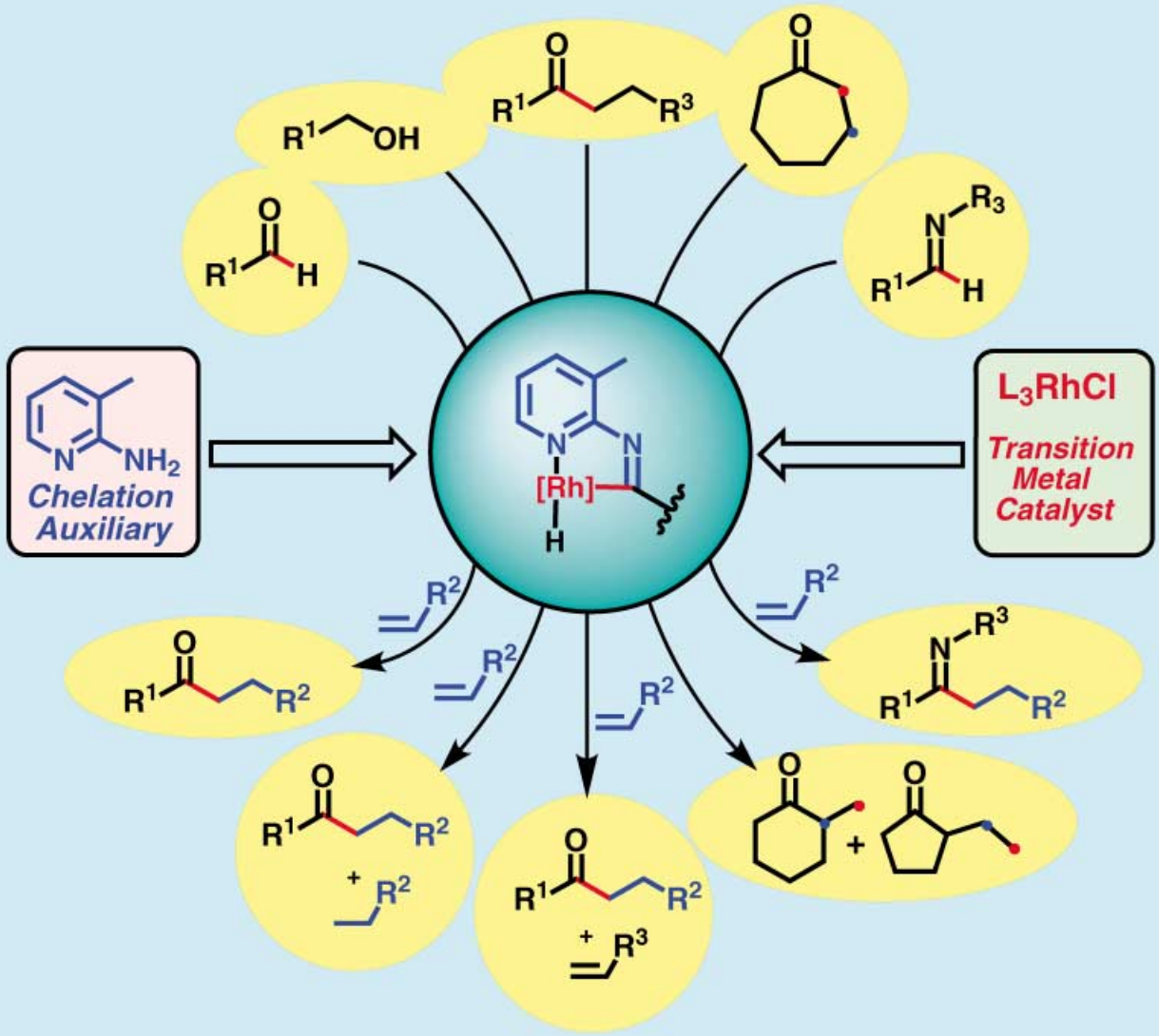
Catalytic C-H and C-C Bond Activation by Chelation-Assistance Strategy



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Chelation-Assisted Carbon–Hydrogen and Carbon–Carbon Bond Activation by Transition Metal Catalysts

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Abstract: Herein we describe the chelation-assisted C–H and C–C bond activation of carbonyl compounds by Rh^I catalysts. Hydroacylation of olefins was accomplished by utilizing 2-amino-3-picoline as a chelation auxiliary. The same strategy was employed for the C–C bond activation of unstrained ketones. Allylamine **24** was devised as a synthon of formaldehyde. Hydroiminoacylation of alkynes with allylamine **24** was applied to the alkyne cleavage by the aid of cyclohexylamine.

Keywords: C–C activation · C–H activation · chelation auxiliary · hydroacylation · rhodium

Introduction

The transition metal catalyzed activation of C–H and C–C bonds has recently attracted increasing attention in organometallic chemistry. For the last two decades, its utility in organic synthesis has been exemplified by valuable applications, for which the beneficial features in the aspect of atom economy and chemoselectivity were highlighted.[1]

Among various strategies to activate the C–H and C–C bonds by transition metal catalysts, a chelation-assistance strategy[2] utilizing cyclometalation[3] is considered to be one of the most promising ways. This strategy requires the existence of a coordination site to facilitate the access of a transition metal to the bond to be cleaved for the formation of a stable metallacycle. Thus, the application of this strategy is limited to the substrates bearing a coordination site.[1, 4]

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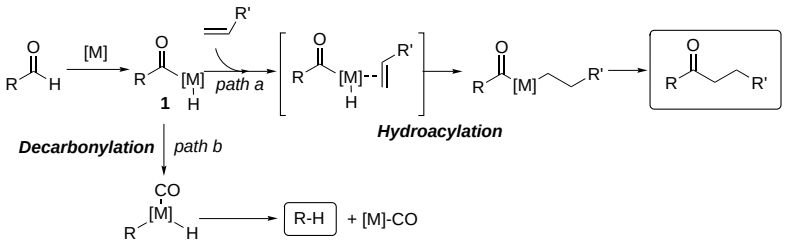
To apply the chelation-assistance strategy to the C–H and C–C bond activation of molecules with no coordination site, it is necessary to utilize a chelation auxiliary to induce cyclometalation. Herein we describe the Rh^I-catalyzed C–H and C–C bond activation of unstrained carbonyl compounds utilizing 2-amino-3-picoline as a chelation auxiliary. The reaction of allylamines derived from 2-amino-3-picoline will be elaborated; this is complementary to the protocol with a chelate auxiliary.

Chelation-Assisted C–H and C–C Bond Activation by Utilizing 2-Amino-3-picoline

General aspects of hydroacylation: Intermolecular hydroacylation of olefins with aldehydes is one of representative examples for the synthetic application of a transition metal catalyzed C–H bond activation (path a in Scheme 1).[5–7]

A key intermediate in hydroacylation is acylmetal hydride **1** generated from the oxidative addition of a transition metal into C–H bond in aldehyde. This intermediate **1** can undergo



Scheme 1. Hydroacylation of olefin with aldehydes by transition metal complexes.

the hydrometalation of the olefin followed by reductive elimination to give a ketone. Nevertheless, the hydroacylation is interrupted by decarbonylation (path b in Scheme 1), which is driven by the stability of a metal carbonyl complex.[8] Thus, the stabilization of the acylmetal hydride intermediate is essential to evade decarbonylation. For such purposes, catalyst systems under the high pressure of carbon monoxide,[5a,b] and ethylene[5c–e] have been devised to stabilize acylmetal hydride.[6] However, these systems lack in generality and efficiency due to the harshness of the reaction conditions and a limitation of olefins that can be used.[7]

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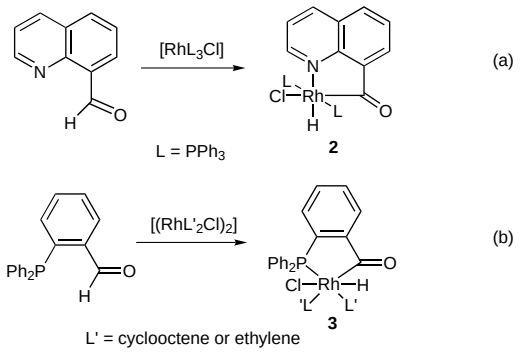
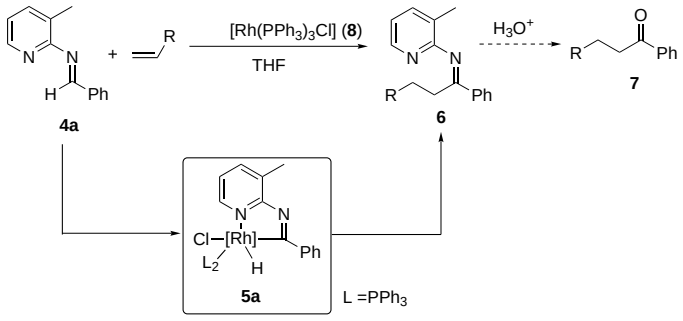
Meanwhile, an epoch-making strategy to utilize cyclometalation was demonstrated by model compounds such as 8-quinolinecarboxaldehyde[9] and 2-(diphenylphosphino)-benzaldehyde (Scheme 2).[10] This strategy is based on the fact that five-membered metalacycles (**2** and **3**) are so stable as to prevent decarbonylation.[11]



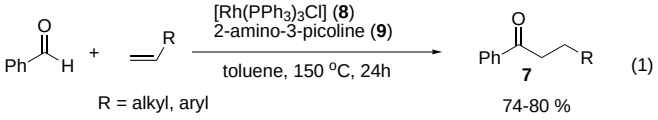
Scheme 2. Cyclometalation models: a) 8-quinolinecarboxaldehyde; b) 2-(diphenylphosphino)benzaldehyde.

Another cyclometalation model, aldimine **4a**, which has no carbonyl group, was designed to make decarbonylation impossible (Scheme 3).[12] The rhodium-catalyzed hydroiminoacylation of an olefin with aldimine **4a** produced ketimine **6**, which could be further acid-hydrolyzed to give ketone **7**. This reaction included the formation of a stable iminoacylrhodium(III) hydride **5a**; this was facilitated by the coordination of the pyridine moiety in **4a** to the rhodium complex **8**. Therefore, this hydroiminoacylation turned out to be a good alternative to the hydroacylation.[13]

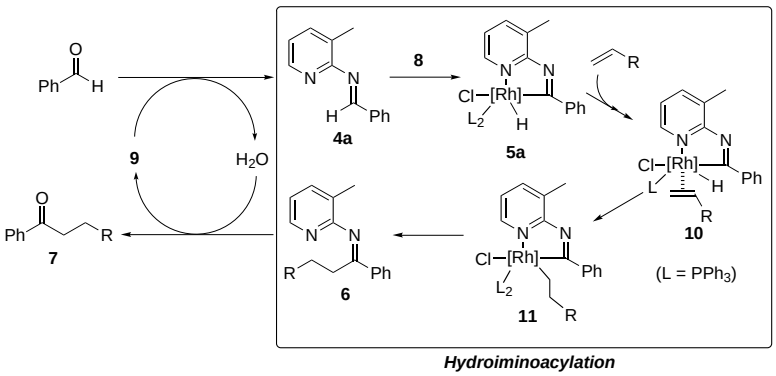


Scheme 3. Rh^{I}-catalyzed hydroiminoacylation of olefins.

Hydroacylation utilizing a chelation auxiliary: From the cyclometalation model aldimine **4a**, we could envisage the introduction of 2-amino-3-picoline (**9**) as a chelation auxiliary in order to directly employ an aldehyde as a substrate for hydroacylation. This protocol was based on the in situ generation of the aldimine from an aldehyde and 2-amino-3-picoline. For example, when the reaction of benzaldehyde and olefins was carried out in the presence of $[Rh(PPh_3)_3Cl]$ (**8**, Wilkinson's complex) and **9**, the corresponding ketones **7** were obtained in fairly good yields [Eq. (1)].[14]



The mechanism of the reaction is depicted in Scheme 4. Initially, benzaldehyde condenses with **9** to form the aldimine **4a**, which then undergoes hydroiminoacylation to afford ketimine **6** via the formation of acylrhodium(III) hydride **5a**, followed by hydrometalation of olefin to form **11** and reductive elimination. Since the ketimine is more susceptible toward hydrolysis compared with the aldimine, it is readily hydrolyzed to ketone **7** by water generated during the condensation step, thus regenerating **9**. Therefore, amine **9** is used as a catalyst to assist chelation with the rhodium complex. In fact, in the absence of **9**, no hydroacylation took place and aldehydes underwent the rapid decarbonylation.



Scheme 4. The mechanism of chelation-assisted hydroacylation of olefins.

The transimination strategy[15] as well as the addition of carboxylic acid turned out to be effective to accelerate the condensation step between an aldehyde and **9**; this is supposed to be the rate-determining step.[16] Thus, a very efficient catalyst system, which consists of **8**, **9**, benzoic acid (**12**), and aniline (**13**), was developed. Under this catalyst system, the reactivity was dramatically enhanced compared with those carried out in the absence of **12** and/or **13** as shown in Figure 1.[16a]

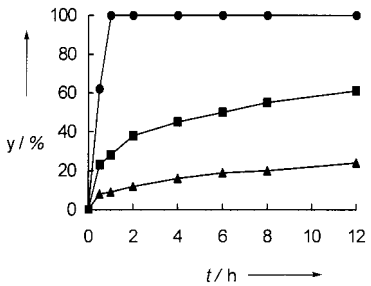


Figure 1. The plot of the GC yield of heptanopheone versus time for the reaction of benzaldehyde and 1-hexene in the presence of **8** (2 mol %) and **9** (20 mol %). The profile for the reaction performed without any additive (▲), in the presence of **12** (6 mol %, ■), and in the presence of both **12** (6 mol %) and **13** (60 mol %, ●) are shown.

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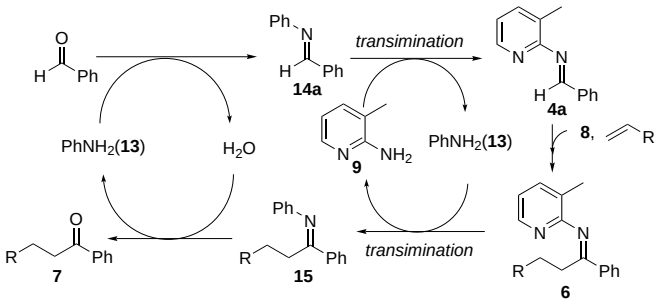
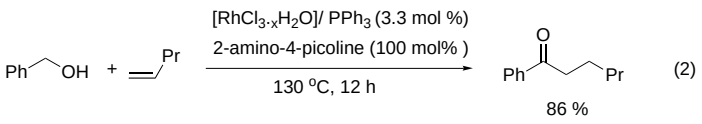
The mechanism of this reaction is illustrated in Scheme 5. Initially, an aldehyde condenses with more reactive aniline to form aldimine **14a**, and the subsequent transimination with **9** generates **4a**,[17] which participates in hydroiminoacylation of



Scheme 5. The mechanism of direct hydroacylation of olefins by transimination.

an olefin. Highly enhanced reactivity of this catalyst system implies that the condensation of an aldehyde with **13** followed by transimination of **14a** into aldimine **4a** is more facile than the direct condensation of an aldehyde and **9**.

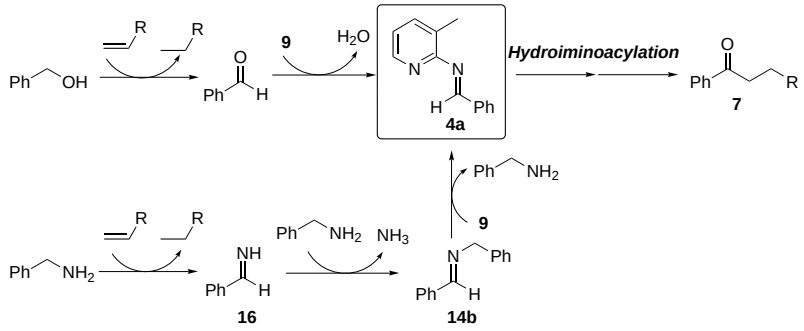
Chelation-assisted hydroacylation with primary alcohols and primary amines: A primary alcohol can be utilized as an aldehyde precursor, since it can be oxidized by hydrogen transfer.[18] For example, the reaction of benzyl alcohol with excess olefin afforded the corresponding ketone in good yield in the presence of a Rh complex and 2-amino-4-picoline [Eq. (2)].[19, 20]



(2)

In this reaction, olefins were required to simultaneously function as not only a substrate for hydroacylation, but also a hydrogen acceptor for a transfer hydrogenation (Scheme 6).

Similarly, primary amines, which could be transformed into imine such as **16** by dehydrogenation,[21] were also employed as a substrate instead of aldehyde (Scheme 6).[22] The unstable imine **16** undergoes transimination with another amine to form more stable aldimine **14b** with the liberation of NH_3.

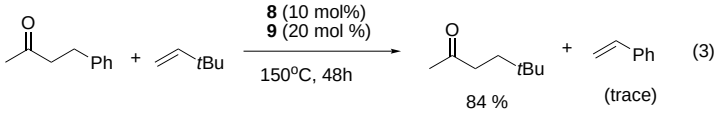


Scheme 6. The formation of ketones from primary alcohols or primary amines.

Similarly to the reaction of **14a** as shown in Scheme 5, aldimine **14b** was treated with olefin to afford corresponding ketone through **4a**.

Chelation-assisted C–C bond activation of unstrained ketones: Ketones have been often used as substrates for C–C bond activation, because the C–C bond adjacent to the carbonyl group is weaker than other C–C bonds.[23] Nevertheless, examples of C–C bond activation of unstrained ketones are quite rare.[24] Therefore, we envisaged the application of the chelation-assistance strategy in our hydroacylation to the C–C bond activation of unstrained ketones, since all the steps from aldimine through ketimines were believed to be reversible. It was realized in the reaction of benzylacetone with olefin under the catalyst system of Wilkinson's complex (**8**) and 2-amino-3-picoline (**9**), which resulted in the replacement of an alkyl group of an unstrained ketone [Eq. (3)].[25]

As illustrated in Scheme 7, initially ketimine **17a** is formed from benzylacetone and **9**. Subsequent C–C bond activation

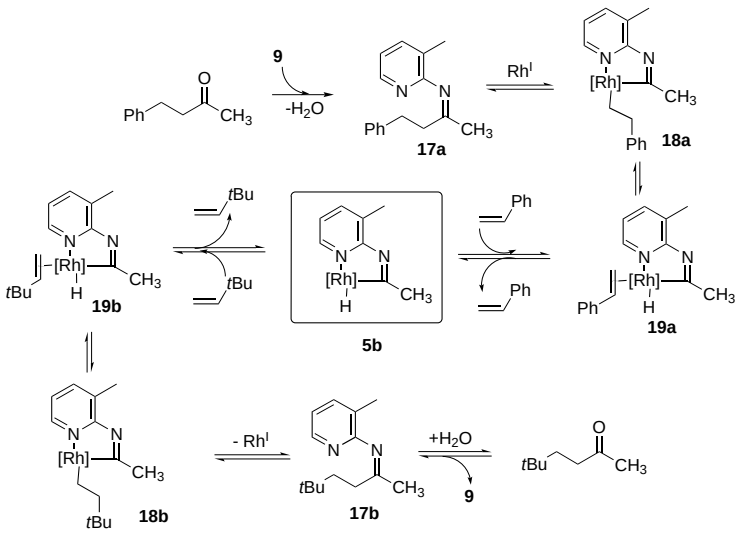


(3)

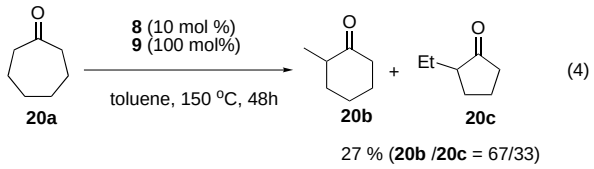
followed by β-hydrogen elimination affords iminoacylrhodium(III) hydride **5b**, which is the net reverse reaction of hydroiminoacylation. The hydrometalation of **5b** with an olefin followed by reductive elimination produces ketimine **17b** and the alkyl-exchanged ketone as a final product. According to the proposed mechanism, there are two requirements for this catalytic cycle to be successfully executed (Scheme 7). First, the ketone substrate should possess a β-hydrogen, because β-hydrogen elimination of complex **18a** affords **5b** via **19a**. The second requirement for completion of this process is to add an excess of external olefin (10 equiv) to drive the forward reaction from complex **5b** to **19b**. In addition, we noticed only the trace amount of styrene remained; this might be attributed to the facile polymerization of styrene at high temperature.[26] Thus, such polymerization also forces this catalytic process to go forward to the production of the alkyl-exchanged ketone.

The C–C bond activation of unstrained cycloalkanones, such as cycloheptanone (**20a**), was also performed in the absence of external olefin to afford ring-contracted products, 2-methylcyclohexanone (**20b**) and 2-ethylcyclopentanone (**20c**) through skeletal rearrangement [Eq. (4)].[27]

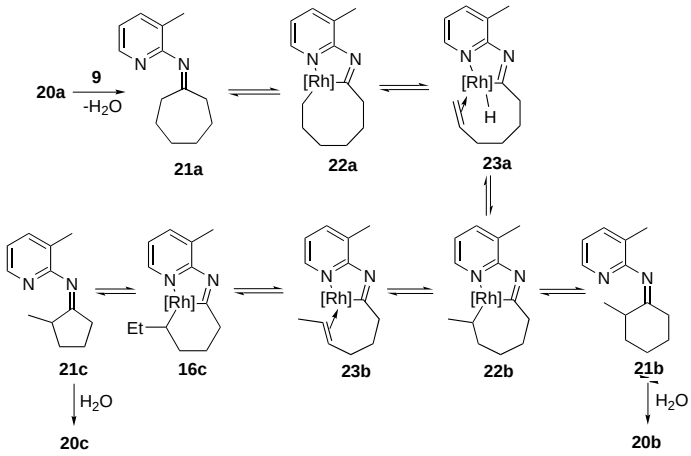
The intermediate iminoacylrhodium(III) hydride **23a**, derived from C–C bond activation of ketimine **21a**, affords an iminoacylrhodium(III) metalacyclic complex **22b** by Markovnikov hydrometalation. Ketimine **21b** is yielded through reductive elimination,



Scheme 7. The proposed mechanism for the C–C bond activation of benzylacetone.

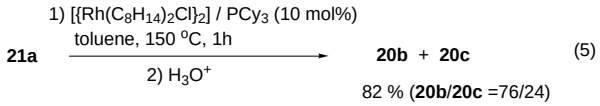


and then hydrolyzed to give ketone **20b**. Similarly, further skeletal rearrangement of **22b** through β-hydrogen elimination followed by hydrometalation and reductive elimination affords cyclopentanone **20c** (Scheme 8).



Scheme 8. The C–C bond activation of cycloalkanone.

When ketimine **21a** instead of **20a** was subjected to this skeletal rearrangement in the presence of $[\{Rh(C_8H_{14})_2Cl\}_2]$ and PCy_3, the ring-contracted products **20b** and **20c** were obtained in a high yield of 82% after hydrolysis [Eq. (5)].



The C–H and C–C Bond Activation by Utilizing Allylamine Derivatives

The introduction of allylamines as a synthon of formaldehyde: The synthesis of dialkyl ketones cannot be realized through the hydroacylation of aliphatic aldehydes; this might be attributed to the occurance of possible side reactions, such as aldol condensation. To overcome such problems, we derived allylamine **24** from 2-amino-3-picoline, which could be readily isomerized by a metal complex to generate aldimine **4b** (Scheme 9).[28]

Then, aldimine **4b** could undergo the hydroiminoacylation of olefins by C–H bond activation to give ketimine **25**, which could be hydrolyzed to afford an unsymmetric ketone **26**. In addition, ketimine **25** bearing a hydrogen β to the imine might be subject to the C–C bond activation to yield a symmetric ketone **28** after acidic hydrolysis. Consequently, allylamine **24** is expected to function as a synthon of formaldehyde for the synthesis of aliphatic ketones.

When the reaction of allylamine **24** with 3,3-dimethylbutene was carried out in the presence of $[\{Rh(C_8H_{14})_2Cl\}_2]$ and PCy_3, a mixture of ketones **26a** and **28a** was obtained. In contrast, the use of $[Ru_3(CO)_{12}]$ instead of the Rh^I complex in the above reaction led to only the monoalkylated ketone **26a** (Scheme 10). Therefore, these results demonstrated that the Rh^I complex is active enough for both C–H and C–C bond activation, whereas the Ru^0 complex acts only for C–H bond activation.

Hydroiminoacylation of alkynes with allylamine 24 and its application to the cleavage of C–C triple bonds: Since the hydroacylation of alkynes has not been studied very well,[11c, 29] we investigated the utilization of allylamine **24** for the hydroiminoacylation of alkynes.[30] Under the catalyst system consisting of **8**, **12**, and cyclohexylamine, the reaction of cinnamylamine **24** with 2-butyne (**29**) yielded 1-phenylpentan-3-one (**32**) after hydrolysis [Eq. (6)].

This transformation begins with the hydroiminoacylation of **29** with **24** to generate α,β-unsaturated ketimine **33** (Scheme 11). Actually, when the reaction was carried out in the absence of cyclohexylamine, α,β-unsaturated ketone **34** was obtained after hydrolysis. The conjugate addition of cyclohexylamine into **33** can take place to form β-aminoketimine **35**. Then, retro-Mannich type fragmentation of **35** leads to enamine **36** along with aldimine **31**.[31] Enamine **36** can be isomerized to give ketimine **37**, which is then transiminated by cyclohexylamine to produce ketimine **30** with liberation of **9**. The final product, ketone **32**, can be obtained by acidic hydrolysis of **30**. Therefore, this one-pot reaction includes 1) hydroiminoacylation of alkynes with allylamine **24** by the Rh^I

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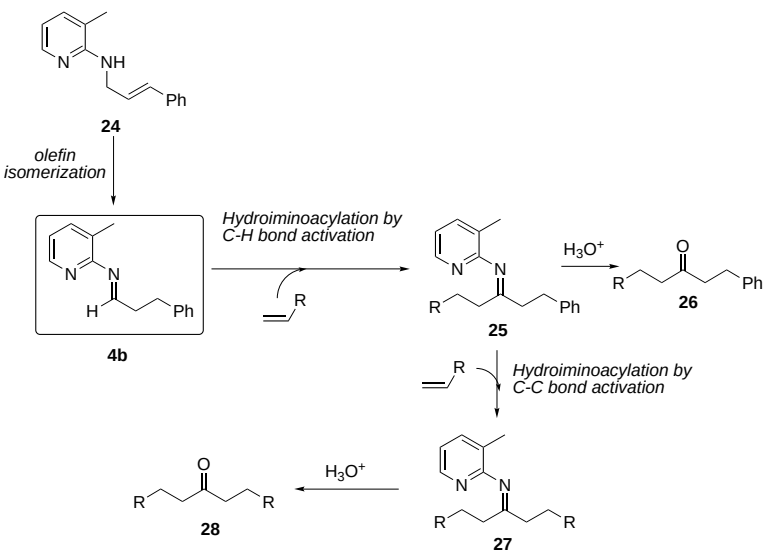
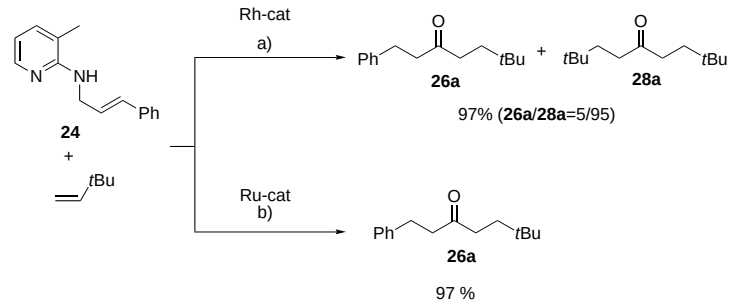
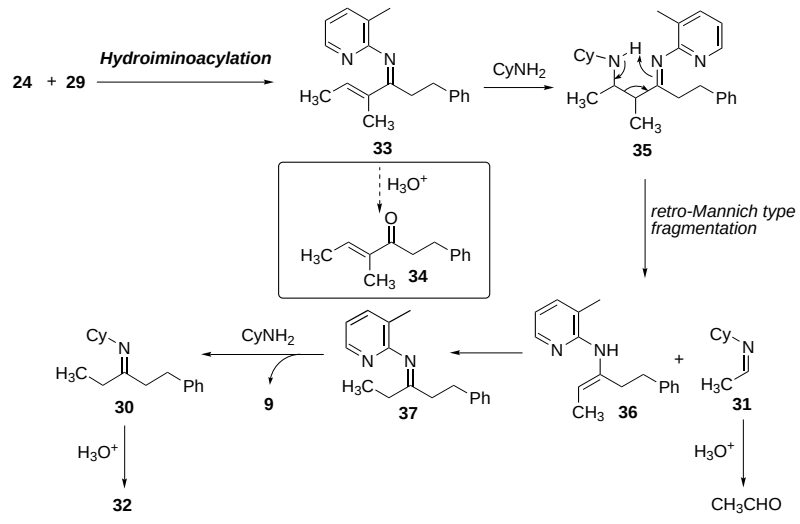


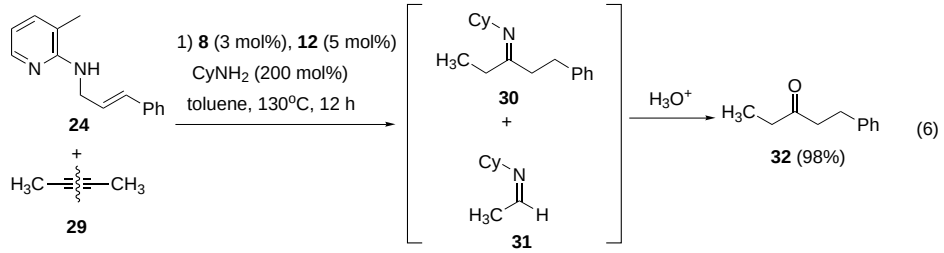
Scheme 9. The C–H and C–C bond activation of allylamine derivative **24**.



Scheme 10. The reaction of allylamine **24** with olefin in the presence of Rh^{I} or Ru^{0} catalyst. Reaction conditions: a) i)3 mol% $[\{Rh(C_8H_{14})_2Cl\}_2]$, 6 mol% PCy_3, 170 °C, 1 h; ii) H^+/H_2O. b) i) 3 mol% $[Ru_3(CO)_{12}]$, 130 °C, 6 h; ii) H^+/H_2O.



Scheme 11. The plausible mechanism of the alkyne cleavage.



catalyst, 2) the conjugate addition of cyclohexylamine into the resulting α,β-unsaturated ketimine, and 3) the retro-Mannich type fragmentation of β-aminoketimine.

Conclusion

The Rh^{I}-catalyzed hydroacylation of unstrained aldehydes has been established by the C–H bond activation utilizing cyclometalation, for which the key aldimine **4a** is generated in situ by introducing 2-amino-3-picoline as a chelation auxiliary. The formation of aldimine **4a** is immensely accelerated by the transimination strategy. In addition, primary alcohols and amines instead of aldehydes can be used as substrates for this hydroacylation, by carrying out dehydrogenation in the presence of an Rh catalyst. The same protocol has been successfully applied to the C–C bond activation of unstrained ketones, which gives rise to a net replacement of an alkyl group in ketones. In the case of an unstrained cycloalkanone, a skeletal rearrangement takes place in the absence of olefins.

Allylamine **24**, derived from 2-amino-3-picoline, was desired to act as a synthon of formaldehyde. The olefin isomerization of **24** followed by a consecutive C–H and C–C bond activation afforded a symmetric ketone. The hydroiminoacylation of alkynes with allylamine **24** generates α,β-unsaturated ketimines, which can then be subjected to the conjugate addition of cyclohexylamine followed by the retro-Mannich type fragmentation to result in the cleavage of the C–C triple bond of alkynes.

Consequently, the Rh-catalyzed activation of the C–H and C–C bonds adjacent to carbonyl functionality is facilitated by utilizing a chelation auxiliary, such as 2-amino-3-

picoline, in which the formation of a stable metallacycle intermediate is driven by the directing group, that is, the nitrogen atom of the pyridine ring. Therefore, this reaction might give access to the activation on an unreactive bond of unactivated substrates, provided that a metal complex can be directed to the bond to be cleaved by an appropriate chelation auxiliary.

Acknowledgements

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