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Chelation-assisted carbon–carbon bond activation by Rh(I) catalysts

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Abstract

Herein described is the chelation-assisted C–C bond activation of unstrained ketones under the co-catalyst system of $Rh(PPh_3)_3Cl$ and 2-amino-3-picoline (**1**). This reaction is based on the strategy we recently developed in hydroacylation with aldehydes in which 2-aminopyridine derivatives function as chelation-assistant tools. Unstrained ketones having a β-hydrogen gave rise to alkyl-exchanged ketones via this C–C bond activation under an excess of external olefins. In the absence of external olefins, cycloheptanone underwent a ring contraction to generate five- and six-membered cyclic ketones. Instead of unstrained ketones, *sec*-alcohols were also employed as a substrate for this C–C bond activation via hydrogen transfer. The reaction of allylamine derivatives under $[Rh(C_8H_{14})_2Cl]_2$ and PCy_3 afforded symmetric dialkyl ketones via a series of reaction such as olefin isomerization, C–H bond activation, and C–C bond activation. The key intermediate, the imine derived from **1** was generated from a primary amine through dehydrogenation followed by transimination. Consequently, the Rh(I)-catalyzed C–C bond activation of unstrained ketones and their equivalents was demonstrated by utilizing a chelation-assistance strategy.

Keywords: C–C bond activation; Rh(I) catalysts; Unstrained ketones; Chelation assistance; 2-Aminopyridines

1. Introduction

The activation of carbon–carbon bonds by transition metal complexes is one of the most challenging areas in chemistry [1–4]. Many chemists are attracted to this fascinating study due to not only the fundamental scientific interest but also its potential utility in synthetic organic chemistry and industrial process. However, the activation of C–C bonds is yet far from practical use, in contrast to many successful applications of carbon–hydrogen bond activation to organic synthesis [5–8].

After the first direct insertion of the transition metal into a C–C bond in cyclopropane [9], many stoichiometric reactions have been developed [1–4]. Consequently, C–C bonds are no longer regarded as inert in the presence of transition metal complexes.

Despite the significant development in a stoichiometric C–C bond activation, only a few catalytic reactions have been reported and the applicable substrates are strictly limited [10–33]. Most of those examples were realized by relieving the ring strain of three- or four-membered ring [10–16]. Carbonyl compounds bearing ring strain such as cyclobutanone were frequently used as a substrate since the C–C bond α to the carbonyl group is weaker than other C–C bonds [17–24].

As for unstrained molecules, a remarkable progress has been achieved by utilizing cyclometalation [25], a

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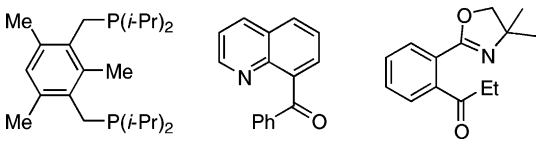

Fig. 1. The designed models for cyclometalation.

formation of a chelate ring containing a metal–carbon σ bond [26–28]. Representative examples of model compounds designed for a chelation are diphosphine pincer-type ligands [26,34–40], 8-quinolinyl alkyl ketones [27,41–45], and aromatic ketones containing an oxazoline group [28] (Fig. 1).

The existence of a coordination site in these molecules facilitates the activation of C–C bond, because it allows the transition metal to easily access the C–C bond to be cleaved so as to bring about the C–C bond cleavage with forming a stable metalacycle. Although such reactions were carried out with specially designed model compounds, a chelation was undoubtedly one of the most powerful tools for the activation of unstrained C–C bonds. Therefore, we were inspired to develop a C–C bond activation of unstrained molecules bearing no coordinating functionality through a temporary installation of an appropriate chelation auxiliary. In the following sections, we will describe the catalytic C–C bond activation of unstrained ketones utilizing a chelation-assistance.

2. Chelation-assisted C–C bond activation of unstrained ketones

2.1. Chelation-assisted hydroacylation via C–H bond activation

In the efforts directed toward the catalytic C–H bond activation, we have developed the chelation-assisted hydroacylation of olefins under the co-catalyst system of $Rh(PPh_3)_3Cl$ and 2-amino-3-picoline (**1**) for the synthesis of ketones [46–49] (Fig. 2).

This C–H bond cleavage process is based on the strategy of a chelation assistance [50]. For the in situ installation of a coordinating functionality, 2-aminopyridine derivative was utilized as a chelation auxiliary. As illustrated in Fig. 3, the condensation of **1** with an aldehyde generates the corresponding

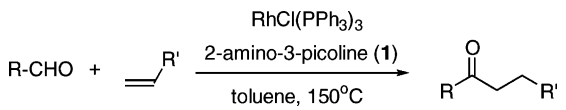

Fig. 2. Chelation-assisted hydroacylation using 2-amino-3-picoline.

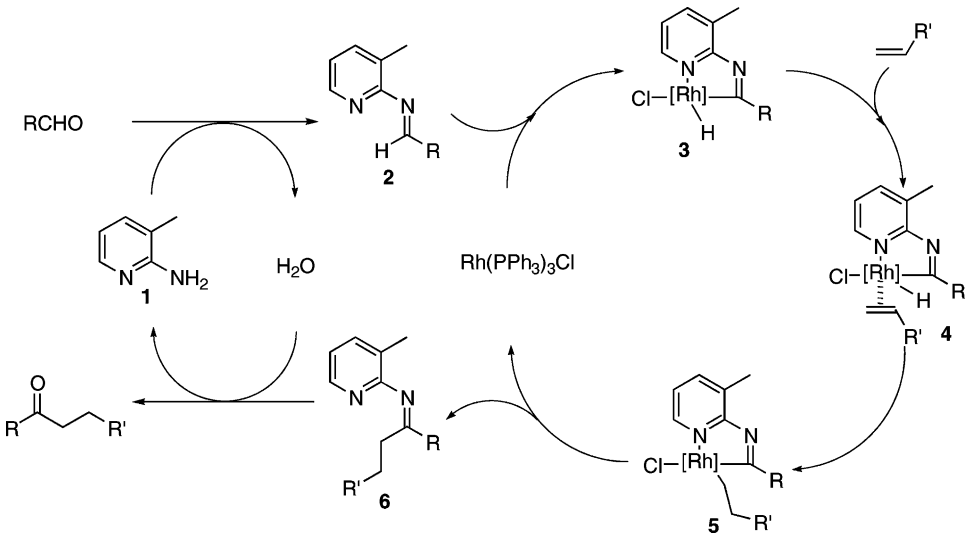

Fig. 3. The mechanism for chelation-assisted hydroacylation of olefin.

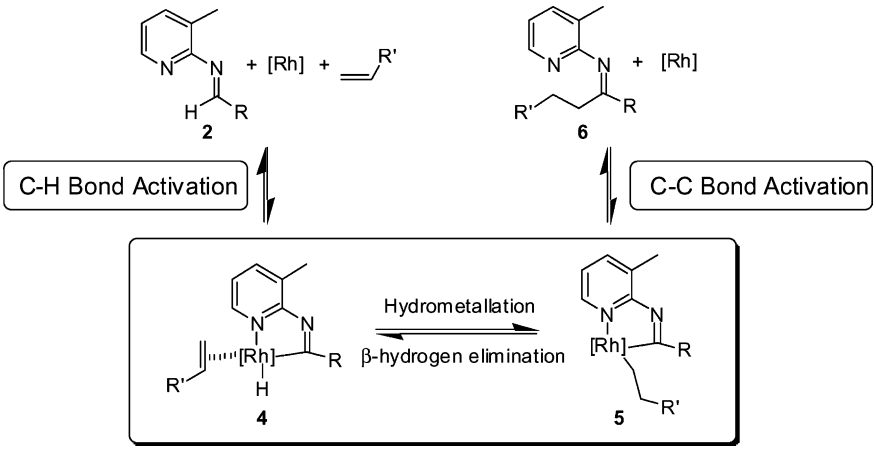

Fig. 4. Reversible process between aldimine and ketimine.

imine **2**. The pre-coordination of pyridinyl group in imine **2** allows a transition metal to locate close to a C–H bond, thereby the cleavage of the C–H bond is promoted to give a stable five-membered metalacycle intermediate **3**. In the presence of external olefins, the coordination of olefins followed by hydrometalation yields (iminoacyl)metal alkyl complex **5**, which results in a C–C bond coupling through reductive elimination.

During this hydroacylation study, we envisioned that the chelation-assistance strategy by means of 2-aminopyridines could be applicable to a C–C bond activation of unstrained ketones since every step from aldimines through ketimines seemed to be a reversible process (see Fig. 4). By the same manner as in a C–H bond activation, the oxidative addition of the a C–C bond of ketimines **6** to transition metals might occur to generate the iminoacylmetal alkyl complex **5**. β-Hydrogen elimination of the complex **5**, which is the net reverse of the hydrometalation step during hydroiminoacylation, could afford iminoacylmetal hydride complex **4**. In the following sections, the C–C bond activation utilizing this type of a chelation-assistance will be discussed in detail.

2.2. The C–C bond activation of unstrained ketones

2.2.1. The C–C bond activation of linear ketones

A chelation-assisted C–C bond activation of unstrained ketones was performed with the reaction of benzylacetone with 3,3-dimethyl-1-butene in the presence of $Rh(PPh_3)_3Cl$ and **1**, which afforded the alkyl-exchanged ketone **7** with a trace amount of styrene [51]. As a result, a phenethyl group in benzylacetone is exchanged with the 3,3-dimethylbutyl group through the cleavage of the C–C bond α to a carbonyl group (Fig. 5).

The reaction begins with the formation of ketimine **8** from the condensation of ketone and **1**, which induces a metal complex to have access to the C–C bond α to an imine by the coordination of its pyridinyl group to the metal complex (Fig. 6). Then the C–C bond in **8** is cleaved by the Rh(I) complex to give an (iminoacyl)rhodium(III) phenethyl **9**, which is followed by β-hydrogen elimination of phenethyl group in **9** to give an (iminoacyl)rhodium(III) hydride **11** with a generation of styrene. The hydrometalation of **11** into olefin followed by reductive elimination produces ketimine **13**. Finally, hydrolysis of the resulting ketimine **13** affords ketone **7**.

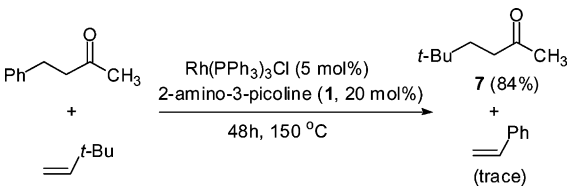

Fig. 5. A chelation-assisted C–C bond activation of unstrained ketone.

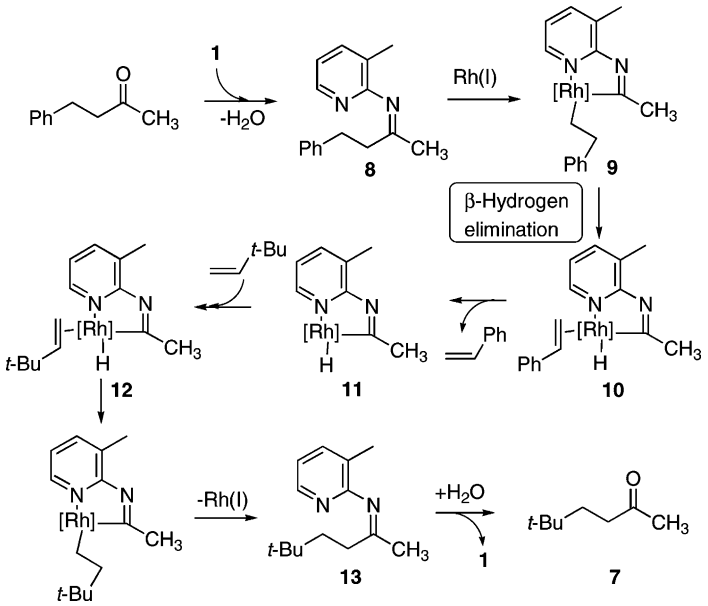

Fig. 6. The mechanism of a chelation-assisted C–C bond activation of unstrained ketone.

According to the above mechanism proposed, there are two requirements for this catalytic cycle to be successfully executed. First, the ketone substrate should possess a β-hydrogen, because β-hydrogen elimination of complex **9** affords the metal hydride complex **11** with generating an olefin such as styrene. The metal hydride intermediate **11** is ready to be coordinated by olefins. At this point, however, there exists a competition between the forward reaction to complex **12** and the backward to complex **10**. Therefore, the second requirement for completion of this process is to add an excess of external olefins to drive the forward reaction from complex **11**, which leads to incorporation with a new alkyl group. Actually, a methyl group having no β-hydrogen available in benzylacetone is inert for this catalytic C–C bond cleavage. And, about 10 equivalents of 3,3-dimethyl-1-butene exhibited the highest yield of ketone **7**. In addition, we noticed only the trace amount of styrene remained, which might be explained by the facile polymerization of styrene, the olefin generated by β-hydrogen elimination of complex **9**, at the reaction temperature [52]. Thus, such polymerization also forces this catalytic process to go forward to the production of the alkyl-exchanged ketone **7**.

To support the proposed mechanism of this reaction, the crossover experiment between two different symmetric dialkyl ketones was carried out in the absence of external olefins as shown in Fig. 7. As expected, we were able to isolate a new ketone **14**, which was generated from the exchange between alkyl groups of both ketones. As a result, each ketone underwent the C–C bond cleavage to generate the olefin, which would serve as a substrate for the alkyl-exchange reaction via a new C–C bond coupling.

2.2.2. The C–C bond activation of cyclic ketones

We investigated, in turn, the C–C bond activation of cyclic ketones [53]. The reaction mixture of cyclooctanone and 1-hexene was heated at 150 °C under $Rh(PPh_3)_3Cl$ and **1** to undergo the C–C bond cleavage reaction. Then, an isomeric mixture of ring-opened alkenyl ketones **15** and a 7-tridecanone (**16**) were obtained in a good yield (Fig. 8).

As shown in Fig. 9, the alkenyl ketones **15** are produced through the C–C bond cleavage followed by hydroacylation with 1-hexene. The terminal olefinic moiety in **15** is possibly isomerized under the reaction condition to give the internal olefin. And 7-tridecanone is the doubly C–C bond activated product which is

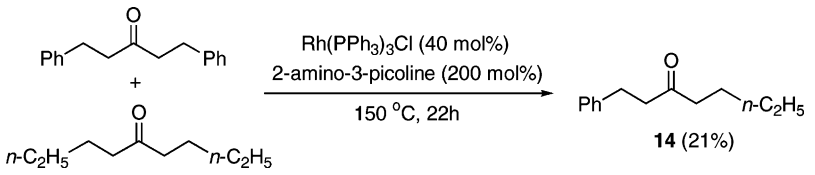

Fig. 7. Alkyl exchange of symmetric dialkyl ketones.

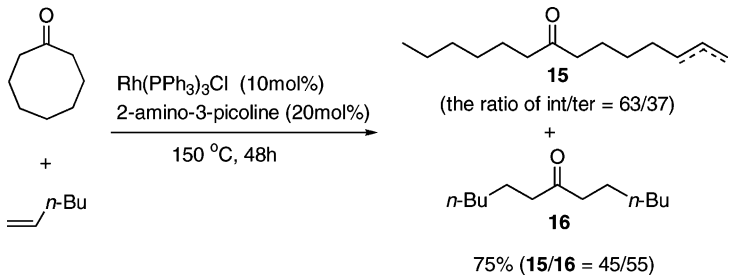

Fig. 8. Ring-opening reaction through C–C bond activation.

derived from **18** via the *syn-anti* isomerization of imine [54] followed by the second C–C bond activation.

When cycloheptanoketimine **20**, a very active substrate for C–C bond activation, was treated with $[Rh(C_8H_{14})_2Cl]_2$ and PCy_3 in the absence of external olefins, a mixture of the ring-contracted cycloalkanones (**21** and **22**) was obtained after hydrolysis without any ring-opened product. (Fig. 10).

The mechanism of this ring contraction is depicted in Fig. 11. The C–C bond cleavage in ketimine **20** by Rh(I) catalyst is followed by β-hydrogen elimination to afford an (iminoacyl)rhodium hydride **23**. A hydride inserts into the terminal olefin in **23** by Markovnikov's rule to give an (iminoacyl)rhodium alkyl **24**, which produces ketimine **25** through reductive elimination. And (iminoacyl)rhodium alkyl **24** is converted to **26**

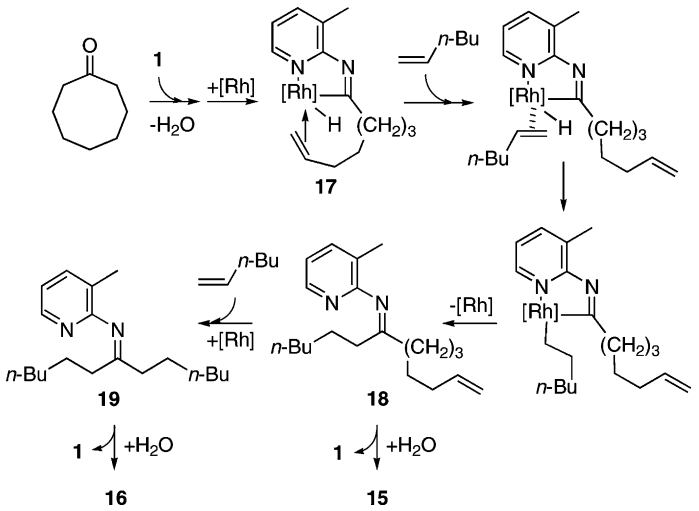

Fig. 9. The mechanism for a C–C bond activation of cycloalkanone.

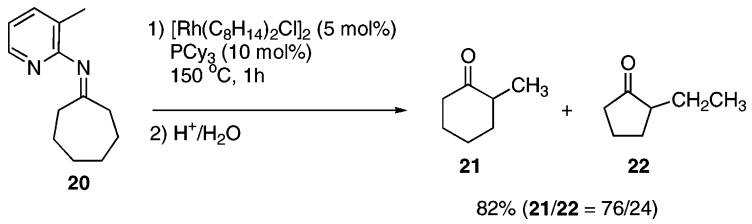

Fig. 10. Ring contraction of cycloheptanoketimine through C–C bond activation.

through the recurrence of β-hydrogen elimination and a hydride insertion. Therefore, the ring-contracted ketones **21** and **22** were produced from hydrolysis of ketimines **25** and **27**, respectively.

This ring rearrangement via the C–C bond activation strongly depends on the ring size of cycloalkanoketimines. Unlike cycloheptanoketimine, cyclohexanoketimine was exclusively rearranged to 2-methylcyclopentanone in a low yield (21%). In the case of cyclooctanoketimine, a mixture of 2-methylcycloheptanone and 2-ethylcyclohexanone was obtained in only 12% yield. And, ketimines larger than cycloctanoketimine showed no reactivity toward the ring rearrangement. Therefore, this ring contraction seems to occur to generate a medium-sized (5–7) cycloalkanone, which is assumed to be energetically favored to bring about the reductive elimination to a branched ring-contraction product. This might be the reason why cycloheptanone is the best substrate for this ring contraction reaction.

Interestingly, bicyclo[3.2.1]octan-2-one (**28**) was subject to the ring rearrangement reaction, because it contains the most reactive seven-membered cyclic ketone structure (see Fig. 12). This bicyclic skeleton has two possible bonds (a and b) to be cleaved. The C–C bond cleavage in ketimine of bicyclo[3.2.1]octan-2-one took place at bond a rather than bond b to afford bicyclo[3.3.0]octan-2-one (**29**), although bond a is sterically more congested. This result might be explained by that the

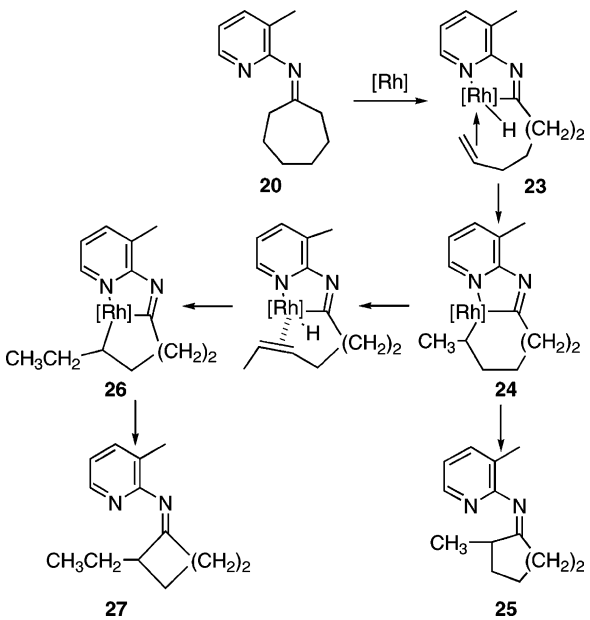

Fig. 11. The mechanism for ring contraction of cycloheptanoketimine.

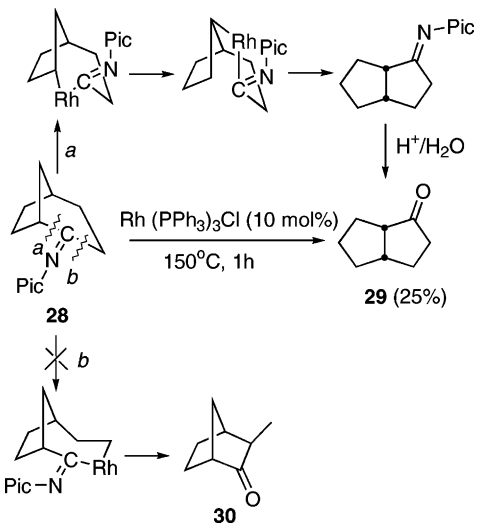

Fig. 12. Rearrangement of bicyclo[3.2.1]octan-2-one through C–C bond activation.

formation of bicyclo[3.3.0]octan-2-one (**29**) is thermodynamically more favorable than that of strained 3-methyl-bicyclo[2.2.1]heptan-2-one (**30**) generated from the cleavage of bond b.

3. Catalytic C–H and C–C bond activation of allylamine derivatives via isomerization

As an extension of our hydroacylation of olefin with aldehydes, we were interested in the synthesis of symmetric dialkyl ketones from formaldehyde through a tandem reaction consisting of a hydroformylation of olefin and a subsequent hydroacylation of the resulting aldehyde. However, our attempts to utilize the chelation-assisted hydroacylation with formaldehyde failed and an alternative route was required to obtain a symmetric dialkyl ketone. So far, we had tried to find a substitute for formaldehyde, and finally aliphatic aldehyde bearing β-hydrogen was found to be good substrates for the synthesis of symmetric dialkyl ketones. An aliphatic aldehyde bearing a β-hydrogen could be hydroacylated with olefin to give a ketone through a C–H bond activation, and further undergo the C–C bond activation to exchange the remaining aliphatic group with olefin and finally generate a symmetric dialkyl ketone. However, this reaction showed a low reactivity, which might be caused by the formation of an aminal instead of an aldimine from the reaction of an aliphatic aldehyde and **1**. To solve such problem with the aliphatic aldehyde, we decided to utilize an allylamine derivative of **1**, which could be easily isomerized to an aldimine by a metal complex [55,56]. As expected, the allylamine derivative turned out to be the most suitable for this reaction, in which the combination of the Rh(I) complex and PCy_3 was the most effective catalytic system [57].

The reaction of an allylamine **31** and 3,3-dimethylbutene under $[Rh(C_8H_{14})_2Cl]_2$ and PCy_3 yielded a mixture of 2,2,8,8-tetramethyl-5-nonanone (**32**) and 6,6-dimethyl-1-phenyl-3-heptanone (**33**) in 97% yield (**32**/**33** = 95/5) within 1 h. It is quite interesting that the reaction rate of this allylamine system is exceptionally fast: a total yield of **32** and **33** is 82% in only 5 min, and 30 min is an enough time to obtain the symmetric dialkyl ketone **32** in over 90% yield (Fig. 13).

Under the Rh(I) catalyst, an allylamine is initially isomerized to aldimine which undergoes the hydroiminoacylation of olefin to form a ketimine. And this ketimine reacts further with olefin to generate a symmetric dialkyl ketimine via the C–C bond activation. This sequential reaction is composed of the following metal-catalyzed reactions: olefin isomerization, hydroiminoacylation via C–H bond activation, and hydroiminoacylation via C–C bond activation (Fig. 14).

The use of $Ru_3(CO)_{12}$ instead of the Rh(I) catalyst as a catalyst led to the mono-alkylated ketone **33**, which results from an olefin isomerization followed by a single hydroiminoacylation via a C–H bond activation (Fig. 15). From this result, it is inferred that the Rh(I) complex is very efficient for both C–H and C–C bond activations while the Ru(0) complex is active only for C–H bond activation and olefin isomerization.

4. Catalytic C–C bond activation of primary amines and *sec*-alcohols via dehydrogenation

4.1. The catalytic C–H and C–C bond activation of primary amines through dehydrogenation

From above results, we found that imines such as aldimines and ketimines are good substrates for C–H

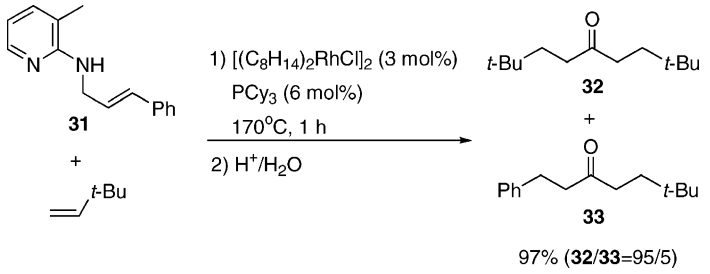

Fig. 13. Synthesis of symmetric dialkyl ketone using allylamine derivative.

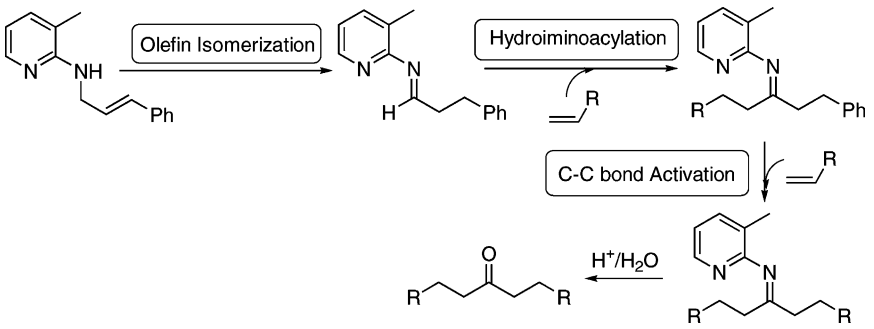

Fig. 14. A series of metal-catalyzed reactions for generating symmetric dialkyl ketone.

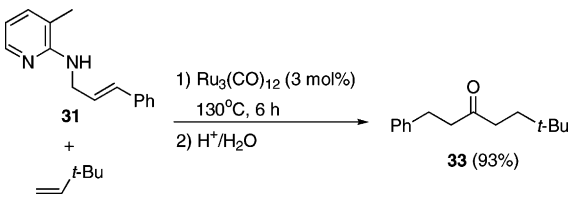

Fig. 15. Hydroiminoacylation of olefin by Ru(0) catalyst.

and C–C bond activations. Since the formation of imines from primary amines under a transition metal catalyst through dehydrogenation was recently utilized for the synthesis of secondary amines [58–60], we have investigated the possibility of primary amine as a substrate for our hydroacylation. When the reaction of primary amine **34** with 3,3-dimethyl-1-butene was carried out at 170 °C for 24 h under the catalyst system of $Rh(PPh_3)_3Cl$ and **1**, the hydroacylated product **36** was obtained in good yields [61] (Fig. 16).

The reaction mechanism is illustrated in Fig. 17. Initially, the primary amine **34** is dehydrogenated by Rh(I) catalyst and olefin to give the imine **37**. The unstable imine **37** is transformed into the more stable imine **38** via transimination [62] by the unreacted amine **34** with the extrusion of NH_3 [59]. The second transimination of the imine **34** by **1** generates the imine **39**, which then undergoes hydroiminoacylation with olefin to give the ketimine **40**. Finally, the resulting ketimine **40** is again transiminated by the amine **34** to afford the ketimine **35**. Then hydrolysis of the ketimine **35** produces the corresponding ketone **36** with liberating the primary amine **34**. Eventually, olefins in this reaction act as a hydrogen acceptor as well as a substrate for hydroiminoacylation.

Furthermore, this method was applied to the synthesis of the symmetric dialkyl ketones. Then, only half of the primary amine **34** is consumed for the formation of the ketone **36** in this reaction since the ketimine **35** consists of 2 mol of the starting primary amine **34**. To solve such problem, H_2O and $AlCl_3$ were added to liberate the amine **34** from the ketimine **35**. Thus, the reaction of 3-phenyl propylamine **41** with olefin

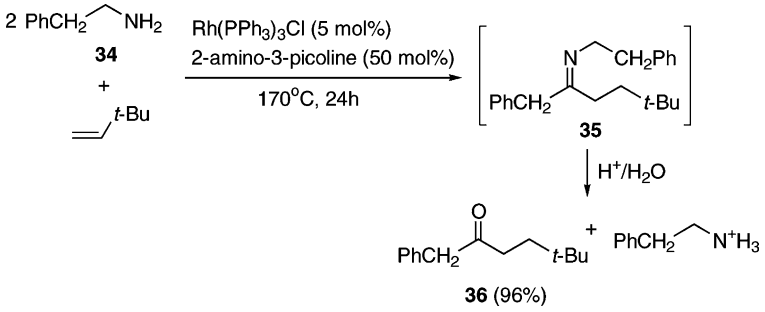

Fig. 16. The generation of ketone from primary amine through dehydrogenation.

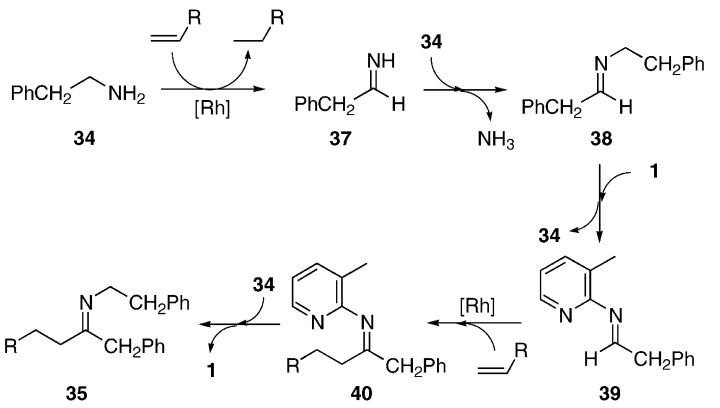

Fig. 17. The mechanism for the transformation of primary amine to ketone.

was performed in the presence of H_2O and $AlCl_3$ under the catalyst system of $Rh(PPh_3)_3Cl$ (10 mol%) and **1** (100 mol%) at 170 °C for 48 h (Fig. 18). As a result, the ketone **32** and the hydroacylated ketone **33** were obtained in 97% yield with a ratio of 1:1. The formation of the symmetric dialkyl ketone **32** is considered to include the chelation-assisted C–C bond cleavage followed by the coupling reaction with olefins. Therefore, this reaction for the synthesis of the symmetric dialkyl ketones demonstrated the consecutive C–H and C–C bond activation via iterative installation of a chelation-assistant tool by transimination.

4.2. The catalytic C–C bond activation of sec-alcohols via hydrogen transfer

A secondary alcohol, just as in the case of a primary amine, is one of the promising candidates for a C–C bond activation since the facile interconversion between alcohols and carbonyl compounds can be achieved through hydrogen transfer [63–67]. In fact, primary alcohols had been already utilized as a substrate for the hydroacylation of olefins in a similar manner [68]. Therefore, as depicted in Fig. 19, *sec*-alcohols would undergo the C–C bond activation of the ketone intermediate that is generated by hydrogen transfer in one-pot. In this reaction, olefins act as hydrogen acceptors as well as a C–C bond coupling partner.

The reaction of 4-phenyl-2-butanol (**42**) and 3,3-dimethyl-1-butene was conducted in the presence of 0.5 mol% of K_2CO_3 to afford the C–C bond activation product, 5,5-dimethyl-2-hexanone (**7**) in a high yield, along with benzylacetone derived from **42** by hydrogen transfer [69] (Fig. 20). Upon optimization of the reaction condition, it was found that the amount of a base such as K_2CO_3 was an important factor to the overall reactivity and only a small amount of a base should be added to prompt the oxidation of *sec*-alcohols with maintaining the reactivity of the C–C bond activation.

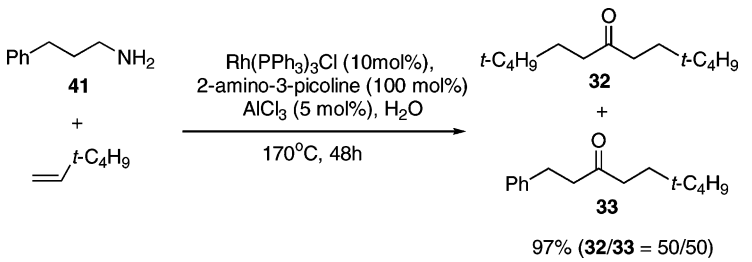

Fig. 18. Synthesis of symmetric dialkyl ketone from primary amine through dehydrogenation.

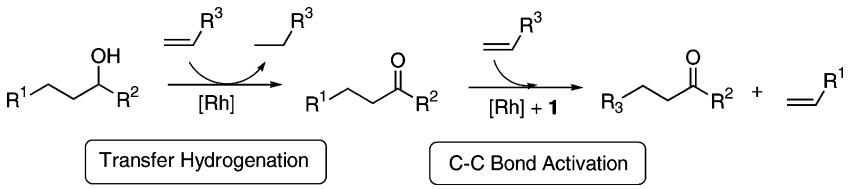

Fig. 19. C–C bond activation of *sec*-alcohol through hydrogen transfer.

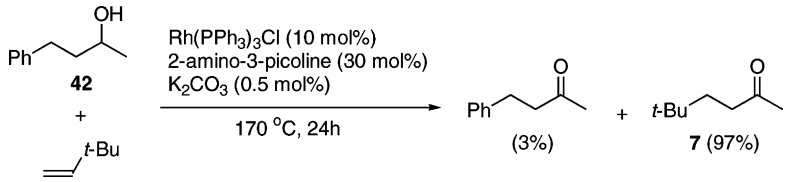

Fig. 20. C–C bond activation of *sec*-alcohol by Rh(I) with a base.

However, it turned out that only 0.5 mol% of potassium carbonate suffices for this reaction unlike the well-known ruthenium catalyzed transfer hydrogenation where a large amount of a base should be loaded. The extent of a C–C bond activation decreases as the amount of K_2CO_3 increases, while the oxidation rate of alcohols increases with K_2CO_3 added. It might be ascribed to the fact that a base could deteriorate the activity of the rhodium complex for the C–C bond activation.

5. Conclusion

To develop the Rh(I)-catalyzed C–C bond activation of unstrained ketones, we utilized a chelation-assistance strategy in which a 2-aminopyridine derivative was employed as a chelation auxiliary so as for the substrates to be equipped with a coordinating functionality. The coordination of the pyridinyl moiety in the imine intermediate to the rhodium complex could direct the cleavage of the C–C bond a to the imine functionality, which is driven by the formation of a stable five-membered metalacycle. For the catalytic alkyl-exchanged process, ketones should possess a β-hydrogen and simultaneously an excess of external olefins was added to replace olefins generated from the preceding β-hydrogen elimination.

The alkyl-exchanged reaction via C–C bond activation was applied to cycloalkanones to produce a mixture of ring opened alkenyl ketones and a symmetric dialkyl ketone by a double C–C bond coupling. In the absence of external olefins, for example, cycloheptanones underwent a ring contraction reaction to afford more stable five- and six-membered rings.

sec-Alcohols instead of unstrained ketones were also subject to this C–C bond activation since the addition of a base facilitated the conversion into the corresponding ketones via hydrogen transfer under the same reaction condition. The synthesis of a symmetric dialkyl ketone was accomplished by a consecutive C–H/C–C bond activation from not only allylamine derivatives via olefin isomerization, but also primary amines via dehydrogenation.

In conclusion, we established the Rh(I)-catalyzed C–C bond activation of unstrained ketones having a β-hydrogen by utilizing a 2-aminopyridine derivative as a chelation assistant tool. This reaction is so efficient and general to be possibly applied to organic synthesis. Therefore, this method strongly demonstrates that a chelation-assistance for the formation of a stable metalacycle is one of the most promising strategies for the activation of C–C bonds.

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