concentration of oxygen vacancy in In_2O_3 at higher temperatures can be controlled by Mn-doping, gaseous oxygen is chemisorbed on oxygen vacancy, and the adsorbed O^- selectively activates CH_4. Methane is activated *via* abstraction of a hydrogen atom at O^- (ads) and then $OH^-_{(ads)}$ ions are formed on the surface of catalyst. The OH^- (ads) ions is desorbed as a form of H_2O in gas phase remaining oxygen vacancy on the surface. The resultant methyl radicals may remain attached to the surface of catalyst where coupling of methyl radicals takes place or be released into the gas phase where methyl radicals are coupled. The methyl radicals can be deeply oxidized to carbon oxides by the reaction with dioxygen in the gas phase or on the surface of the catalyst.

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Synthesis of β,γ-Unsaturated Ketones through Ligand-Promoted Hydroiminoacylation of Dienes by Rh

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Chlorobis(isoprene)rhodium(I) (**3**), prepared by olefin-exchange reaction of chlorobis(cyclooctene)rhodium dimer (**2**) with isoprene, reacted with benzaldimine **4** to give iminoacylrhodium(III) η^3-1,2-dimethylallyl complex **6**. Ligand-promoted reductive elimination of **6** by pyridine and $P(OMe)_3$ produced β,γ-unsaturated ketimine **8**, which was readily hydrolyzed to give β,γ-unsaturated ketone **9**. Other methyl branched dienes such as 2,3-dimethylbutadiene, 3-methyl-1,3-pentadiene, 2-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 3-methyl-1,4-pentadiene and 2-methyl-1,4-pentadiene, were applied the synthesis of β,γ-unsaturated ketones. In case of 2,4-dimethyl-1,3-pentadiene, only γ,δ-unsaturated ketone **25**, 1,2-addition product, was obtained, maybe due to the mono-olefin coordination.

Introduction

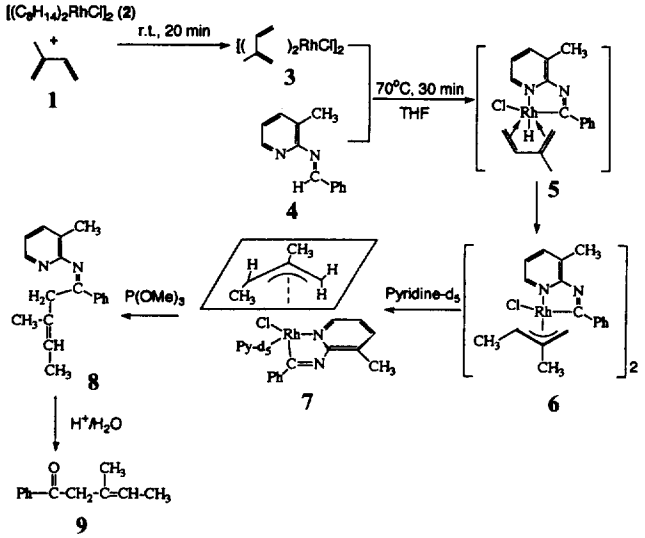
The activation of the C-H bond by transition metal complexes is one of current interests in organometallic chemistry.[1] Especially the aldehydic C-H bond can be readily cleaved by transition metals such as Wilkinson's complex. Subsequent decarbonylation of the acylmetal hydride and reductive elimination of the resulting alkylmetal hydride gives alkane.[2] This decarbonylation can be prevented through cyclometallation due to the formation of stable 5-membered ring metallacycle as an intermediate.[3] One of good substrates is 8-quinolinecarboxaldehyde, which is reacted with Rh(I) to give acyl-

rhodium hydride, followed by the hydride addition to olefins to generate acylrhodium alkyl complex. The acylrhodium alkyl complex undergoes ligand-promoted reductive elimination by $P(OMe)_3$ to give 8-quinolinyl alkyl ketones.[4] When diene was used instead of mono-olefin, the resulting ketone was 8-quinolinyl β,γ-unsaturated ketone *via* the acylrhodium π-allyl complexes.[5] One of the major problems to synthesize β,γ-unsaturated ketones by this method is that the quinoline group is hard to be discarded in order to apply the general ketone synthesis from aldehyde. To solve this problem, aldimine, prepared from condensation of 2-amino-3-picoline and aldehyde, has been used for the hydroiminoacylation substrate to give ketimine, in which 2-amino-3-picoline can be easily eliminated by the hydrolysis of the resulting ketimine to give the corresponding ketone.[6] In hydroiminoacylation, aldimine reacted with monoolefins and dienes, catalytically[7] and stoichiometrically.[8] This report explains that β,γ-unsaturated ketone can be synthesized through the ligand promoted reductive elimination of the π-allylrhodium(III) complexes, formed from C-H bond activation of aldimine by diene-rhodium(I) chloride.

Results and Discussion

It has been reported that many dienes can readily coordinate to Rh by olefin-exchange reaction under mild conditions.[9] 2-Methyl-1,3-butadiene rhodium(I) complex dimer (**3**) can be generated *in situ* from the reaction of bis(cyclooctene) rhodium(I)chloride dimer (**2**) and isoprene (**1**) (Scheme 1).

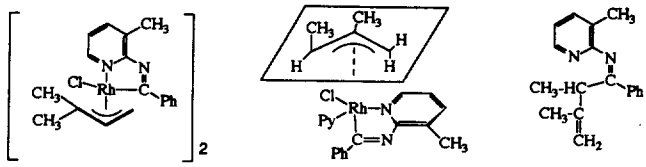
3-Methyl-2-aminopyridyl benzaldimine (**4**) was allowed to react with a solution of **3** in THF at 70 ℃ for 30 min. A brown precipitate was obtained with pentane in 82% yield. This brown solid was supposed to be chlorine-bridged η^3-1,2-dimethylallyl rhodium(III) complex dimer **6**, which is not soluble in chloroform. The addition of pyridine-d_5 to **6** in $CDCl_3$ solution gives soluble iminoacylrhodium(III)-η^3-1-*anti*-2-dimethylallyl complex **7**, which must be five-coordinate species. The ^1H NMR chemical shifts for the 1-*anti*-methyl and meso-methyl group in **7** appear at 0.42 (J=6.4 Hz) and 1.2 ppm



Scheme 1. Reaction of chlorobis(2-methyl-1,3-butadiene)rhodium(I) with 3-methyl-2-aminopyridyl benzaldimine.

(J=2.8 Hz) as doublets, respectively.[10] The ^{13}C NMR chemical shifts for the allyl group in **7** appear at 124.7 (J_{Rh-C}=8.8 Hz, C-2 of the allyl group), 61.7 (J_{Rh-C}=9.1 Hz, C of the allyl group adjacent to the *anti*-methyl group) and 53.6 (J_{Rh-C}=10.2 Hz, C-3 of the allyl group) as doublets, indicating that all three carbons in the allyl group are coupled with Rh while those of the meso- and *anti*-methyl groups appear at 16.9 and 12.7 ppm as singlets, respectively.[11] Trimethylposphite causes facile ligand-promoted reductive elimination of **7** to give β,γ-unsaturated ketimine **8** in 88% yield. Since ketimine is susceptible for hydrolysis, treatment of **8** with 1 N-HCl aq. solution produced β,γ-unsaturated ketone **9** in 88% yield after chromatographic isolation.

Complex **5** is regarded as an intermediate in the reaction of **3** and **4** *via* C-H bond activation. The hydride addition to 2-methyl-1,3-butadiene takes place only at the 4-position to give η^3-1,2-dimethylallylrhodium(III) complex **6**. If the hydride addition takes place at the 1-position in 2-methyl-1,3-butadiene, it should have given η^3-1,1-dimethylallylrhodium (III) complex **10**.



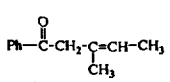
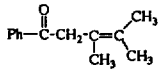
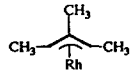
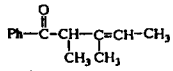
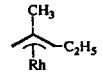
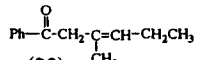
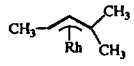
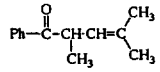
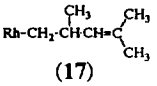
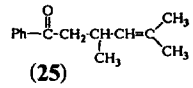
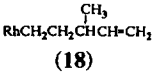
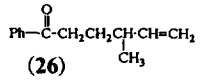
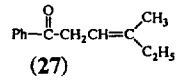
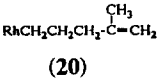
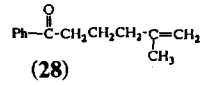
10 **11** **12**

But any evidence for the formation of **10** has not been observed. The reason must be that since this system is very susceptible for steric congestion, the hydride addition takes place at the sterically less hindered 4-position than the 1-position in **5**. The selectivity is also shown in the formation of **7**. Two geometrical isomers, **7** and **11**, are possible for structures of η^3-1,2-dimethylallyl rhodium(III) complex. The ^1H NMR spectrum shows only that of η^3-1-*anti*-2-dimethylallyl rhodium(III) complex **7**, not η^3-1-*syn*-2-dimethylallyl rhodium(III) complex **11** even though thermal stability of **11** is better than that of **7**.[10] The final selectivity is observed in reductive-elimination of **7** by trimethylphosphite. Compound **12** as well as **8** should have been produced, but only **8** was generated by reductive-elimination of **7**, maybe due to the steric differences of the primary-alkyl and the secondary-alkyl site. Above three selectivity results in **6**, **7** and **8** comparing with **10**, **11** and **12** seem to indicate that the sterically congested picoline system makes it possible for the more stable structure selection.

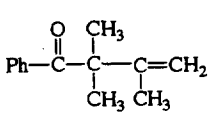
Another interesting point is that by looking at the structure of the final hydrolysis product **9**, it is possible to infer the ketimine **8** and its precusor complex **6**. Actually reductive-elimination of the chlorine-bridged dimer **6** by trimethylphosphite gives **8** without isolating or identifying **7**. All of these reactions can be done by the continuous process. That is, isoprene is added to complex **2**, followed by addition of **4** under the above reaction condition gives a brown suspension. Without isolation of the intermediate complex, reductive elimination with pyridine and trimethylphosphite, and subsequent hydrolysis with 1 N-HCl aq. solution gives β,γ-unsaturated ketone **9** in 81% yield.

Other dienes were also applied for this continuous process without isolating intermediates, as shown in Table 1. Entries

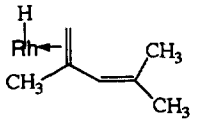
Table 1. Reaction Intermediate of Chlorobis(diene)rhodium(I) and benzaldimine (**4**), and Hydrolysis Product of the Reductive-Eliminated Ketimine of Rh(III) Intermediate

Entry	Diene	Rh(III) Intermediate complex	Hydrolysis product of the resulting ketimine	Product ratio	Yield (%)
1		 **(6)**	 **(9)**		81
2		 **(13)**	 **(21)**		46
3		 **(14)**	 **(22)**		52
4		 **(15)**	 **(23)**	63	57
		 **(16)**	 **(24)**	37	
5		 **(17)**	 **(25)**		49
6		 **(18)**	 **(26)**	60	71
		 **(19)**	 **(27)**	40	
7		 **(20)**	 **(28)**	7	81
		15	**23**	93	

2-5 are the conjugate diene used instead of **1**, while entries 6 and 7 are the non-conjugate dienes. Symmetric conjugate-diene, 2,3-dimethyl-1,3-butadiene (entry 2) generates one kine of π-allyl complex as expected, η^3-1,1,2-trimethylallyl complex **13**. Hydrolysis product after reductive-elimination of **13** is one kind of β,γ-unsaturated ketone **21**. In reductive-elimination of **13**, another possible product, **29**, has not been found in the reaction product.

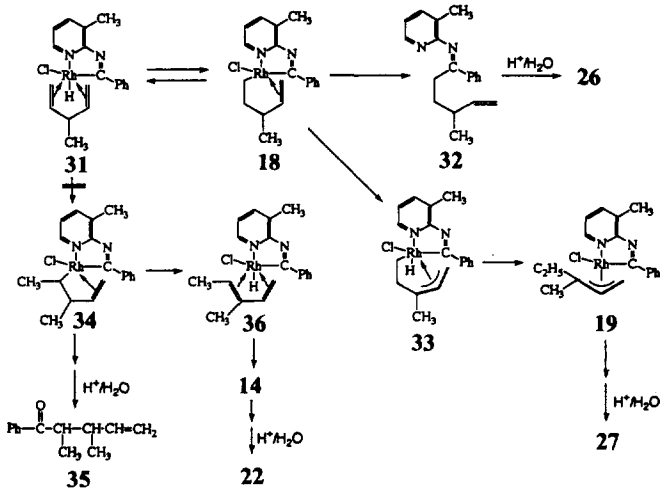


29



30

The reason must be that the C-C bond coupling of the primay carbon of the 3-position in **13** is much more facile than that of the tertiary carbon of the 1-position due to the steric hindrance. This result indicates that the least substituted alkyl site in the π-allyl group is much more favorable for the reductive-elimination reaction.



Scheme 2. Formation mechanism of **26** and **27** through **18** and **33**.

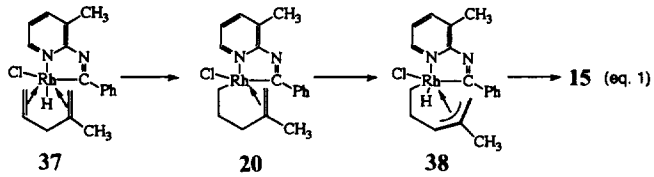
In the case of 3-methyl-1,3-pentadiene (entry 3), the hydride addition takes place at the least sterically hindered 1-position to give the symmetrically methyl-substituted 1,2,3-trimethylallyl complex **14**. Reductive-elimination of **14** gives one kind of β,γ-unsaturated ketone **22**. However the hydride addition of 2-methyl-1,3-pentadiene (entry 4) generates two kinds of π-allyl complexes, **15** and **16**, as inferred from the product mixtures, **23** and **24**. The hydride addition ratio at the 1- and 4-position in 2-methyl-1,3-pentadiene can be measured as 63 : 37 by analyzing the ratio of **23** and **24**.

Another interesting molecule is 2,4-dimethyl-1,3-pentadiene (entry 5) which is very sterically hindered diene. In this case, any β,γ-unsaturated ketone has not been found in the reaction product, but only γ,δ-unsaturated ketone **25** is produced in 49% yield under the above reaction conditions. Prereductive-elimination complex was inferred as **17**, which means that the 1,2-hydride addition takes place instead of the 1,4-addition to form π-allyl complexes. Therefore the coordinated diene intermediate can be presumed as **30**, which is different from other conjugate diene complexes such as **5**. This result shows that 2,4-dimethyl-1,3-pentadiene acts as a monoolefin since the gem-dimethyl-substituted olefin site is hard to be coodinated to the metal due to the steric hindrance.

With non-conjugate diene, 3-methyl-1,4-pentadiene (entry 6), two intermediate complexes, **18** and **19**, are inferred from the two final products, **26** and **27**. The second step must be the hydride addition of 3-methyl-1,3-pentadiene to form the complex **18** which forms a stable 5.5-membered ring metallacycle structure. Reductive elimination of **18** and hydrolysis of the resulting ketimine **32** give **26** as one of the products. Another intermediate complex **19** must be formed from isomerization of the initial intermediate complex **18**. Two possible mechanism should be considered for the isomerization of **18** to **19**[12]; a hydride addition-elimination mechanisim[13] and a π-allyl hydrido mechanism.[14] Many olefin-isomerization process can be explained in terms of the hydride addition-elimination mechansim. However, the hydride addition-elimi-

nation mechanism can not explain the formation of **19**. The hydride addition-elimination mechanism allows **18** to form intermediate **36**. A subsequent hydride addition to 3-methyl-1,3-pentadiene should have formed **14**, followed by reductive-elimination and hydrolysis to give **22**, which was already characterized in entry 3. Compound **35** formed from the presumed intermediate **34** has not been detected. Therefore altrenative π-allyl hydrido mechanism may be possible to be operating even though Rh in the intermediate **33** is in its high oxidation state, as rhodium(V). Some examples of high oxidation state for rhodium(V) metal complexes have been reported.[15] This kind of π-allyl hydrido mechanism has been also reported in the isomerization of the 4-pentenylrhodium(III) complex to the η^3-1-ethylallyl rhodium(III) complex in quinoline system.[5a]

Even unsymmetrical non-conjugate diene, 2-methyl-1,4-pentadiene (entry 7), produces one kind of β,γ-unsaturated ketone **23** with **28** throughout the reaction. This reaction clearly shows that the π-allyl hydrido mechanism is operating in the isomerization of the first alkyl intermediate **20**, a pre-reductive elimination complex of **28**, to **15** *via* **38** (Eq. 1).



37 **20** **38**

Since the hydride addition of olefin in this picoline system is strongly regio-selective, a hydride addition in **37** takes place at 4-position to give only **20**. The reason must be that the 2-position is sterically more hindered than the 4-position.

On the basis of the above results, it is possible to synthesize the β,γ-unsaturated ketones selectively from the conjugate dienes or non-conjugate diens with the isomerization process.

Experimental

Chlorobis(cyclooctene)rhodium(I) (**2**)[16] and **4**[6] were prepared by published procedure. Rhodium(III)chloride trihydrate, isoprene, 2,3-dimethylbutadiene, 2-methyl-1,3-pentadiene, 3-methyl-1,3-pentadiene, 2,4-dimethyl-1,3-pentadiene, 3-methyl-1,4-pentadiene and 2-methyl-1,4-pentadiene were purchased from Aldrich Chemical Co. and used without further purification. All solvents were distilled and stored over molecular sieves (4 Å). NMR spectra were recorded with either a Bruker AC-200 (200 MHz), a Bruker AM-300 (300 MHz) or a Varian FT-80 A (80 MHz) spectrometer. The chemical shifts (δ) of the ^{1}H NMR and ^{13}C NMR resonances are in ppm relative to internal Me_4Si. Infrared spectra were recorded with a Perkin-Elmer 683 spectrometer. Mass spectra were obtained with either a Jeol JMS-DX 303 GC/MS or Shimadzu GC/MS-QP5000. Column-Chromatography was performed on Merck Silica Gel-60 (70-230 and 230-400 mesh). IR spectra and Mass spectra of **23**, **24**, **26**, **27** and **28** were obtained from the mixture compounds of **23** and **24**, **26** and **27**, **28** and **23** by using GC-IR spectrometer (HP-5965B IR detector equipped with a HP 5890 series II Gas Chromatograph).

Reaction of Chlorobis(2-methyl-1,3-butadiene)rhodium(I) (3) and 3-methyl-2-aminopyridyl benzaldimine (4). A screw-capped pressure vial was charged with 0.100 g (0.28 mmol) of chlorobis(cyclooctene)rhodium(I) (**2**) and 0.300 g (4.4 mmol) of isoprene (**1**) was added under nitrogen. After the reaction mixture was stirred at room temperature for 10 min during which time the color changed brown into red, 0.055 g (0.28 mmol) of 3-methyl-2-aminopyridyl benzaldimine **4** dissolved in 3 m*l* THF was added. The reaction mixture was heated at 70 ℃ for 30 min and allowed to room temperature. A brown precipitate was obtained with 20 m*l* of pentane, filtered and dried *in vacuo* to give 0.185 g (82% yield) of chloro-η^3-1,2-dimethylallyl-(3-methyl-2-aminopyridyl benzketimine-C,N)rhodium(III) dimer (**6**). **6**: mp. 246 ℃; IR (KBr) 3060, 2960, 1615, 1520, 1470, 1380, 1220, 950, 920, 775, 700 cm^{-1}. To a suspension of 0.097 g (0.24 mmol) of **6** in 2 m*l* of $CDCl_3$ was added 0.02 g (0.25 mmol) of pyridine-d_5. The resulting mixture was stirred at room temperature for 1 h, and the precipitate was obtained with 20 m*l* pentane, filtered, and dried *in vacuo* to give 0.105 g (91% yield) of iminoacylrhodium(III)-η^3-1-*anti*-2-dimethylallyl rhodium(III) pyridine-d_5 complex **7**. **7**: mp. 155 ℃; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.65 (d, J=5.4 Hz, 1H, H-6 in picoline) 8.5-7.0 (m, 7H, Hs of picoline and phenyl groups) 4.0 (q, J=6.3 Hz, 1H, syn-H-1 of η^3-allyl group) 3.8 (s, 1H, syn-H-3 of η^3-allyl group) 3.48 (s, 1H, *anti*-H-3 of η^3-allyl group) 2.7 (s, 3H, CH_3 in picoline group) 1.2 (d, $J_{Rh\text{-}Me}$=2.8 Hz, 3H, *meso*-CH_3) 0.42 (d, J=6.4 Hz, *anti*-CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm), 165.4 (C=N), 153.3-119.7 (Cs of picoline and phenyl group), 124.7 (d, $J_{Rh\text{-}C}$=8.8 Hz, *meso*-C of allyl group), 61.7 (d, $J_{Rh\text{-}C}$=9.1 Hz, C-1 of allyl group), 53.6 (d, $J_{Rh\text{-}C}$=10.2 Hz, C-3 of allyl group), 19.2 (CH_3 in picoline group), 16.9 (*meso*-CH_3 of allyl group), 12.7 (*anti*-CH_3 of C-1 in allyl group); IR (KBr) 3060, 2960, 2920, 1615, 1565, 1475, 1450, 1320, 1220, 1070, 1025, 840, 775, 700 cm^{-1}.

Reductive Elimination of Iminoacylrhodium(III)-η^3-1-anti-2-dimethyl allyl rhodium(III) pyridine-d_5 complex (7) by trimethylphosphite. To a solution of 0.097 g (0.2 mmol) of **7** in 3 m*l* THF was added 1 m*l* of trimethylphosphite upon which time the color changed from brown to red. After stirring for 2 h, the mixture was concentrated at 50 ℃ under reduced pressure, leaving a dark brown residue. The residue was purified by column-chromatography on silica gel (hexane : ethyl acetate=5 : 1) to give 46.7 mg (88% yield) of 3-methyl-2-amino-pyridyl(2-methylbut-2-enyl-benzketimine (**8**). **8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.27 (d, J=3.9 Hz, 1H, 6-H in picoline), 8.0-7.4 (m, 6H, Hs of picoline and phenyl groups), 6.95 (dd, J=7.4 & 4.9 Hz, 1H, 5-H in picoline) 5.08 (q, J=6.6 Hz, 1H, =CH-), 3.45 (s, 2H, α-CH_2 to CN), 2.12 (s, H, CH_3 in picoline), 1.49 (brs, 3H, =C-CH_3), 1.42 (d, J=6.6 Hz, 3H, -CH-CH_3); IR (film) 2080, 3020, 2920, 1630 (C=N), 1580, 1445, 1410, 1230, 1110, 985, 785, 690 cm^{-1}; mass spectrum; m/e (relative intensity) 264 (M^+, 49), 249 (56), 235 (7), 222 (9), 209 (38), 195 (100), 172 (16), 146 (6), 92 (68), 77 (5); TLC R_f=0.32, hexane : ethyl acetate=5 : 2, SiO_2.

Hydrolysis of 3-methyl-2-amino-pyridyl(2-methylbut-2'-enyl)benzketimine (8). 0.063 g (0.24 mmol) of **8** was dissolved in 5 m*l* chloroform and 10 m*l* 1 N HCl aq. solution was added. The mixture was stirred at room temperature for 1 h. The organic layer was separated and dried over magnesium sulfate. The solution was concentrated at 50 ℃ under reduced pressure, leaving a brown residue.

The residue was purified by column-chromatography on silica gel to give 36.6 mg (88% yield) of 2-methylbut-2-enyl phenyl ketone (**9**)[17]. **9**: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 7.95 (dd, J=8.3 & 1.72 Hz, 2H, 2,6-Hs of phenyl group), 7.6-7.4 (m, 3H, 3,4,5-Hs of phenyl group), 5.39 (q, J=6.9 Hz, 1H, =CH-), 3.65 (s, 2H, α-CH_2 to CO), 1.69 (s, 3H, =C-CH_3), 1.64 (d, J=6.8 Hz, 3H, =CH-CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 196.7 (C=O), 137.0-128 (Cs of phenyl group), 130.0 (-C=), 49.2 (α-CH_2 to CO), 36.4 (=C-CH_3), 16.2 (=CH-CH_3); IR (film) 3040, 2970, 1680 (C=O), 1630, 1595, 1445, 1380, 1330, 1275, 1200, 965, 750, 690 cm^{-1}; mass spectrum; m/e (relative intensity) 174 (M^+, 11), 173 (M^+-1, 22), 159 (6), 147 (14), 131 (7), 105 (100), 77 (26); TLC R_f=0.65, hexane : ethyl acetate=5 : 1.

General Procedure for the Synthesis of β,γ-Unsaturated Ketone from Dienes. A screw-capped pressure vial is charged with 0.1 g (0.28 mmol) of chlorobis(cyclooctene)rhodium(I) (**2**), and 0.3 g of diene was added under nitrogen. After the reaction mixture was stirred at room temperature for 20 min during which time the color changed brown into yellowish red, 0.055 g (0.28 mmol) of 3-methyl-2-aminopyridyl benzaldimine (**4**) dissolved in 3 m*l* THF was added. The reaction mixture was heated at 70 ℃ for 1 h and allowed to room temperature. To the solution was added 0.022 g (0.28 mmol) of pyridine. After the resulting mixture was stirred for 1 h, 1 m*l* of trimethylphosphite was added upon which the color changed from brown to red. After stirring for 2 h, a mixture of 10 m*l* chloroform and 20 m*l* 1 N HCl aq. solution was added. The mixture was stirred at room temperature for 1 h. The organic layer was separated and dried over magnesium sulfate. The solution was concentrated at 50 ℃ under reduced pressure, leaving a brown residue. The residue was purified by column-chromatography on silica gel to give phenyl β,γ-unsaturated alkyl ketone (46-81% yield).

Preparation of 2,3-dimethylbut-2-enyl phenyl ketone (21) from 2,3-dimethyl-1,3-butadiene and 4. **21**[17]: 46% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm), 7.96 (dd, J=7.9 & 1.6 Hz, 2H, 2,6-Hs of phenyl group), 7.6-7.4 (m, 3H, 3,4,5-Hs of phenyl group), 3.75 (s, 2H, α-CH_2 to CO), 1.74 (s, 3H, 2-CH_3 in 2,3-dimethylbut-2-enyl group), 1.70 (s, 6H, =C(CH_3)$_2$); ^{13} C NMR (50.5 MHz, $CDCl_3$) δ (ppm), 198.7 (C=O), 137.3-122.4 (Cs of phenyl group & C-2 & C-3 in 2,3-dimethylbut-2-enyl group), 44.5 (α-CH_2 to CO), 30.29 (CH_3 attached to C-2 in 2,3-dimethylbut-2-enyl group), 20.7 & 19.75 (=C-(CH_3)$_2$); IR (film), 3060, 2980, 1680 (C=O), 1595, 1575, 1445, 1370, 1330, 1280, 1200, 1175, 985, 860, 750, 690 cm^{-1}; mass spectrum; m/e (relative intensity), 188 (M^+, 9), 187 (M^+-1, 14), 173 (7), 158 (21), 145 (24), 119 (20), 105 (100), 77 (23); TLC R_f=0.65, hexane : ethyl acetate=5 : 1, SiO_2.

Preparation of 1,2-dimethylbut-2-enyl phenyl ketone (22) from 3-methyl-1,3-pentadiene and 4. **22**: 52% yield; ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm), 7.99-7.93 (m, 2H, 2,6-Hs of phenyl group), 7.52-7.4 (m, 3H, 3,4,5-Hs of phenyl group), 5.44 (q, J=7.0 Hz, 1H, =CH-), 4.60 (q, J=6.7 Hz, 1H, α-CH to CO), 1.59 (s, 3H, =C-CH_3), 1.57 (d, J=7.0 Hz, 3H, =CH-CH_3), 1.29 (d, J=6.7 Hz, 3H, CO-CH-CH_3); ^{13}C NMR (50.5 MHz, $CDCl_3$), δ (ppm), 198.7 (C=O), 137.3-128.1 (Cs of phenyl group & C-2 & C-3 in 1,2-dimethylbut-2-enyl group), 49.4 (α-CH to CO), 26.2 (CH_3 attached to C-2 in 1,2-dimethylbut-2-enyl group), 17.7 (=CH-CH_3), 13.6 (COCH-CH_3); IR (film), 3060, 3020, 2960, 2920, 1680 (C=O), 1595, 1575, 1445, 1365, 1330, 1255, 1220, 1175, 960, 920, 745, 690 cm^{-1}; mass spectrum; m/e (relative intensity), 188 (M^+, 42), 173 (68), 161 (5), 145 (8), 133 (2), 118 (4), 105 (100), 77 (87); TLC R_f=0.71, hexane : ethyl acetate=5 : 2, SiO_2.

Preparation of a mixture of 1,3-dimethylbut-2-enyl phenyl ketone (24) and 2-methylpent-2-enyl phenyl ketone (23) from 2-methyl-1,3-pentadiene and 4. Yield: 57% (the ratio of **24** and **23**=37 : 63); **24**[18] : ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm), 7.96 (d, 2H, 2,6-Hs of phenyl group), 7.47 (m, 3H, 3,4,5-Hs of phenyl group), 5.2 (dm, J=9.5 Hz, 1H, =CH-), 4.26 (qd, J=6.8 & 2.7 Hz, 1H, α-CH to CO), 1.75 (d, J=1.30 Hz, 3H, =C-CH_3), 1.70 (d, J=1.38 Hz, 3H, =C-CH_3), 1.25 (d, J=6.7 Hz, 3H, CO-CH-CH_3); IR (film), 3073, 2974, 1702 (CO), 1595, 1450, 1274, 1196, 993 cm^{-1}, mass spectrum; m/e (assignment, relative intensity), 188 (M^+, 2.22), 173 (M^+-CH_3, 0.78), 160 (M^+-CO, 0.26), 159 (M^+-CHO, 1.96), 145 (1.32), 105 ($PhCO^+$, 100); **23**: ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm), 8.0 (d, J=6.0 Hz, 2H, 2,6-Hs of phenyl group), 7.6-7.4 (m, 3H, 3,4,5-Hs of phenyl group), 3.64 (s, 2H, α-CH_2 to CO), 2.05 (q, J=7.5 Hz, 2H, =C-CH_2-), 1.7 (s, 3H, =C-CH_3), 0.97 (t, J=7.5 Hz, 3H, -CH_2-CH_3); IR (film), 3073, 2982, 1705 (C=O), 1596, 1453, 1381, 1219, 1067, 972, 847 cm^{-1}; mass spectrum; m/e (relative intensity), 188 (M^+, 2.55), 173 (M^+-CH_3, 0.59), 105 ($PhCO^+$, 100); TLC R_f=0.66, hexane : ethyl acetate=5 : 1, SiO_2.

Peparation of 2,4-dimethylpent-3-enyl phenyl ketone (25) from 2,4-dimethyl-1,3-pentadiene and 4. **25**[19]: 49% yield; ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm), 7.94 (dd, J=8.5 & 1.7 Hz, 2H, 2,6-Hs of phenyl group), 7.46 (m, 3H, 3,4,5-Hs of phenyl group), 4.98 (dt, J=9.28 & 1.45 Hz, 1H, -CH=), 3.1 (m, 1H, β-CH to CO), 2.90 (d, J=2.1 Hz, 1H, one of diastereotopic CH_2), 2.86 (d, J=3.6 Hz, 1H, one of diastereotopic CH_2), 1.64 (d, J=1.3 Hz, 3H, =C-CH_3), 1.58 (d, J=1.37 Hz, 3H, =C-CH_3), 1.02 (d, J=6.53 Hz, 3H, -CH-CH_3); IR (film), 3060, 2960, 2920, 1680 (C=O), 1595, 1580, 1445, 1275, 1070, 1000, 945, 890, 840, 750, 690 cm^{-1}; mass spectrum; m/e (relative intensity), 202 (1), 188 (6.8), 187 (1.6), 173 (0.7), 159 (2), 149 (3), 131 (1), 120 (4), 106 (8), 105 (100), 77 (31); TLC R_f=0.67, hexane : ethyl acetate=5 : 1, SiO_2.

Preparation of a mixture of 3-methylpent-4-enyl phenyl ketone (26) and 3-methylpent-2-enyl phenyl ketone (27) from 3-methyl-1,4-pentadiene and 4. Yield: 71% (the ratio of **26** and **27**=60 : 40); **26**[20]: ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm), 7.95 (d, J=7.1 Hz, 2H, 2,6-Hs of phenyl group), 7.6-7.4 (m, 3H, 3,4,5-Hs of phenyl group), 5.7 (m, 1H, -CH=), 4.95 (m, 2H, ABX system of =CH_2), 2.95 (td, J=6.7 & 1.8 Hz, 2H, α-CH_2 to CO), 2.25 (m, 1H, γ-CH to CO), 1.82 (m, 2H, β-CH_2 to CO), 1.02 (d, 3H, -CH-CH_3), 0.95 (t, J=7.3 Hz, 3H, -CH_2-CH_3); IR (neat), 3079, 2972, 1704 (CO), 1596, 1453, 1265, 1004, 920 cm^{-1}; mass spectrum, m/e (assignment, relative intensity), 188 (M^+, 5.55), 173 (M^+-CH_3, 3.16), 160 (M^+-CO, 0.6), 159 (M^+-CHO, 3.36), 133 (Ph-$COCH_2CH_2^+$, 5.31), 105 ($PhCO^+$, 100). **27**[21]: ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm), 7.95 (d, J=7.1 Hz, 2H, 2,6-Hs of phenyl group), 7.6-7.4 (m, 3H, 3,4,5-Hs of phenyl group), 5.45 (t, J=66.8 Hz, 1H, -CH=), 3.7 (d, J=6.8 Hz, 1H, α-CH_2 to CO), 2.11 (q, J=7.5 Hz, 2H, =C-CH_2-), 1.71 (s, 3H, =C-CH_3), 1.03 (t, J=7.6 Hz, 3H, CH_2-CH_3); IR (film), 3075, 2981, 1684

(C=O), 1454, 1289, 1214, 1015 cm^{-1}; mass spectrum; m/e (relative intensity), 188 (M^+-2, 3.47), 175 (45.32), 161 (100), 129 (44.31), 105 ($PhCO^+$, 76.90); TLC R_f=0.62, hexane : ethyl acetate=5 : 1, SiO_2.

Preparation of a mixture of 4-methylpent-4-enyl phenyl ketone (28) and 2-methylpent-2-enyl phenyl ketone (23) from 2-methyl-1,4-pentadiene and 4. Yield: 81% (the ratio of **28** and **23**=7 : 93); **28**[22]: ^1H NMR (300 MHz, $CDCl_3$) δ (ppm), 8.0 (d, J=6.0 Hz, 2H, 2,6-Hs of phenyl group), 7.6-7.4 (m, 3H, 3,4,5-Hs of phenyl group), 4.75 (d, J=9.2 Hz, 2H, AB system of $=CH_2$), 2.97 (t, J=7.3 Hz, 2H, α-CH_2 to CO), 2.1-1.85 (m, 4H, β,γ-CH_2 to CO), 1.72 (s, 3H, $=C-CH_3$); IR (neat), 3078, 2947, 1702, 1622, 1453, 1364, 1227, 991, 896 cm^{-1}. mass spectrum, m/e (assignment, relative intensity), 188 (M^+, 8.53), 173 (M^+-CH_3, 3.01), 170 (6.52), 160 (M^+-CO, 1.22), 159 (M^+-CHO, 10.28), 145 (4.72), 120 ($PhC(OH)=CH_2^+$, 58.87), 105 ($PhCO^+$, 100). TLC R_f= 0.66, hexane : ethyl acetate=5 : 1, SiO_2.

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