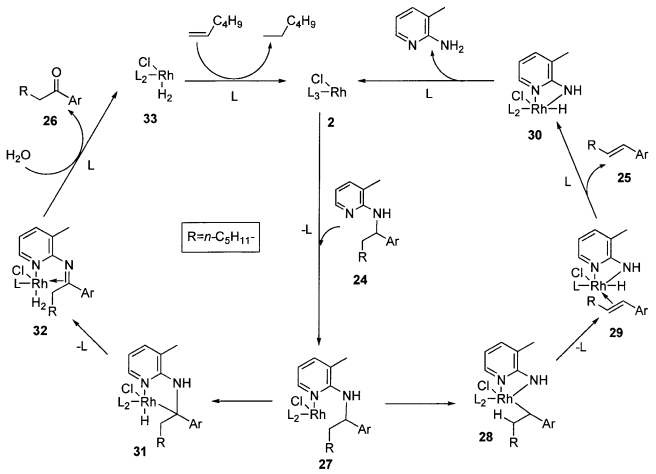
The catalytic cycle of these two competitive reactions is shown in Scheme 3. The electron-rich group assists the carbon-nitrogen bond cleavage to generate the intermediate **28**,

Table 1. Catalytic Reaction of **24** and H_2O by 10 mol% of Complex **2**



24 **25** **26**

Entry	R(1)	Reactant	Product	Isolated Yield
1		**24a**	**25a**	94%
2		**24b**	**25b**	93%
3		**24c**	**26c**	9%
4		**24d**	**26d**	8%



Scheme 3. Catalytic Cycle for the Carbon-Nitrogen Bond Cleavage and Dehydrogenation (L=PPh_3).

followed by β-elimination to give **29**. Compound **25** could be liberated from **29** with the formation of **30**, which undergoes reductive elimination to give 2-amino-3-picoline and the starting catalyst **2**. Since the electron-withdrawing group weakens the benzylic carbon-hydrogen bond, it is easier for the chelation-assisted cleavage of the carbon-hydrogen bond to give **31**. β-Elimination in **31** produces ketimine **32**, which is hydrolyzed to give **26** along with the hydride complex **33**. Complex **33** hydrogenates alkene to alkane with regeneration of catalyst **2**.

In conclusion, chelation assists the carbon-nitrogen bond cleavage as well as olefin isomerization. The nitrogen-carbon bond near the electron-rich group in the alkylamine system is readily cleaved by the transition metal catalyst while that bearing the electron-withdrawing group is not cleaved, but dehydrogenated. For allylamine system, only olefin-isomerization is observed, although it contains the electron-donating substituent.

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3. Compound **1** was prepared by the published procedure. (a) Suggs, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 489. (b) Wakefield, B. J. *Organomagnesium Methods in Organic Synthesis*; Academic Press: Sandiego, **1995**, p 87; Spectral Data for **1**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*= 5.1 Hz, 1H), 7.2-6.1 (m, 6H), 5.9 (m, 1H), 4.9 (m, 3H), 4.4 (q, *J*=6.9 Hz, 1H), 2.9 (s, 6H), 2.1 (m, 5H), 1.9 (q, *J*=6.9 Hz, 2H).; IR (neat) 3415 (NH), 3246, 3085, 2920, 1614, 1524, 1351, 1181; Mass (70 eV) m/z 295 (20) [M^+], 240 (100), 147 (56), 122 (50).
4. **13**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.0-6.4 (m, 8H), 5.8 (m, 1H), 5.3 (q, *J*=7.4 Hz, 1H), 5.0 (m, 2H), 4.4 (d, *J*= 7.6 Hz, 1H), 2.3-1.9 (m, 7H); IR (neat) 3454 (NH), 3079, 2934, 2861, 1604, 1499, 1420, 1130, 926; Mass (70 eV) m/z 252 (14) [M^+], 211 (67), 197 (100), 108 (14), 92 (17).
5. **15**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*=5.1 Hz, 1H), 7.3-6.2 (m, 6H), 6.0 (m, 1H), 5.2 (m, 3H), 4.8 (q, *J*= 6.3 Hz, 1H), 2.9 (s, 6H), 2.2 (m 3H).; IR (neat) 3420 (NH), 3241, 2985, 1617, 1524, 1356, 1182; Mass (70 eV) m/z 267 (8) [M^+], 253 (100), 160 (23), 92 (14).
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9. **24a**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.0 (d, *J*=4.9 Hz, 1H), 7.3-6.4 (m, 6H), 5.1 (q, *J*=7.2 Hz, 1H), 4.3 (d, *J*= 7.5 Hz, 1H), 2.9 (s, 6H), 2.0-1.8 (m, 5H), 1.3-0.8 (m, 13H).; IR (neat) 3457 (NH), 2933, 2859, 1611, 1482, 1346, 1167; Mass (70 eV) m/z 325 (10) [M^+], 240 (100), 160 (72), 134 (66). **24b**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 8.0 (d, *J*=4.8 Hz, 1H), 7.3-6.5 (m, 2H), 5.2 (q, *J*=6.7 Hz, 1H), 4.4 (d, *J*=8.3 Hz, 1H), 4.3-4.1 (m, 9H), 2.2 (s, 3H), 2.0-0.9 (m, 13H).; IR (neat) 3448 (NH), 3096, 2936, 2862, 1608, 1473, 1337; Mass (70 eV) m/z 390 (76) [M^+], 305 (80), 228 (100), 163 (63), 121 (47). **24c**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.9 (d, *J*=3.9 Hz, 1H), 7.4-6.4 (m, 7H), 5.2 (q, *J*=7.2 Hz, 1H), 4.3 (d, *J*=7.5 Hz, 1H), 2.1 (s, 3H), 1.9-0.8 (m, 13H).; IR (neat) 3458 (NH), 3036, 2934, 2862, 1604, 1502, 1418, 1334, 1123.; Mass (70 eV) m/z 282 (10) [M^+], 211 (21), 197 (100), 92 (16). **24d**: ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.8 (d, *J*=5.0 Hz, 1H), 7.5-6.4 (m, 6H), 5.1 (q, *J*=7.1 Hz, 1H), 4.3 (d, *J*=7.1 Hz, 1H), 2.1 (s, 3H), 1.8-0.8 (m, 13H).; IR (neat) 3457 (NH), 2938, 2860, 1605, 1496, 1333, 1171, 1134.; Mass (70 eV) m/z 350 (9) [M^+], 279 (30), 265 (100), 108 (35).