Catalytic Carbon-Nitrogen Bond Cleavage by Rh(I)

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Received September 24, 1998

Carbon-nitrogen bond cleavage by transition metal complexes has been one of the recent developments in organometallic chemistry. Recently we found the chelation-assisted olefin-isomerization in homoallylamine model systems. 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), reacted with H2O (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-dimethylaminophenyl)-3-pentanone (4) in 92% and 5% yields along with a trace amount (1%) of 4-N,N-dimethylaminophenyl butyl ketone (5).

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. When (4-Methyl-2-pyridyl)-N-{1-phenyl-4-pentenyl}amine (13) bearing no electron-donating 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) was applied to the catalytic carbon-nitrogen bond cleavage at 130 °C for 6 h with H2O (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 allylamine6, allyl alcohol7 and allyl ether8. 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 allylamine 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, 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 allylamine 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.

Acknowledgement. The support of this research by the Korea Science and Engineering Foundation (Grant No. 97-05-01-05-01-3) is greatly acknowledged.

References
3. Compound 1 was prepared by the published procedure. (a) Suggs, J. W. J. Am. Chem. Soc. 1979, 101, 489. (b) Wakefield, B. J. Organometallics Methods in Organic Synthesis; Academic Press: Sandiego, 1995, p 87; Spectral Data for 1: 1 H NMR (250 MHz, CDCl$_3$) $\delta$ (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$_3$) $\delta$ (ppm) 7.8 (d, $J = 7.1$ Hz, 1H), 7.0-7.4 (m, 6H), 5.9 (m, 1H), 4.4 (q, $J = 7.4$ Hz, 1H), 3.6 (s, 3H), 1.9 (s, 3H).; IR (neat) 3415 (NH), 3245, 3085, 2920, 1614, 1524, 1351, 1181; Mass (70 eV) m/z 295 (20) [M$^+$], 240 (100), 147 (56), 122 (50).


24a: 1 H NMR (250 MHz, CDCl$_3$) $\delta$ (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$_3$) $\delta$ (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$_3$) $\delta$ (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$_3$) $\delta$ (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).