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Application of C–H and C–C bond activation in organic synthesis*

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Abstract: Herein we describe the chelation-assisted C–H and C–C bond activation by Rh(I) catalysts and its application directed toward the formation of C–C bonds in organic synthesis.

INTRODUCTION

Transition metal-catalyzed C–H bond activation has received considerable attention in synthetic organic chemistry since the cleavage of an unreactive C–H bond and subsequent addition of the C–H unit into unsaturated substrates such as olefins and alkynes could lead to the formation of a new C–C bond [1]. The formation of C–C bond is one of the most fundamental projects in organic chemistry. Much effort has naturally been devoted to develop more convenient and efficient strategies for the formation of C–C bonds. During the last two decades, many successful applications of catalytic C–H bond activation directed toward the construction of C–C bonds have been reported in synthetic communities [2]. Compared to C–H bond activation, however, the activation of C–C bonds is more challenging in chemistry [3]. A limited number of the homogeneous catalytic activation of C–C bonds has been reported. Most examples are dependent on the benefit of the releasing ring strain of small ring-sized molecules.

Over the past several years, we have developed some useful Rh(I)-catalyzed C–H and C–C bond activation processes using 2-aminopyridine derivatives as a chelation-assisted auxiliary [4]. In this account, we present some of our recent works focusing on various kinds of C–C bonds that can be constructed efficiently using the chelation-assisted C–H and C–C bond activation protocols.

HYDROACYLATION OF OLEFIN VIA C–H BOND ACTIVATION

The transition metal-catalyzed intermolecular hydroacylation of olefin is one of the most useful C–H bond activation processes. Regio- and chemoselective insertion of an aldehydic C–H bond into the C–C double bond of olefins leads to the formation of a new C–C bond, and the corresponding ketones can be obtained as a coupling product. The major limitation of hydroacylation is the instability of the acylmetal hydride intermediate and the resulting competitive decarbonylation pathway [5]. To stabilize the acylmetal hydride and suppress decarbonylation, some catalytic reactions were carried out under the high pressure of ethylene or CO [6]. To overcome the harsh reaction conditions of these systems, cyclometallation has been introduced as a directing strategy for the hydroacylation with aldehydes such as quinoline-8-carboxaldehyde [7a] and *o*-diphenylphosphinobenzaldehyde [7b], which are able to form a stable five-membered metallacycle with a transition metal.

Another strategy based on cyclometallation was ingeniously developed by Suggs in 1979 [8]. This strategy is conceptually different from that of hydroacylation. In place of aldehydes, an aldimine

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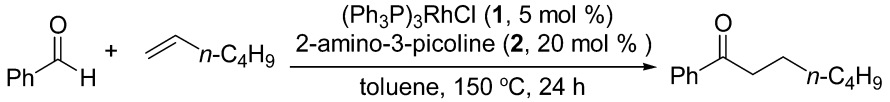
was utilized in the Rh(I)-catalyzed hydroiminoacylation to prevent decarbonylation. A stable (imino)acylrhodium(III) hydride is believed to be a key intermediate of this reaction. Recently, we have developed a more convenient hydroiminoacylation protocol using not only chlorotris(triphenylphosphine)rhodium (**1**) but also 2-amino-3-picoline (**2**) as a chelation auxiliary [9]. An aldimine could be generated in situ from a condensation of the corresponding aldehyde with **2**, and it would be further transformed into the corresponding ketimine by a transition-metal catalyst. For example, when benzaldehyde was treated with 1-hexene in the presence of **1** and **2** as a cocatalyst, the corresponding linear ketone, heptanophenone, was obtained as a sole product in a good yield (eq. 1).



(1)

The proposed mechanism for this reaction is speculated in Fig. 1 [9a]. The first step might consist of the condensation of benzaldehyde with **2** to give the corresponding aldimine **3** and H_2O. Formation of a five-membered (iminoacyl)rhodium(III) hydride **4** via C–H bond activation can be facilitated by the precoordination of the pyridine moiety in **3** onto the rhodium catalyst, which allows the transition metal to be situated with proximity to the sp^2 C–H bond. Coordination of olefin **5** to the metallacycle **4** gives **6**. An (iminoacyl)rhodium alkyl **7** is obtained from **6** through hydrometallation in an anti-Markovnikov way. Reductive elimination in **7** furnishes ketimine **8** as a coupling product. Subsequent hydrolysis of **8** with H_2O, generated in the condensation step, gives ketone **9** with the regeneration of **2**. As a result, a one-step synthesis of ketones from aldehydes has been developed without the isolation of aldimines and the hydrolysis of ketimines using a cocatalyst system of **1** and **2**.

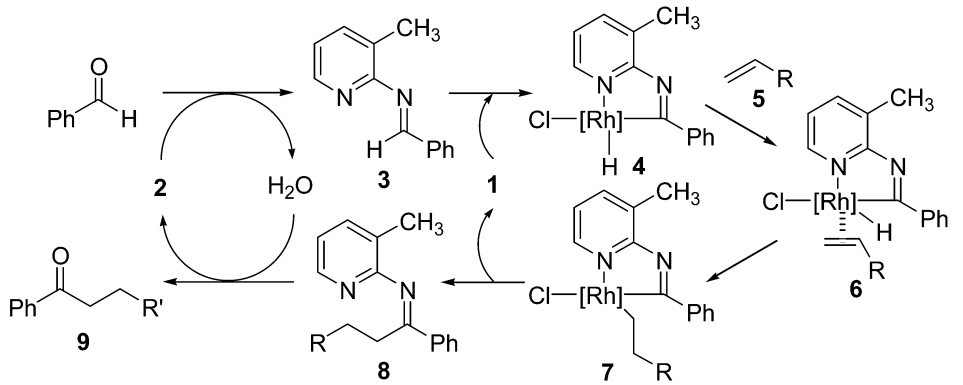
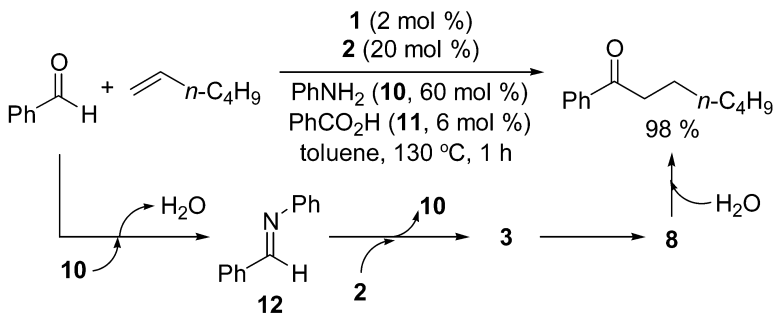


Fig. 1 The mechanism of chelation-assisted hydroacylation of olefins.

During the course of investigation, it was found that two more additives, aniline (**10**) and benzoic acid (**11**), dramatically accelerated the rate of the catalytic intermolecular hydroacylation reaction [10]. When a mixture of benzaldehyde and hex-1-ene was heated in the presence of **1**, **2**, **10**, and **11**, heptanophenone was isolated in a nearly quantitative yield after 1 h (eq. 2). In the presence of the acid catalyst **11**, aniline (**10**), more nucleophilic than 2-amino-3-picoline (**1**), is condensed with benzaldehyde to give aldimine **12**. Subsequent transimination of the aldimine **12** with **1** gives another aldimine **3** with the liberation of **10**. The aldimine **3** is then transformed into ketimine **8** by the hydroiminoacylation mechanism [10]. Finally, **8** is hydrolyzed by H_2O, generated from the condensation, to afford a ketone (eq. 2). Highly enhanced reactivity of this cocatalyst system strongly suggests that both the condensation of an aldehyde with **10** and subsequent transimination are facilitated by the acid catalyst **11**.



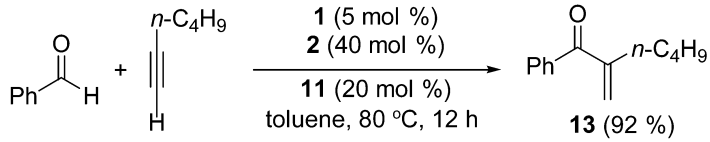
(2)

Some alcohols, which can be oxidized into the corresponding aldehydes by transition metals, can be utilized in the chelation-assisted Rh(I)-catalyzed hydroacylation of olefins. For example, various benzyl and allylic alcohols can be converted into ketones via the corresponding aldehyde through the reaction with olefins under a cocatalyst system of **1**, **2**, and **11** [11]. A primary amine can also be used as a substrate in the chelation-assisted Rh(I)-catalyzed C–H bond activation, because it can be readily dehydrogenated to give the corresponding aldimine by the transition-metal catalyst [12].

HYDROACYLATION OF ALKYNE VIA C–H BOND ACTIVATION

Relatively less attention has been paid to the intermolecular hydroacylation of alkynes with aldehydes, and only a few nonselective examples have been reported with limited applications to internal alkynes [13] or specific aldehydes [14]. A new C–C bond between sp^2-hybridized carbonyl group and sp^2-hybridized olefinic carbon can be formed through this reaction.

We have recently reported a highly regio- and stereoselective intermolecular hydroacylation of 1-alkynes with aldehydes using the chelation-assisted catalytic system. Benzaldehyde was treated with hex-1-yne in the presence of the cocatalysts consisting of **1**, **2**, and **11** to give a branched α,β-enone **13** as a sole product in an excellent yield (eq. 3) [15]. It was found that most aromatic aldehydes tested underwent smooth hydroacylation with 1-alkynes to produce branched α,β-enones exclusively in good to excellent yields. At the present time, this system seems to be the most efficient for the selective synthesis of branched α,β-enone from aromatic aldehydes and 1-alkynes.



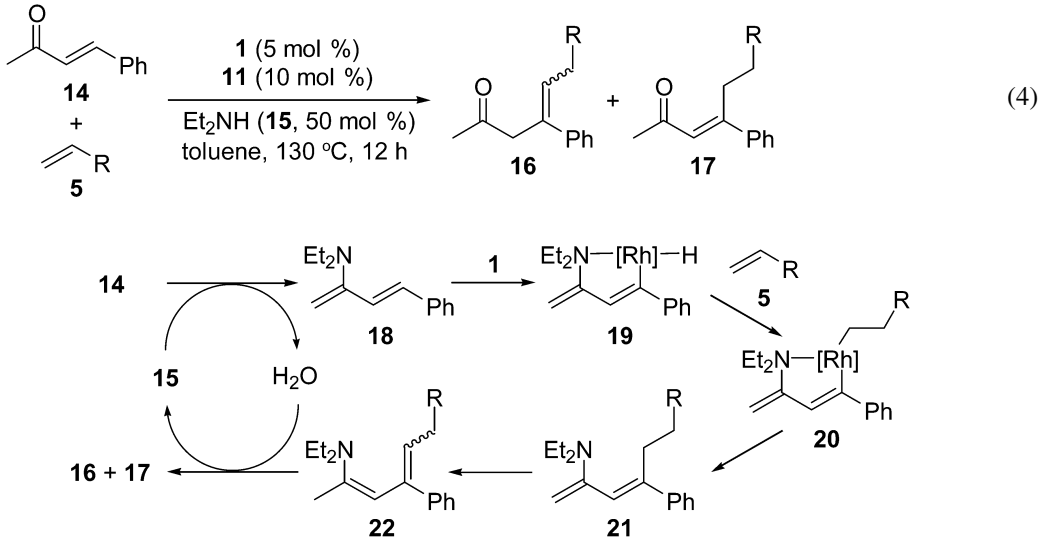
(3)

β-ALKYLATION OF α,β-UNSATURATED KETONES

Selective formation of C–C bonds at the β-position of α,β-unsaturated carbonyl compounds by the addition of the β vinylic C–H bond across unsaturated molecules is called as β-alkylation, and it constitutes a very useful strategy for the elaboration of simple alkenes into more complex ones. A few catalytic systems for the β-alkylation of α,β-unsaturated carbonyl compounds using Ru(II) complex were reported by Trost and Murai [16]. Though the Ru(II)-catalyzed reaction shows a high reactivity with vinylsilane or styrene, other common olefins seem not to be adequate for this catalytic reaction.

The successful application of a chelation-assistant tool into the Rh(I)-catalyzed *ortho*-alkylation of aromatic ketimines [17] prompted us to develop a new catalytic system for the β-alkylation of carbonyl compounds using a chelation auxiliary. Using 4-phenylbut-3-en-2-one (**14**) as a model substrate, we investigated the β-alkylation of α,β-unsaturated ketones with various olefins. The reactions of enone **14** with terminal olefin **5** were performed in the presence of diethylamine (**15**) as well as **1** and **11**. All reactions tested proceeded smoothly to give a mixture of β,γ-enone **16** and α,β-enone **17** in good to ex-

cellent yields (eq. 4) [18]. Some experimental results support the proposed mechanism, which is shown in Fig. 2. (1) In the absence of **15**, β-alkylation did not proceed at all and only the starting enone **14** was completely recovered. This result implies that dienamine **18**, which is derived in situ from the condensation of the enone **14** with **15**, might be a key intermediate of the reaction. (2) Steric requirement of dialkylamine also affects strongly on the overall catalysis that no β-alkylated product is obtained when sterically more hindered diisopropylamine is used instead of **15**. This result strongly suggests that the facile chelation of a rhodium species to the nitrogen functionality of **18** is a decisive factor for the efficiency of the reaction, and thereby a vinylic C–H bond could be cleaved to generate five-membered metallacycle **19**. Alkylation of **19** with **5** followed by reductive elimination in **20** furnishes β-alkylated dienamine **21** that equilibrates with regioisomer **22**. Hydrolysis of both **21** and **22** affords the β-alkylated products **16** and **17**.



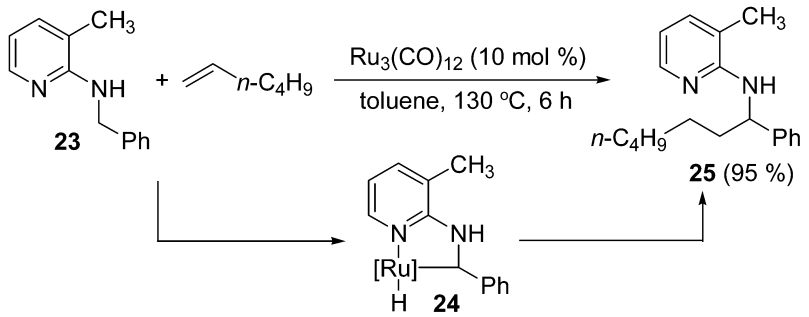
(4)

Fig. 2 A plausible mechanism for the Rh(I)-catalyzed β-alkylation of **14** with olefin.

ALKYLATION OF BENZYLAMINE DERIVATIVES VIA sp^3 C–H BOND ACTIVATION

Most catalytic C–H activations that have been developed to date are focused on the cleavage of sp^2 C–H bonds. In contrast, catalytic reactions involving the cleavage of sp^3 C–H bonds are still rare [19]. In fact, development of new catalytic processes including the activation of sp^3 C–H bonds is one of the most challenging subjects in organic chemistry. It is believed that the cleavage of sp^3 C–H bonds is thermodynamically and kinetically unfavorable. In the past decade, however, some transition metal-catalyzed reactions, which involve the cleavage of sp^3 C–H bond adjacent to heteroatoms such as oxygen and nitrogen, have been reported [20]. These examples suggest that a heteroatom can make the adjacent sp^3 C–H bond kinetically labile by allowing a transition metal to be sufficiently close to the bond, and thereby the sp^3 C–H bond can be cleaved to form a thermodynamically stable metallacycle.

To develop a new catalytic reaction, which involves the cleavage of an unreactive sp^3 C–H bond, we turned our attention to *N*-pyridylbenzylamine derivatives possessing nitrogen functionalities on the reactive benzylic position. When *N*-benzyl-*N*-(3-methylpyridin-2-yl)amine (**23**) was reacted with an excess of 1-hexene in the presence of catalytic amount of $Ru_3(CO)_{12}$, the corresponding alkylated product **25** was obtained (eq. 5). The intermediate of this reaction might be the five-membered metallacycle **24**, which could be formed by the oxidative addition of a Ru(0) catalyst to the benzylic C–H bond in **23** [21]. It is demonstrated that the presence of both the 3-methyl group and the pyridyl group in **23** is the critical prerequirement for the successful cleavage of the benzylic C–H bond. The 3-methyl group



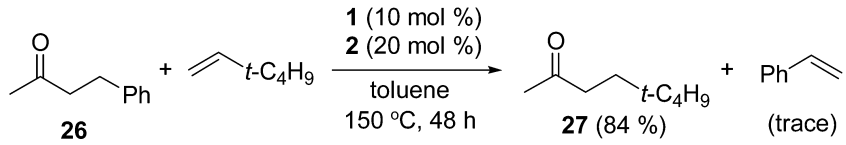
(5)

of **23** can restrict the conformation of the benzyl group, and helps the Ru catalyst to approach to the benzylic C–H bond after the precoordination of the catalyst onto the pyridyl nitrogen atom of **23**.

C–C BOND ACTIVATION OF UNSTRAINED KETONES

A variety of chemical bonds can be activated by transition-metal complexes. However, the activations of carbon–carbon sigma bonds are much more difficult than those of carbon–hydrogen bonds. It is well known that the inertness of C–C sigma bond originates not only from its thermodynamic stability, but also from its kinetic inertness. Highly ring-strained cyclopropanes have frequently been used as a substrate for C–C bond activation since the use of them is beneficial kinetically as well as thermodynamically [3a]. Strained carbonyl compounds such as cyclobutanones are also used since the strained C–C single bond α to a carbonyl group is weaker than other C–C bonds [22].

Recently, it was demonstrated that the carbon–carbon bond of unstrained ketones could be cleaved by a rhodium catalyst using the chelation-assisted strategy. For example, when benzylacetone (**26**) was heated with 3,3-dimethylbut-1-ene in the presence of **1** and **2**, 5,5-dimethylhexan-2-one (**27**) was isolated as a major product along with a trace amount of styrene (eq. 6) [23]. The alkyl-exchanged ketone **27** must be derived from the replacement of a phenethyl group of **26** with the 3,3-dimethylbutyl group through the cleavage of an C–C bond α to the carbonyl group. As illustrated in Fig. 3, the reaction commences with the formation of ketimine **28** from the condensation of **26** with **2**. Precoordination of a rhodium complex to the pyridyl group in **28** can facilitate the cleavage of the C–C bond α to the imino group. Thus, the α C–C bond in **28** could be cleaved by the Rh(I) complex to afford metallacycle **29**. β-Hydride elimination in **29** followed by the hydrometallation of **31** onto 3,3-dimethylbut-1-ene furnishes (iminoacyl)rhodium(III) alkyl **32**. Reductive elimination in **32** produces ketimine **33**, which is hydrolyzed into the alkyl-exchanged ketone **27**.



(6)

As shown in eq. 7, C–C bond activations of unstrained cycloalkanone derivatives were also investigated. A mixture of ring-contracted cycloalkanones, 2-methylcyclohexanone (**37**) and 2-ethylcyclopentanone (**38**), was obtained after hydrolysis when cycloheptanoketimine **34** was treated with $[Rh(C_8H_{14})_2Cl]_2$ (**35**) and tricyclohexylphosphine (**36**) in the absence of any external olefins [24]. Interestingly, any ring-opened product was not detected. The ring-contracted products **37** and **38** seem to be formed via (imino)acylrhodium(III) hydride **39**, which could be generated through the C–C bond cleavage in **34** by a Rh(I) catalyst and subsequent β-hydride elimination in the resulting intermediate.

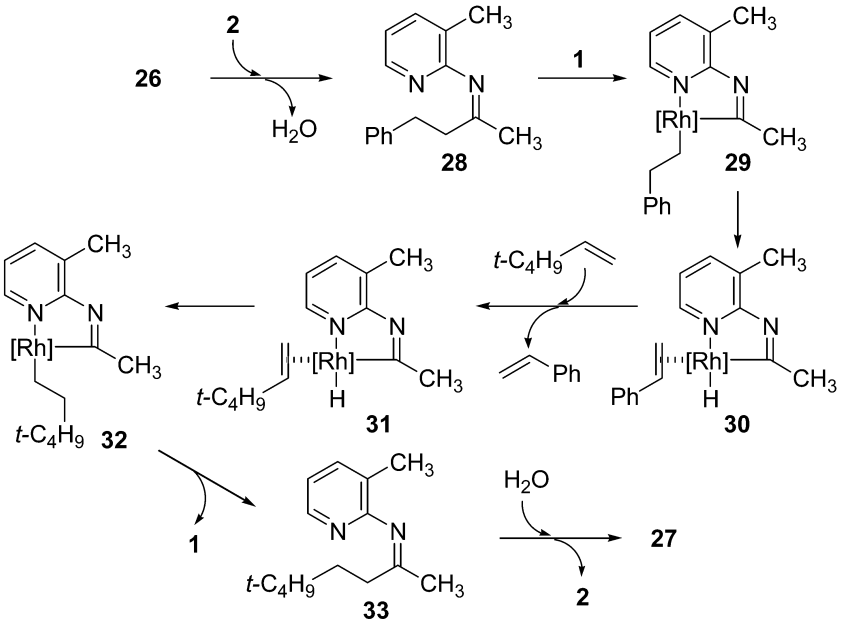
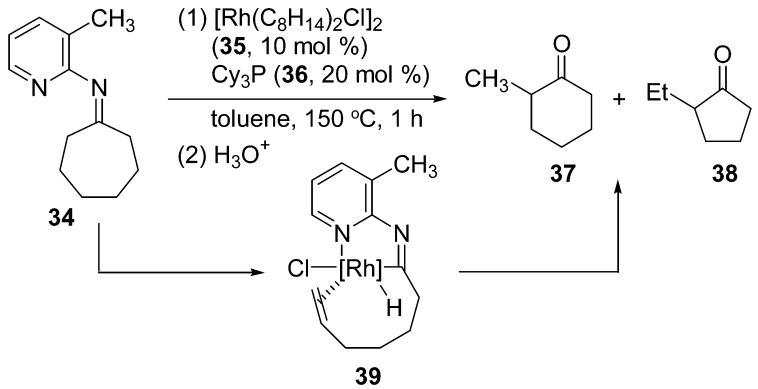


Fig. 3 The proposed mechanism for a chelation assisted C–C bond activation of unstrained ketone.

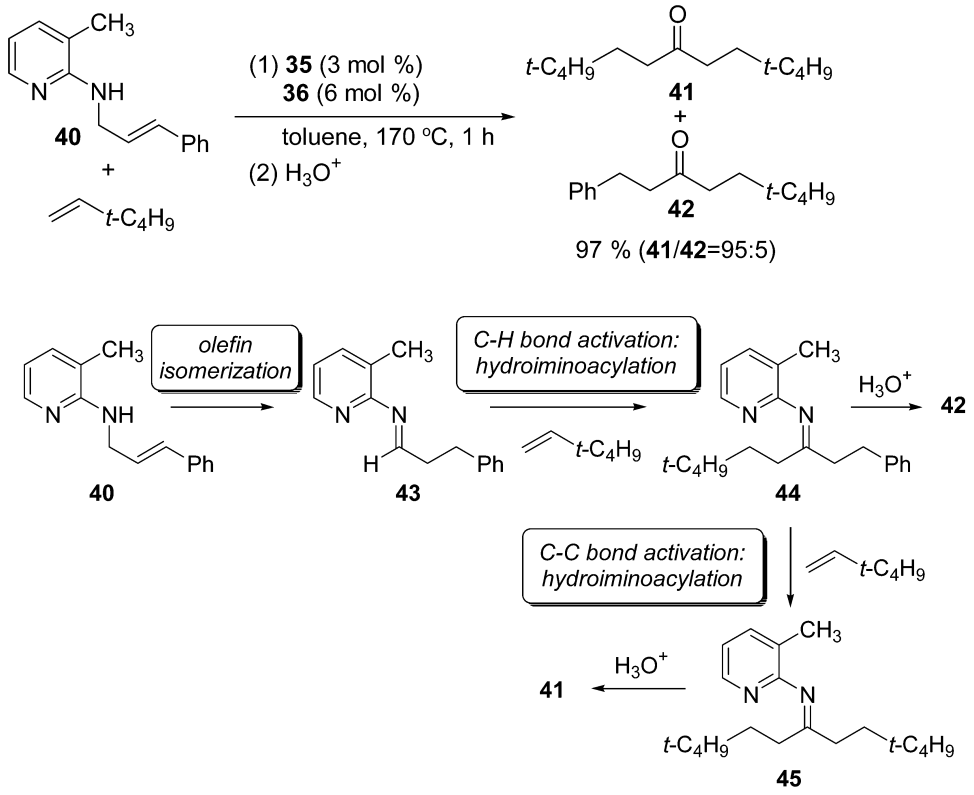


(7)

C–H AND C–C BOND ACTIVATION OF ALLYLAMINE DERIVATIVES

As discussed above, the hydroacylation of olefins with aromatic aldehydes using the cocatalyst system of **1** and **2** is very useful for the preparation of various unsymmetrical alkyl aryl ketones. For the preparation of symmetrical dialkyl ketones, however, the hydroacylation of aliphatic aldehydes seems to be unsuitable because a side reaction, such as aldol condensation, could be problematic under the applied reaction condition. To overcome such a problem with aliphatic aldehydes, allylamine **40** was selected as an aldimine precursor since it could be readily isomerized into the corresponding aldimine through olefin isomerization by transition-metal complexes. When the reaction of **40** with 3,3-dimethylbut-1-ene under a Rh(I) catalyst gave symmetrical 2,2,8,8-tetramethylnonan-5-one (**41**) as a major product along with a small amount of unsymmetrical 6,6-dimethyl-1-phenylheptan-3-one (**42**) (eq. 8) [25]. A plausible explanation for the formation of both **41** and **42** is shown in Fig. 4. Aldimine **43**, derived from **40** through an olefin isomerization, could be transformed into ketimine **44** through the hydroiminoacylation of an olefin via C–H bond activation. Further hydroiminoacylation of **44** via C–C bond

activation would give another ketimine **45**. Finally, hydrolysis of both **44** and **45** produces the unsymmetrical ketone **42** and the symmetrical ketone **41**, respectively.



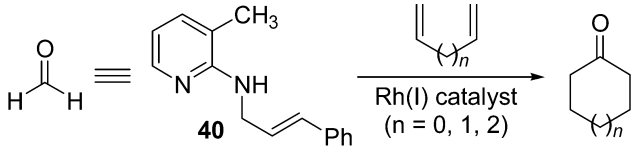
(8)

Fig. 4 A plausible explanation for the formation of both **41** and **42**.

SYNTHESIS OF CYCLOALKANONES FROM DIENES AND ALLYLAMINES

Intramolecular hydroacylation provides the most promising way to prepare cyclopentanones from pent-4-enal [26]. However, its application has been limited to the preparation of five-membered rings because the competing decarbonylation of the acyl metal hydride intermediate prevails during the formation of other larger rings.

Attempts to utilize formaldehyde as a substrate in the chelation-assisted double hydroacylation failed. Since decarbonylation cannot occur in the reaction with allylamine **40**, we envisaged that its application, as a synthetic equivalent of formaldehyde, into the cyclization with dienes could furnish cycloalkanones with various sizes through the consecutive C–H and C–C bond activation (eq. 9). When **40** was allowed to react with nonsubstituted dienes such as penta-1,4-diene and hexa-1,5-diene, not only the corresponding cycloalkanones, but ring-contracted products were also obtained. For example, the reaction of **40** with penta-1,4-diene was performed in the presence of $[Rh(C_8H_{14})_2Cl]_2$ (**35**) and PCy_3 (**36**) to afford cyclohexanone and 2-methylcyclopentanone in a 87 and 13 % yield, respectively [27]. Cycloheptanone, 2-methylcyclohexanone, and 2-ethylcyclopentanone were obtained in a ratio of 38:40:22 from the reaction of **40** with hexa-1,5-diene. However, the reaction with 1,4- or 1,5-dienes bearing substituents at C2 or C3 position gave substituted cyclohexanones or cycloheptanones, respectively, as a sole product without forming ring-contracted products.

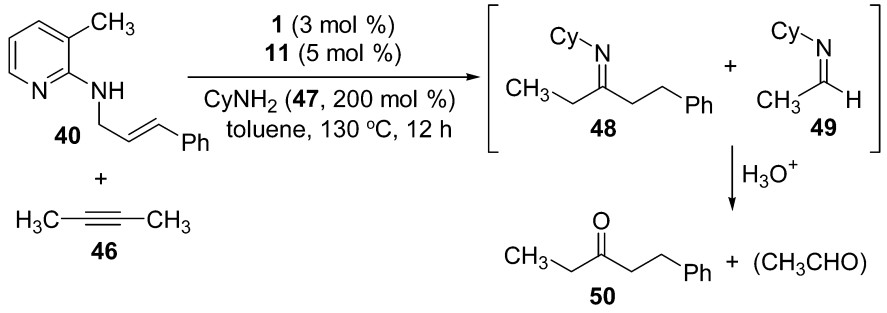


(9)

CLEAVAGE OF C–C TRIPLE BOND

A carbon–carbon triple bond of alkynes is one of the strongest chemical bonds. Therefore, the cleavage of alkyne triple bonds is restricted to a few examples including alkyne-ligand scission on transition-metal complexes [28a], oxidative cleavage [28b], alkyne metathesis [28c], and others [28d]. During the course of our investigation of the chelation-assisted activation of C–H and C–C bond, we found that the C–C triple bond of alkynes could be cleaved through the hydroiminoacylation of alkynes using allylamine derivatives.

The reaction of allylamine **40** with but-2-yne (**46**) in the presence of **1**, cyclohexylamine (**47**), and **11** afforded a mixture of ketimine **48** and aldimine **49** determined by a GC-analysis (eq. 10) [29]. Acidic hydrolysis of **48** yielded 1-phenylpentan-3-one (**49**) in a quantitative yield. It is obvious that both ethylidene moiety of **49** and ethyl group of **48** are derived from the cleavage of the C–C triple bond of **46**. The proposed mechanism for this unusual transformation is depicted in Fig. 5. The transformation begins with the isomerization of **40** to **43**, which could undergo hydroiminoacylation with **46** to give α,β-unsaturated ketimine **51**. The conjugate addition of **47** into **51** followed by retro-Mannich-type fragmentation in the resulting β-amino ketimine **52** furnishes enamine **53** along with aldimine **49**. The enamine **53** is isomerized into ketimine **54**, which is then transiminated by cyclohexylamine **47** to give another ketimine **48** with the regeneration of **1**. Finally, acidic hydrolysis of both **48** and **49** furnishes the final product **50** and acetaldehyde, respectively.



(10)

A variety of alkynes can be successfully applied into this unique transformation to afford various ketones in good to excellent yields. However, an allylamine as a substrate cause a limitation to its versatile use. We were intrigued by the possibility of development of a more common protocol for the C–C triple bond cleavage using aldehyde instead of allylamine **40**. It is speculated that the key intermediate of the alkyne triple bond cleavage reaction, an α,β-unsaturated ketimine such as **51** (Fig. 5), could also be derived from an aldehyde and an alkyne using a cocatalyst of **1** and **2**. To examine this hypothesis, acetaldehyde was allowed to react with dodec-6-yne in the presence of **1**, **2**, **47**, and aluminum chloride. As expected, octan-2-one was obtained in a good yield after hydrolysis (eq. 11) [30].

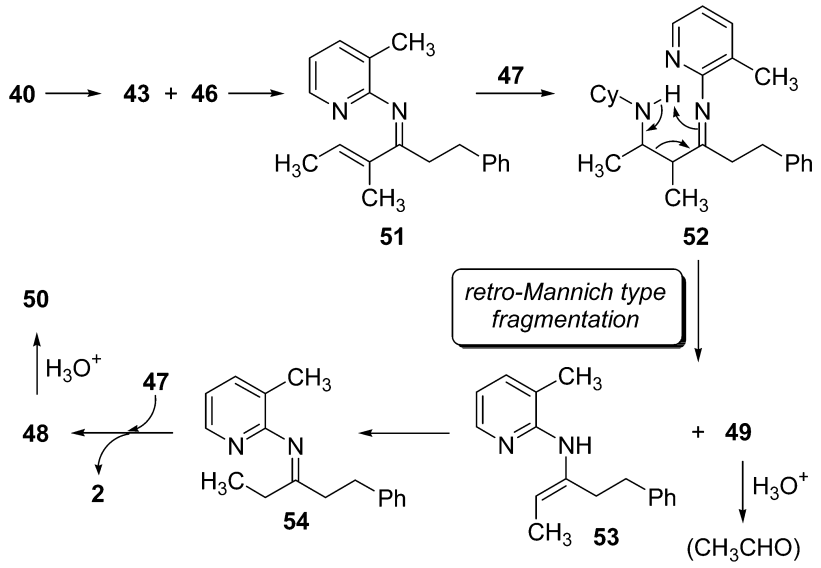
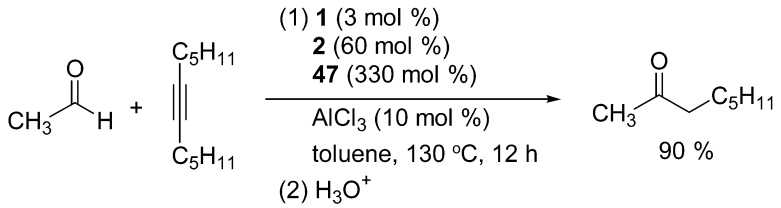


Fig. 5 A proposed mechanism for the cleavage of alkyne triple bonds.



(11)

CONCLUSION

As described above, some catalytic C–H and C–C bond activation processes have been developed based on a chelation-assisted cyclometallation strategy. It has been demonstrated that some kinds of chemically unreactive bonds could be easily activated by a reaction system employing Wilkinson's complex (**1**) and 2-amino-3-picoline (**2**). Some successful applications of catalytic C–H bond activation directed toward the construction of C–C bonds have been realized using this cocatalyst system. The usefulness of the chelation-assisted C–H bond activation process is indicated by its applications by other researchers [31].

The chelation-assisted cyclometallation strategy has also been successfully applied to the C–C bond activation of unstrained ketones, which leads to the formation of a new C–C bond at the α position of the carbonyl group. Allylamine **40**, which is readily isomerized to the corresponding aldimine by transition-metal complexes, can be used as a masked form of formaldehyde in the Rh(I)-catalyzed C–H and C–C bond activation processes. Thus, it was successfully utilized for the preparation of symmetrical diakyl ketones with 1-alkenes, and cycloalkanones with dienes. The chelation-assisted hydroacylation of alkyne with allylamine **40** has been further applied to the cleavage of C–C triple bond of alkyne through the retro-Mannich-type fragmentation with cyclohexylamine (**47**).

ACKNOWLEDGMENT

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