Catalytic Carbon−Carbon Bond Activation of *sec*-Alcohols by a Rhodium(I) Complex

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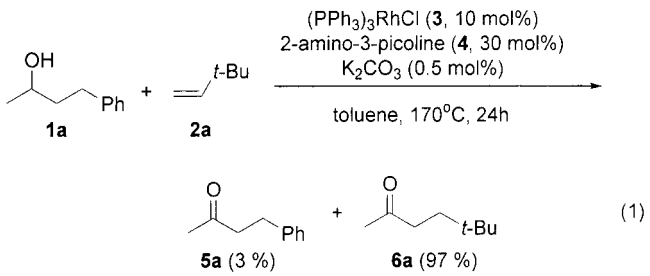
Summary: Various unstrained sec-alcohols, including cycloalkanols, reacted with alkenes under a catalytic system of Rh(I) complex, 2-amino-3-picoline, and K_2CO_3 to give the alkyl-group-exchanged ketones through transfer hydrogenation and consecutive carbon−carbon bond activation. The presence of base is essential to enhance the rate of the oxidation step, and alkene acts as a hydrogen acceptor and a substrate of the carbon−carbon coupling reaction.

Introduction

The activation of the carbon−carbon bond is a current challenge in organometallic chemistry.[1] There are several ways to activate C−C bonds using transition-metal complexes, including the relief of ring strain,[2] the induction of aromaticity,[3] the formation of a stable metallacycle complex,[4] and so on. Most methods involve stoichiometric reactions; only a few catalytic reactions have been reported.[5−9] In particular, the activation of an unstrained C−C bond is quite rare. Recently we reported the chelation-assisted activation of a carbon−carbon bond in unstrained ketone with Rh(I) catalyst.[9] As for an unstrained alcohol, the ruthenium-catalyzed deallylation of tertiary homoallyl alcohol via β-allyl group elimination was reported.[8c] Here, we wish to explain the unprecedented catalytic activation of a C−C bond of an unstrained secondary alcohol through hydrogen transfer.

Results and Discussion

In our experiment, 4-phenyl-2-butanol (**1a**) reacted with 3,3-dimethyl-1-butene (**2a**; 10 equiv based on **1a**) in the presence of $(PPh_3)_3RhCl$ (**3**; 10 mol %), 2-amino-3-picoline (**4**; 30 mol %), and K_2CO_3 (0.5 mol %) to yield 4-phenyl-2-butanone (**5a**) and 5,5-dimethyl-2-hexanone (**6a**) in a 3% and a 97% yield, respectively (eq 1). Ketone **5a** is the oxidation product of **1a**, and **6a** is formed by the activation of C−C bond α to the carbonyl group in **5a**.



(1)

The proposed mechanism for the formation of **5a** and **6a** is depicted in Scheme 1. The first step is the oxidation of **1a** to generate **5a** via hydrogen transfer,[10,11] in which **2a** acts as a hydrogen acceptor, giving off 2,2-dimethylbutane. The resulting ketone **5a** condenses with **4** to generate the intermediate ketimine **7**, of which the C−C bond α to the imino group is cleaved by **3** to afford an (iminoacyl)rhodium hydride complex (**8**), liberating styrene. Ketimine **9a** is formed by a hydrometalation of **8** into **2a** and a subsequent reductive elimination. It is then hydrolyzed to give **6a**.[9a]

The role of a base, K_2CO_3, is to promote the initial hydrogen transfer step. When the reaction was carried

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(1) For reviews, see: (a) Murakami, M.; Ito, Y. In *Topics in Organometallic Chemistry*; Murai, S., Ed.; Topics in Organometallic Chemistry 3; Springer: Berlin, Germany, 1999; pp 97−129. (b) Rybtchinski. B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (c) Jennings, P. W.; Johnson, L. L. *Chem. Rev.* **1994**, *94*, 2241.

(2) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.

(3) (a) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Halt, E. M. *J. Am. Chem. Soc.* **1986**, *108*, 7222. (b) Hemond, R. C.; Hughes, R. P.; Locker, H. B. *Organometallics* **1986**, *5*, 2391.

(4) (a) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699. (b) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774. (c) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1995**, 1965. (d) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1986**, *108*, 4679. (e) Suggs, J. W.; Jun, C.-H. *J. Am. Chem. Soc.* **1984**, *106*, 3054.

(5) (a) Chatani, N.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **1999**, *121*, 8645. (b) Mitsudo, T.; Suzuki, T.; Zhang, S.-W.; Imai, D.; Fujita, K.; Manabe, T.; Shiotsuki, M.; Watanabe, Y.; Wada, K.; Kondo, T. *J. Am. Chem. Soc.* **1999**, *121*, 1839. (c) Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *Chem. Commun.* **1998**, 687. (d) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843. (e) Harayama, H.; Kuroki, T.; Kimura, M.; Tanaka, S.; Tamaru, Y. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2352. (f) Lin, M.; Hogan, T.; Sen, A. *J. Am. Chem. Soc.* **1997**, *119*, 6048. (g) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc.* **1994**, *116*, 3647.

(6) (a) Murakami, M.; Tsuruta, T.; Ito, Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 2484. (b) Murakami, M.; Itahashi, T.; Amii, H.; Takahashi, K.; Ito, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9949. (c) Murakami, M.; Takahashi, K.; Amii, H.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 9307. (d) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285. (e) Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540.

(7) (a) Baba, A.; Ohshiro, Y.; Agawa, T. *J. Organomet. Chem.* **1976**, *110*, 121. (b) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 4895. (c) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1991**, *113*, 2771.

(8) (a) Nishimura, T.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 11010. (b) Nishimura, T.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **1999**, *121*, 2645. (c) Kondo, T.; Kodoi, K.; Nishinaga, E.; Okada, T.; Morisaki, Y.; Watanabe, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **1998**, *120*, 5587.

(9) (a) Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880. (b) Jun, C.-H.; Lee, H.; Park, J.-B.; Lee, D.-Y. *Org. Lett.* **1999**, *1*, 2161. (c) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun.* **1985**, 92.

(10) For reviews, see: (a) Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129. (b) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (c) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97. (d) Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2045.

(11) (a) Bäckvall, J.-E.; Chowdhury, R. L.; Karlsson, U. *J. Chem. Soc., Chem. Commun.* **1991**, 473. (b) Wang, G.-Z.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1992**, 337. (c) Yang, H.; Alvarez, M.; Lugean, N.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1995**, 1721. (d) Hashiguchi, S.; Fijii, A.; Takehera, J.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 7562. (e) Aranyos, A.; Csjernyik, G.; Szabo, K. J.; Bäckvall, J.-E. *Chem. Commun.* **1999**, 351.

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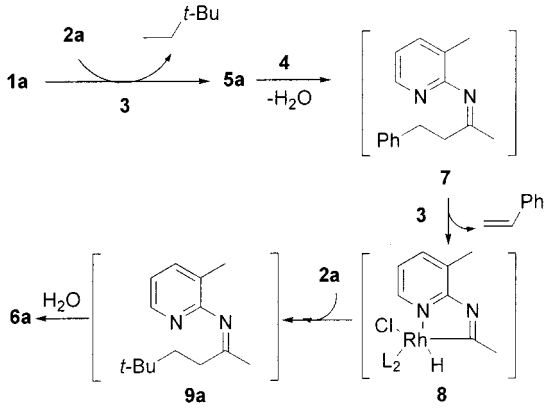
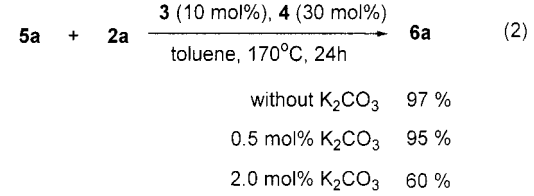
Scheme 1



out in the absence of K_2CO_3, **6a** was obtained in only 78% yield and 8% of **1a** remained. The rate acceleration effect of a base in hydrogen transfer has been studied extensively.[11] To investigate the effect of K_2CO_3 in the oxidation of alcohol, the reaction of **1a** and **2a** was carried out in the absence of **4** (Figure 1).

With 0.5 mol % of K_2CO_3, **1a** was completely converted into **5a** in 18 h, while only 17% of **5a** was obtained in 24 h without K_2CO_3. Furthermore, the rate of oxidation increases as the amount of K_2CO_3 increases; the oxidation was almost completed within 1 h when K_2CO_3 was added up to 5 mol %.

The reactivity of C−C bond activation of **1a**, in contrast, was not enhanced by the addition of a large amount of K_2CO_3. For example, the yield of **6a** decreased to 74% as 2 mol % of K_2CO_3 was added. The reason for this result might be that the C−C bond activation of ketone was suppressed by the base. To confirm this assumption, the catalytic C−C bond activation of ketone **5a** was carried out in the presence of K_2CO_3 (eq 2).



(2)

While the reaction of **5a** proceeded well to give **6a** in a 97% yield in the absence of K_2CO_3, the yield of **6a** from **5a** decreased down to 60% with 2 mol % of K_2CO_3.[12] Although the presence of K_2CO_3 is essential, only a small amount, e.g. 0.5 mol %, suffices for a complete oxidation of *sec*-alcohol in order to maintain the reactivity of the C−C bond activation.

Various 2-aminopyridine derivatives and bases other than K_2CO_3, such as Na_2CO_3, Cs_2CO_3, $NaHCO_3$, KOH, and NaOH, were examined for this C−C bond activation. It turned out that the combination of **4** and K_2CO_3 was most effective (see the Supporting Information). $HRh(PPh_3)_4$ and ruthenium complexes, such as $Ru_3(CO)_{12}$, $(H_2)Ru(PPh_3)_4$, and $RuCl_2(PPh_3)_3$, were inactive in C−C bond activation. The oxidation of alcohol, on the other hand, proceeded completely to afford **5a**.

(12) In the case of ruthenium-catalyzed hydrogen transfer, chlorides in the ruthenium complex are removed to give active species in the presence of base.[11] We anticipate that this type of removal of chloride deteriorates the rhodium catalyst in the C−C bond activation.

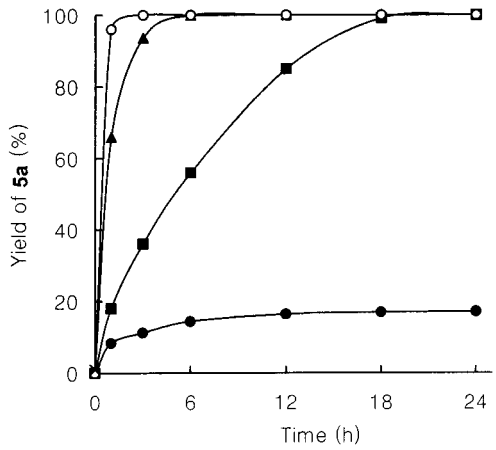
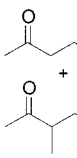
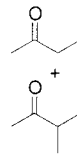


Figure 1. Effect of K_2CO_3 in the oxidation of **1a** to **5a**. The reactions of **1a** were carried out at 170 °C in the presence of **2a** (**1a**:**2a** = 1:10) and **3** (10 mol %) with 0 mol % (●), 0.5 mol % (■), 2 mol % (▲), and 5 mol % (○) of K_2CO_3.

Table 1. Catalytic C−C Bond Activation of 1a with Alkenes 2[a]

Entry	Alkenes (**2**)	Product(s) (**6**)	Yield (%)[b]
1	 (**2a**)	 (**6a**)	86[c]
2[d]	(**2b**)	 (**6b**) + (**6c**)	79 (**6b**/**6c** =95/5)[e]
3[d]	2-Hexene (**2c**)	(**6b**) + (**6c**)	64 (**6b**/**6c** =94/6)[e]
4[d]	 (**2d**)	 (**6d**) + (**6e**)	(72) (**6d**/**6e** =95/5)[e]
5	 (**2e**)	 (**6f**) (*exo*/*endo*=73/27)[f]	(73)
6[d,g]	 (**2f**)	 (**6g**)	51

[a] The reaction of **1a** and **2** (**1a**:**2** = 1:10) was carried out at 170 °C for 24 h under **3** (10 mol %), **4** (30 mol %), and K_2CO_3 (0.5 mol %) in toluene. [b] The yield of product was determined by GC, and isolated yields are shown in parentheses. **1a** was fully converted into ketones, except for entry 6. [c] The reaction time was 18 h. [d] A small amount (~2%) of **10** was detected by GC. [e] Determined by GC. [f] Determined by ^1H NMR. [g] 3% of **1a** was left. 13% of **11a** and 5% of **11b** were detected.

The reactions of **1a** with various alkenes were carried out, and the results are summarized in Table 1. Of the olefins examined, **2a** showed the highest reactivity (entry 1). 1-Hexene (**2b**) reacted with **1a** to give a 79% yield of the ketones 2-octanone (**6b**) and 3-methyl-2-heptanone (**6c**) in a ratio of 95:5 along with a small amount of 3-phenyl-2-butanone (**10**), the skeletal rearrangement product of **5a** (entry 2). The branched alkyl ketone **10** might be formed through the hydrometalation of **8** into styrene generated from C−C bond cleavage of

Table 2. Oxidation of 1a Using Alkenes (2) as Hydrogen Acceptors[a]

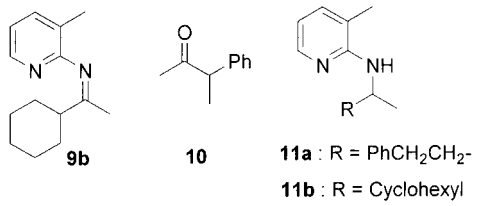
entry	alkene **2**	yield of **5a** (%)[b]
1	**2a**	85
2	**2b**	57
3	**2c**	52
4	**2d**	56
5	**2e**	53
6	**2f**	13

[a] The reaction of **1a** and **2** (**1a**:**2** = 1:10) was carried out at 170 °C for 12 h under **3** (10 mol %) and K_2CO_3 (0.5 mol %) in toluene. [b] GC yields.

7 according to Markownikoff's rule, instead of reacting with external alkene substrate.[13]

When 2-hexene (**2c**) was used, the linear alkyl ketone **6b** was obtained as a major product; the terminal alkene **2b** also gave a similar ratio of **6b** and **6c** (entry 3). The induction of a linear alkyl group from an internal olefin has been studied in the ruthenium-catalyzed alkylation of benzylamine derivatives.[14]

Among cyclic alkenes, norbonylene (**2e**) exhibited high reactivity to give 1-(bicyclo[2.2.1]hept-2-yl)ethanone (**6f**) in 73% yield, and cyclohexene (**2f**) yielded 51% of cyclohexylethanone (**6g**) along with *N*-(3-methyl-2-pyridyl)-*N*-(3-phenyl-2-butyl)amine (**11a**) and *N*-(1-cyclohexylethyl)-*N*-(3-methyl-2-pyridyl)amine (**11b**), which



were generated through the hydrogenation of the intermediate ketimines **7** and **9b**, respectively.[15] The formation of these amines results in decreased reactivity, because **4** cannot be regenerated from **11a** or **11b**.

The reactivity of alkene is also influenced by its capability as a hydrogen acceptor, as alkene participates in hydrogen transfer (from **1a** to **5a** in Scheme 1) as well as in C−C bond coupling (from **8** to **9a** in Scheme 1). The reactivity of the alkene as a hydrogen acceptor was examined by the reaction of **1a** and alkenes without **4** (Table 2).

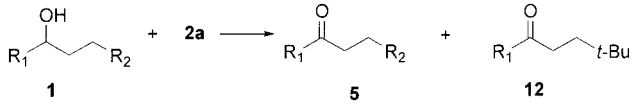
Among the alkenes tested, **2a** turned out to be the most effective hydrogen acceptor (entry 1). Other linear alkenes, **2b**, **2c**, and **2d**, are less reactive than **2a** (entries 2−4). The reactivity of **2e** was comparable to that of linear olefins (entry 5), but **2f** was a weak hydrogen acceptor; the conversion of **1a** to **5a** was limited to only 13% (entry 6). The inferior reactivity of **2f** as a hydrogen acceptor resulted in hydrogenation of the intermediate ketimine to form amines such as **11a** and **11b**.

(13) This type of skeletal rearrangement was identified by the fact that **5a** was heated with **3** and **4** without alkene to afford **10** in 7% yield. Similarly, **10** was also isomerized to **5a** under the same reaction conditions to give a mixture of **5a** and **10** in a ratio of 11:89.

(14) Jun, C.-H.; Hwang, D.-C.; Na, S.-J. *Chem. Commun.* **1998**, 1405.

(15) Imine is thought to be an intermediate in ruthenium-catalyzed N-alkylation of amine by alcohol: (a) Watanabe, Y.; Tsuji, Y.; Ohsugi, Y. *Tetrahedron Lett.* **1981**, *22*, 2667. (b) Murahashi, S.-I.; Kondo, K.; Hakata, T. *Tetrahedron Lett.* **1982**, *23*, 229. (c) Watanabe, Y.; Tsuji, Y.; Ige, H.; Oshugi, T. *J. Org. Chem.* **1984**, *49*, 3359.

Table 3. Catalytic C−C Bond Activation of Various *sec*-Alcohols 1 with 2a[a]



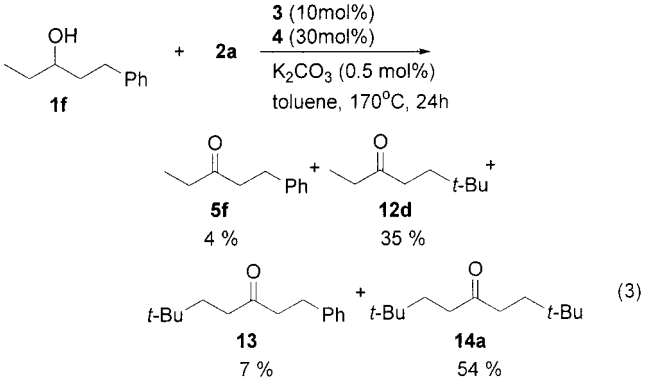
1 **5** **12**

Entry	Alcohol (**1**) R1	R2		Products (Isolated Yield, %) 5	12
1	Ph-	H-	(**1b**)	**5b** (53)	**12a** (43)
2	Ph-	Ph-	(**1c**)	**5c** (30)	**12a** (68)
3	F_3C-	Ph-	(**1d**)	**5d** (21)	**12b** (73)
4[b]	MeO-	Ph-	(**1e**)	**5e** (42)	**12c** (46)

[a] The reaction of **1** and **2a** (**1:2a** = 1:10) was carried out at 170 °C for 24 h under **3** (10 mol %), **4** (30 mol %), and K_2CO_3 (0.5 mol %) in toluene. [b] Dehydration of **1e** occurred to give a mixture of 3-phenyl-1-(4-methoxyphenyl)propene and 3-(4-methoxyphenyl)-1-phenylpropene in 7% yield (detected by GC).

Other *sec*-alcohols also underwent C−C bond activation to yield the corresponding ketones (Table 3).

The difference of reactivities between 1-phenylpropanol (**1b**) and 1,3-diphenylpropanol (**1c**) implies that the phenethyl group is more easily cleaved than the ethyl group (entry 1 and 2), which can be also identified by the reaction of 5-phenyl-3-pentanol (**1f**) that has two possible sites for C−C bond activation, the ethyl group and the phenethyl group. The reaction of **1f** and **2a** afforded a mixture of the ketones, **5f**, **12d**, **13**, and **14a** in 4%, 35%, 7%, and 54% yields, respectively (eq 3).

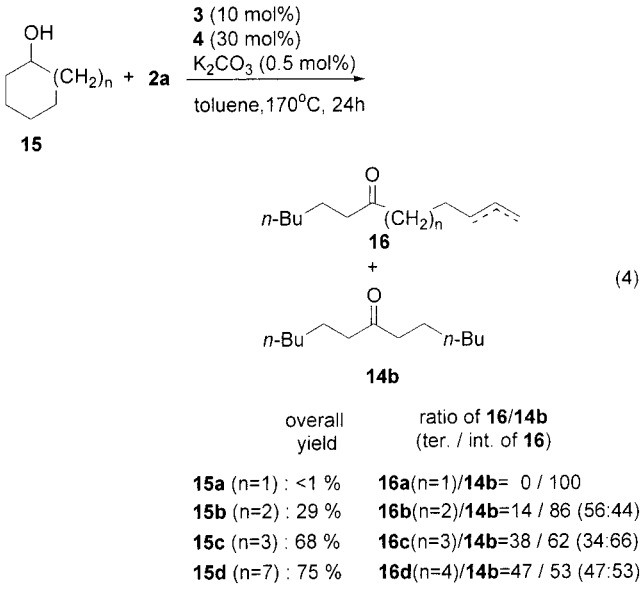


Ketone **5f** is an initial oxidation product of **1f**, while **12d** and **13** are formed through the C−C bond activation of the phenethyl group and ethyl group in **5f**. The symmetric ketone **14a** is generated from the C−C bond activations of both the phenethyl and the ethyl group. The difference between the yield of **12d** and that of **13** also confirmed that the phenethyl group is more reactive than the ethyl group.

An electron-withdrawing substituent, such as the trifluoromethyl group in **1d**, improves the yield of a C−C bond cleaved product (**12b**) compared with electron-donating substituent in **1e** (entries 3 and 4 in Table 3).

In addition to open chain *sec*-alcohols, cycloalkanols **15** with various ring sizes were also applied to this reaction to give a mixture of the ring-opened alkenyl ketone **16** and the symmetric ketone **14b**, which derives

from the consecutive C−C bond activations of **16** (eq 4).



(4)

overall yield	ratio of **16**/**14b** (ter. / int. of **16**)
15a (n=1) : <1 %	**16a**(n=1)/**14b**= 0 / 100
15b (n=2) : 29 %	**16b**(n=2)/**14b**=14 / 86 (56:44)
15c (n=3) : 68 %	**16c**(n=3)/**14b**=38 / 62 (34:66)
15d (n=7) : 75 %	**16d**(n=4)/**14b**=47 / 53 (47:53)

These results exhibit a similar tendency in comparison with the C−C bond activation of cycloalkanone imine according to ring size.[16] When cyclohexanol (**15a**) was used, only a trace (<1%) of **14b** was detected. As the size of the ring increases from cycloheptanol (**15b**) to cyclododecanol (**15d**), the yield of the C−C bond cleaved products increases from 29% to 75%.[17]

In conclusion, we effected the carbon−carbon bond activation of *sec*-alcohols to obtain an alkyl-group-exchanged product from the catalytic system of Rh(I) complex, 2-amino-3-picoline, and K_2CO_3. The reaction consisted of two steps: the oxidation of alcohol through hydrogen transfer and the chelation-assisted carbon−carbon bond activation of the resulting ketone. Cycloalkanol also underwent C−C bond activation to afford ring-opened ketones.

Experimental Section

The reagents and toluene used in the experiments were purified by standard procedures.[18] $(PPh_3)_3RhCl$ was prepared as described in the literature.[19] Other transition-metal complexes were purchased from Aldrich Co. and used as received. ^1H NMR and ^{13}C NMR spectra were recorded at 250 and 62.5 MHz. Samples were analyzed in $CDCl_3$, and the chemical shift was expressed in ppm relative to TMS. GC analyses were conducted using a Donam DS 2000 gas chromatograph. Mass spectra were obtained using a G1800A GCD system. *sec*-Alcohols **1** and **15** were either purchased or prepared according to the known procedures (see the Supporting Information).

Typical Procedure for the Catalytic Reaction. The Reaction of 1a and 1-Octene (2d) (Table 1, Entry 4). A screw-capped pressure vial (1 mL) was charged with 43.6 mg (0.29 mmol) of **1a**, 325 mg (2.9 mmol) of 1-octene (**2d**), 9.4 mg (0.087 mmol) of 2-amino-3-picoline (**4**), 0.2 mg (0.0015 mmol) of K_2CO_3, 26.8 mg (0.029 mmol) of $(PPh_3)_3RhCl$ (**3**), and 130 mg of toluene. The mixture was stirred for 24 h in an oil bath that was preheated to 170 °C. After the reaction, the mixture was cooled to room temperature and purified by column chromatography (SiO_2, *n*-hexane:ethyl acetate = 5:1) to yield 32.8 mg (72%) of a mixture of 2-decanone (**6d**) and 3-methyl-2-nonanone (**6e**), which were identified by GCD. The ratio of **6d** and **6e** was determined as 95:5 by GC.

For the other volatile ketones, the yields of products were also determined by GC. Among the products, commercially available compounds such as **5a**,**b**, **6b**,**d**,**g**, **12a**, and **14b** were identified by comparison with authentic specimens. Other compounds, **5c**,[20] **5d**,[21] **5e**,[21] **5f**,[22] **6a**,[9a] **6c**,[23] **6e**,[24] **6f**,[25] **10**,[26] **12c**,[27] **12d**,[28] **13**,[9b] **14a**,[9b] and **16a**−**d**,[16] have already been reported. All of the new compounds are characterized below.

(3-Methyl-2-pyridinyl)(3-phenyl-2-butyl)amine (11a). ^1H NMR (250 MHz, $CDCl_3$): δ 8.01 (d, J = 4.9 Hz, 1H), 7.33−7.08 (m, 6H), 6.47 (dd, J = 7.1 Hz, 5.1 Hz, 1H), 4.33 (m, 1H), 3.86 (d, J = 7.1 Hz, 1H), 2.72 (m, 2H), 1.98 (s, 3H), 1.89 (m, 2H), 1.27 (d, J = 6.4 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 156.6, 145.6, 142.5, 136.8, 128.5, 125.9, 116.3, 112.3, 46.4, 39.2, 32.8, 21.6, 17.1. IR (neat): 3443, 3058, 3025, 2926, 2857, 1600, 1496, 1469, 1412, 1144, 771, 698 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{16}H_{20}N_2$ (M^+) 240.1622, found 240.1640.

(1-Cyclohexylethyl)(3-methyl-2-pyridinyl)amine (11b). ^1H NMR (250 MHz, $CDCl_3$): δ 8.00 (d, J = 4.9 Hz, 1H), 7.18 (d, J = 7.1 Hz, 1H) 6.43 (dd, J = 7.1 Hz, 5.1 Hz, 1H), 4.13 (m, 1H), 3.95 (d, J = 7.1 Hz, 1H), 2.06 (s, 3H), 1.89−1.00 (m, 11H), 1.16 (d, J = 6.6 Hz, 3H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 156.9, 145.6, 136.8, 116.2, 111.9, 50.4, 43.6, 29.8, 29.0, 26.8, 26.6, 26.5, 18.4, 17.3. IR (neat): 3452, 2966, 2851, 1600, 1581, 1495, 1469, 1449, 1411, 1334, 1244, 1138, 989, 770 cm^{-1}. HRMS (EI): *m*/*z* calcd for $C_{14}H_{22}N_2$ (M^+) 218.1788, found 218.1791.

4,4-Dimethyl-1-(4-(trifluoromethyl)phenyl)-1-pentanone (12b). Mp: 38 °C. ^1H NMR (250 MHz, $CDCl_3$): δ 8.06 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H), 2.96 (t, J = 8.1 Hz, 2H), 1.65 (t, J = 8.1 Hz, 2H), 0.97 (s, 9H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 200.1, 139.9, 134.6−125.8, 121.7, 38.1, 34.8, 30.4, 29.4. IR (KBr): 2957, 1693, 1600, 1471, 1410, 1363, 1326, 1160, 1132, 1067, 1015 cm^{-1}. HRMS (CI): *m*/*z* calcd for $C_{14}H_{18}OF_3$ ($M + 1^+$) 259.1305, found 259.1313.

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Supporting Information Available: Text giving synthetic procedures for the preparation of starting materials and results of experiments in varying 2-aminopyridine derivatives and bases. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Jun, C.-H.; Lee, H.; Lim, S.-G. *J. Am. Chem. Soc.* **2001**, *123*, 751. The catalyst system consisting of $[(C_8H_{14})_2RhCl]_2$ and Cy_3P, which had been used in the reaction of cycloalkanone imine, was not effective in the reaction of alcohol because this catalyst system was inactive in the hydrogen transfer reaction.

(17) In cases of small-ring cycloalkanols such as **16a** and **16b**, skeletal rearrangement products such as 2-methylcyclopentanone (1%, from **16a**), 2-methylcyclohexanone (8%, from **16b**), and 2-ethylcyclopentanone (4%, from **16b**) were obtained.

(18) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, U.K., 1996.

(19) Osborn, J. A.; Wilkinson, G. In *Reagents for Transition Metal Complex and Organometallic Synthesis*; Angelich, R., Ed.; Wiley: New York, 1989; Vol. 28, pp 77−79.

(20) Skene, W. G.; Scaiano, J. C.; Yap, P. A. *Macromolecules* **2000**, *33*, 3536.

(21) Spogliarich, R.; Farnetti, E.; Graziani, M. *Tetrahedron Lett.* **1991**, *47*, 1965.

(22) Mattson, M. N.; Rapoport, H. *J. Org. Chem.* **1996**, *61*, 6071.

(23) Clarke, T. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 7934.

(24) Collman, J. P.; Winter, S. R.; Clark, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 1788.

(25) Moron, J.; Roussi, G. *J. Org. Chem.* **1978**, *43*, 4215.

(26) Sakai, T.; Matsumoto, S.; Hidaka, S.; Imajo, N.; Tsuboi, S.; Utaka, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3473.

(27) Russell, G. A.; Shi, B. *Synlett* **1993**, 701.

(28) Seyferth, D.; Hui, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 4551.