First Intermolecular Hydroacylation of 1,3-Dienes with Aldehydes Catalyzed by Ruthenium

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Summary: Ru(cod)(cot)−PPh_3 (cod = 1,5-cyclooctadiene, cot = 1,3,5-cyclooctatriene) is an effective catalyst system for the intermolecular hydroacylation of 1,3-dienes with aromatic and heteroaromatic aldehydes to give the corresponding β,γ-unsaturated ketones in reasonable yields. In this reaction, carbon monoxide is not needed to suppress decarbonylation of aldehydes. The key intermediate is an (acyl)(η^3-allyl)ruthenium complex which undergoes reductive elimination to give the corresponding ketones.

Introduction

Hydroacylation is an intriguing catalytic process because of its potential usefulness in the general synthesis of ketones from alkenes and aldehydes. Although activation of the formyl C−H bond by transition-metal complexes often leads to decarbonylation,[1] a hydrido−acyl intermediate could hydroacylate an unsaturated bond if the rate of hydroacylation is faster than the rate of decarbonylation. With rhodium-based catalysts, conversion of 4-pentenals to cyclopentanones via intramolecular hydroacylation has been extensively studied[2,3] and has been extended to asymmetric cyclization of substituted 4-pentenals into chiral cyclopentanones.[4,5] Recently, several examples of rhodium-catalyzed hydroiminoacylation were also reported as analogues of hydroacylation.[6] However, the catalytic systems reported so far are strictly limited to rhodium, and there are still only a few examples of transition-metal-catalyzed *intermolecular* hydroacylation reactions,[7,8] each of which has some limitations. We have recently been interested in the reactivity of (η^3-allyl)-ruthenium complexes[9] as well as ruthenium-catalyzed activation of the formyl C−H bond.[10] In this paper, we report the first example of ruthenium-catalyzed intermolecular hydroacylation of 1,3-dienes with aldehydes (eq 1).[11]

The reaction of 1,3-dienes with aldehydes catalyzed by transition-metal complexes, especially those involving palladium, generally yields tetrahydropyran derivatives and/or open-chain homoallyl alcohols.[12] Therefore, the present reaction represents the first method for

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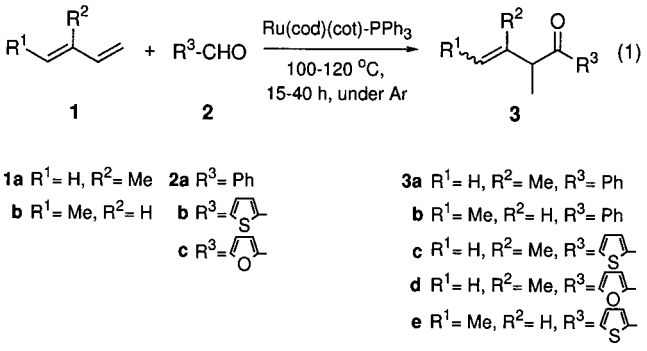

preparing β,γ-unsaturated ketones from readily available 1,3-dienes and aldehydes.

Results and Discussion

We initially examined the reaction of isoprene (**1a**) with benzaldehyde (**2a**) in the presence of a variety of ruthenium complexes. The reaction of **2a** (5.0 mmol) with **1a** (4.0 mL) in the presence of a catalytic amount of Ru(cod)(cot) and PPh_3 (4.0 mol % each) at 100 °C for 40 h under an argon atmosphere gave the corresponding β,γ-unsaturated ketone (**3a**) in an isolated yield of 54%. Conversion of benzaldehyde was 80%, and the only byproduct derived from benzaldehyde was benzene. Other catalyst systems, such as $RuH_2(PPh_3)_4$, $Ru_3(CO)_{12}$, $Ru_3(CO)_{12}-PPh_3$, Cp*RuCl(cod)$-PPh_3$, and $RuCl_2(PPh_3)_3$, were totally ineffective.

The effect of the molar ratio of PPh_3 to Ru(cod)(cot) was examined in the hydroacylation of **1a** with **2a** at 120 °C for 15 h under an argon atmosphere. As can be readily seen from Figure 1, the catalytic activity of Ru(cod)(cot) was greatly affected by the amount of PPh_3 ligand added. The best result was obtained when the PPh_3/Ru(cod)(cot) ratio was 1.0. Ratios higher and lower than 1.0 both led to a low conversion of aldehyde **2a** and a low yield of the product **3a**. The combination of Ru(cod)(cot) with suitable tertiary phosphine ligands can provide many useful catalytic systems,[13] but there is no information available regarding the reaction of Ru(cod)(cot) with bulky phosphines such as PPh_3. In the early stage of the present catalytic process, PPh_3 could react with Ru(cod)(cot) to give Ru(η^4-cod)(η^4-cot)(PPh_3) in a manner similar to the reaction with PMe_3 and $P(OMe)_3$.[14,15]

As for phosphorus ligands, with the use of more electron-donating ligands such as PBu_3 and PCy_3 instead of PPh_3, only Tishchenko-type dimerization of **2a** proceeded to give the corresponding ester, benzyl benzoate, as the main product.[16] In addition, the combination of Ru(cod)(cot) with electron-withdrawing ligands such as $P(OPh)_3$ showed no catalytic activity for the hydroacylation of **1a** with **2a** or for Tishchenko-type dimerization of **2a**.

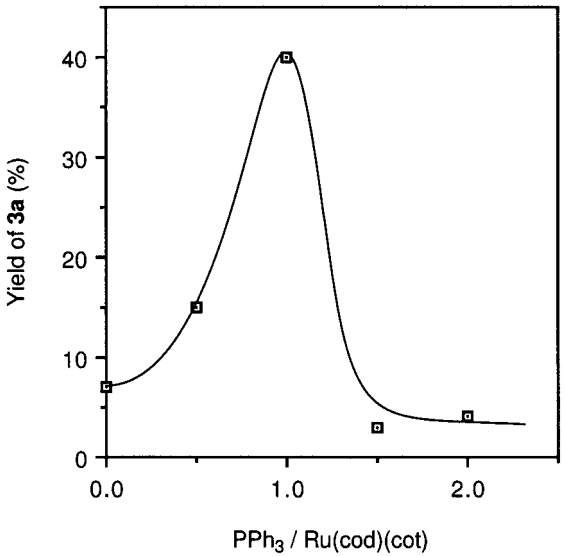

Figure 1. Effect of the PPh_3/Ru(cod)(cot) molar ratio on the hydroacylation of **1a** with **2a**. Reaction conditions: **1a** (4.0 mL), **2a** (5.0 mmol), Ru(cod)(cot) (0.20 mmol) at 120 °C for 15 h under an argon atmosphere.

Table 1. Ru(cod)(cot)/PPh_3-Catalyzed Intermolecular Hydroacylation of 1,3-Dienes with Aldehydes[a]

run	1,3-diene	aldehyde	product	yield (%)[b]	*E*:*Z*[c]
1[d]	**1a**	**2a**	**3a**	54	
2	**1b**	**2a**	**3b**	60	61:39
3	**1a**	**2b**	**3c**	43[e]	
4	**1a**	**2c**	**3d**	40[e]	
5	**1b**	**2b**	**3e**	43	56:44

[a] A mixture of 1,3-diene (4.0 mL), aldehyde (5.0 mmol), Ru(cod)(cot) (0.20 mmol), and PPh_3 (0.20 mmol) in a 50-mL stainless steel autoclave was heated at 120 °C for 15 h under an argon atmosphere. [b] Isolated yields based on the aldehyde charged. [c] Determined by ^{1}H NMR. [d] At 100 °C for 40 h. [e] GLC yield.

The results obtained from the reactions of several 1,3-dienes with aromatic and heteroaromatic aldehydes are summarized in Table 1. In all cases, the starting aldehydes were almost completely consumed to give the corresponding β,γ-unsaturated ketones (**3a**−**e**) in reasonable yields. The reaction of *trans*-1,3-pentadiene (**1b**) with benzaldehyde (**2a**) gave the corresponding β,γ-unsaturated ketone (**3b**) in an isolated yield of 60% (run 2 in Table 1). Heteroaromatic aldehydes such as thiophene-2-carbaldehyde and furan-2-carbaldehyde were also useful (runs 3−5). Unfortunately, the reactions with aliphatic aldehydes were unsuccessful. For example, the reaction of **1a** with dodecanal gave the corresponding ketone in only 10% yield together with various byproducts,[17] while the conversion of dodecanal was 70%.

It is noteworthy that the hydroacylation of *trans*-1,3-pentadiene (**1b**) with benzaldehyde (**2a**) gave the cor-

(13) For example, see: (a) Mitsudo, T.; Nakagawa, Y.; Watanabe, K.; Hori, Y.; Misawa, H.; Watanabe, H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 565. (b) Mitsudo, T.; Hori, Y.; Watanabe, Y. *J. Organomet. Chem.* **1987**, *334*, 157. (c) Watanabe, Y.; Morisaki, Y.; Kondo, T.; Mitsudo, T. *J. Org. Chem.* **1996**, *61*, 4214. (d) Wakatsuki, Y.; Yamazaki, H.; Kumegawa, N.; Satoh, T.; Satoh, J. Y. *J. Am. Chem. Soc.* **1991**, *113*, 9604.

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(15) In the present reaction, the impediment to catalytic turnover frequency is the formation of a catalytically inactive ruthenium carbonyl species (ν_{CO} = 2025 (w), 1994 (vs), 1955 (s), and 1933 (vs) cm^{-1}). To suppress decarbonylation of aldehydes leading to the formation of this species, the PPh_3 ligand is essential and should attach to Ru during the reaction. Efforts are currently underway to prepare the more efficient modified catalysts.

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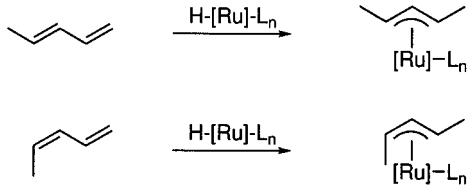
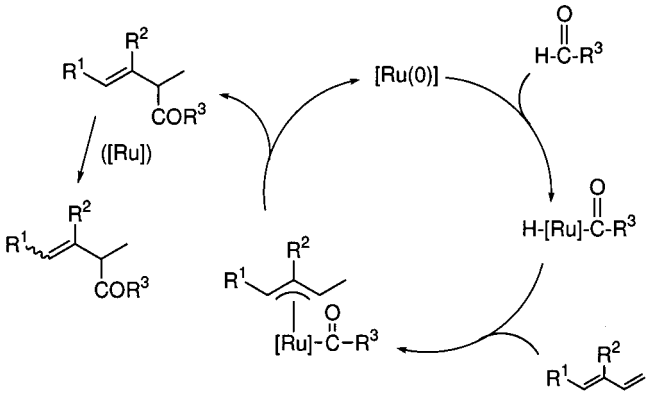
Scheme 1



Scheme 2



responding β,γ-unsaturated ketone (**3b**) in 60% yield (run 2 in Table 1), while no reaction occurred with *cis*-1,3-pentadiene. This result strongly suggests that an (η^3-allyl)ruthenium species is a key intermediate in the present reaction. A stable *syn*,*syn*-(η^3-allyl)ruthenium intermediate could be obtained from the reaction of *trans*-1,3-pentadiene with a (hydrido)ruthenium(II) species, while *cis*-1,3-pentadiene would give an unstable *anti*,*syn*-(η^3-allyl)ruthenium intermediate (Scheme 1).

Considering all of our findings, the most plausible mechanism is illustrated in Scheme 2. First, an (acyl)(hydrido)ruthenium(II) species is generated by the oxidative addition of aldehyde to an active ruthenium(0) species. Next, insertion of the less-substituted double bond in 1,3-diene into a hydrido−ruthenium bond occurs to give an (acyl)(η^3-allyl)ruthenium(II) intermediate. Successive regioselective reductive elimination between the acyl and η^3-allyl ligands[18,19] gives the β,γ-unsaturated ketone with regeneration of an active ruthenium(0) species.

In conclusion, we have developed a novel method for preparing β,γ-unsaturated ketones by the ruthenium-catalyzed intermolecular hydroacylation of 1,3-dienes with aldehydes. This reaction does not require ethylene,[2b,d,e,3a] hydrogen,[2f,4f,g,5b] or carbon monoxide[8] to activate the catalyst or to suppress the decarbonylation of aldehydes. Since hydroacylation is now a powerful tool in organic synthesis,[20] the present reaction should open new opportunities in this field.

Experimental Section

Materials. The reagents used in this study were dried and purified before use by standard procedures. $Ru_3(CO)_{12}$ was obtained commercially and used without further purification. Ru(cod)(cot),[21] $RuH_2(PPh_3)_4$,[22] Cp*RuCl(cod),[23] and $RuCl_2(PPh_3)_3$[24] were prepared as described in the literature.

Analytical Procedures. GLC analyses were carried out on gas chromatographs equipped with a glass column (3 mm i.d. × 3 m) packed with Silicone OV-17 (2% on Chromosorb W(AW-DMCS), 80−100 mesh) and a capillary column (Shimadzu capillary column HiCap-CBP10-M25-025 (polarity similar to that of OV-1701): 0.22 mm i.d. × 25 m). The ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz. Samples were analyzed in $CDCl_3$, and the chemical shift values are expressed relative to Me_4Si as an internal standard. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

General Procedures. A mixture of 1,3-diene (**1**) (4.0 mL), aldehyde (**2**) (5.0 mmol), Ru(cod)(cot) (63.0 mg, 0.20 mmol), and PPh_3 (52.5 mg, 0.20 mmol) was placed in a 50-mL stainless steel autoclave under an argon atmosphere. The mixture was magnetically stirred at 120 °C for 15 h. After cooling, the products were isolated by Kugelrohr distillation and/or recycling preparative HPLC. All of the products are characterized below.

2,3-Dimethyl-1-phenylbut-3-en-1-one (3a):[18] colorless oil, bp 70 °C (5.0 mmHg, Kugelrohr). IR (neat): 1683.7 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34 (d, 3H, CH_3, J = 6.83 Hz), 1.74 (s, 3H, CH_3), 4.13 (q, 1H, CH, J = 6.83 Hz), 4.89 (s, 1H, CH_2=), 4.90 (s, 1H, CH_2=), 7.42−7.46 (m, 2H, Ph), 7.51−7.56 (m, 1H, Ph), 7.96−7.99 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.0, 20.5, 49.1, 113.6, 128.4 (two overlapping signals), 132.8, 136.7, 145.3, 200.9 (C=O). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.65; H, 8.24.

(*E*)-2-Methyl-1-phenylpent-3-en-1-one (3b): pale yellow oil, bp 120 °C (5.0 mmHg, Kugelrohr). IR (neat): 1687.9 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.21 (d, 3H, CH_3, J = 6.83 Hz), 1.58 (d, 3H, CH_3, J = 4.88 Hz), 4.03 (dq, 1H, CH, J = 4.88, 6.35 Hz), 5.44 (dd, 1H, CH=, J = 17.09, 6.35 Hz), 5.48 (dq, 1H, CH=, J = 17.09, 6.83 Hz), 7.33−7.46 and 7.85−7.90 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.1, 17.5, 44.5, 125.4, 128.3, 128.4, 128.5, 132.8, 136.5, 201.6 (C=O). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found (for a 61:39 mixture of **3b** and **3b′**): C, 82.46; H, 8.13.

(*Z*)-2-Methyl-1-phenylpent-3-en-1-one (3b′): pale yellow oil, bp 120 °C (5.0 mmHg, Kugelrohr). IR (neat): 1684.1 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.20 (d, 3H, CH_3, J = 6.84 Hz), 1.68 (dd, 3H, CH_3, J = 6.83, 1.46 Hz), 4.31 (dq, 1H, CH, J = 9.03, 6.84 Hz), 5.36−5.50 (m, 2H, 2CH=), 7.26−7.48 and 7.81−7.90 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.7, 18.0, 40.2, 117.5, 129.7, 130.6, 130.9, 132.9, 137.0, 201.9 (C=O).

1-(2-Thienyl)-2,3-dimethylbut-3-en-1-one (3c): pale yellow oil, bp 80 °C (5.0 mmHg, Kugelrohr). IR (neat): 1659.6 cm^{-1} ($\nu_{C=O}$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34 (d, 3H, CH_3, J = 6.84 Hz), 1.75 (d, 3H, CH_3, J = 0.98 Hz), 3.99 (q, 1H, CH, J = 6.84 Hz), 4.93 (s, 1H, CH_2=), 4.97 (s, 1H, CH_2=), 7.11 (dd, 1H, thienyl, J = 5.13, 3.90 Hz), 7.61 (dd, 1H thienyl, J = 5.13, 0.97 Hz), 7.78 (dd, 1H, thienyl, J = 3.90, 0.97 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.9, 20.2, 50.8, 113.6, 128.0, 132.0,

(17) Careful analysis of the byproducts by GC-MS showed the formation of undec-1-ene (obtained by decarbonylation/β-hydride elimination, 4% yield), undecane (obtained by decarbonylation, 2% yield), and 1-dodecanol (obtained by reduction, 9% yield). Other high-boiling byproducts may contain the aldol-type condensation products but cannot be characterized fully.

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(24) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth*. **1970**, *12*, 237.

133.4, 143.8, 145.1, 193.7 (C═O). Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71; O, 8.88. Found: C, 66.83; H, 6.92; O, 9.18.

1-(2-Furyl)-2,3-dimethylbut-3-en-1-one (3d):[18] colorless oil, bp 70 °C (5.0 mmHg, Kugelrohr). IR (neat): 1673.0 cm^{-1} ($\nu_{C=O}$). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.31 (d, 3H, CH_3, J = 6.84 Hz), 1.76 (s, 3H, CH_3), 3.94 (q, CH, J = 6.84 Hz), 4.90 (s, 1H, CH_2═), 4.92 (s, 1H, CH_2═), 6.52 (dd, 1H, furyl, J = 3.42, 1.47 Hz), 7.23 (d, 1H, furyl, J = 3.42 Hz), 7.58 (d, 1H, furyl, J = 1.47 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 15.3, 20.5, 49.2, 112.1, 113.3, 117.5, 144.6, 146.2, 152.3, 189.8 (C═O). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.85; H, 7.64.

(*E*)-1-(2-Thienyl)-2-methylpent-3-en-1-one (3e): pale yellow oil, bp 80 °C (5.0 mmHg, Kugelrohr). IR (neat): 1659.8 cm^{-1} ($\nu_{C=O}$). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.31 (d, 3H, CH_3, J = 6.84 Hz), 1.67 (d, 3H, CH_3, J = 5.37 Hz), 3.92 (dq, 1H, CH, J = 7.32, 6.84 Hz), 5.59 (dd, 1H, CH═, J = 16.85, 7.32 Hz), 5.65 (dq, 1H, CH═, J = 16.85, 5.37 Hz), 7.11−7.13 (m, 1H, thienyl), 7.61−7.62 (m, 1H, thienyl), 7.73−7.76 (m, 1H, thienyl). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.1, 17.5, 46.4, 125.5, 128.0, 131.8, 132.0, 133.5, 143.7, 194.5 (C═O). Exact mass: calcd for $C_{10}H_{12}OS$, 180.0609; found, 180.0608. Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71. Found (for a 56:44 mixture of **3e** and **3e′**): C, 66.69; H, 6.75.

(*Z*)-1-(2-Thienyl)-2-methylpent-3-en-1-one (3e′): pale yellow oil, bp 80 °C (5.0 mmHg, Kugelrohr). IR (neat): 1659.8 cm^{-1} ($\nu_{C=O}$). ^1H NMR ($CDCl_3$, 400 MHz): δ 1.29 (d, 3H, CH_3, J = 6.84 Hz), 1.77 (d, 3H, CH_3, J = 5.37 Hz), 4.14 (dq, 1H, CH, J = 8.79, 6.84 Hz), 5.56 (dd, 1H, CH═, J = 9.28, 8.79 Hz), 5.57 (dq, 1H, CH═, J = 9.28, 5.37), 7.11−7.13 (m, 1H, thienyl), 7.61−7.62 (m, 1H, thienyl), 7.73−7.76 (m, 1H, thienyl). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.7, 17.9, 41.6, 117.6, 127.5, 130.5, 130.8, 133.5, 143.6, 194.7 (C═O).

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Additions and Corrections

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Judith C. Gallucci, Olivier Gobley, Florence Zaegel, Philippe Meunier, Bernard Gautheron, Holger Lange, Rolf Gleiter, Natasha Kozmina, and Leo A. Paquette*: Solid-State Structural Analysis of the "Naked" Isodicyclopentadienide Anion.

Page 112. The space groups for the Na(isodiCp)(15-crown-5) and the [K-cryptand(2.2.2)]$^+$(isodiCp)$^-$ structures were incorrectly reported in refs 13 and 14 as $P1$. Both space groups are $P\bar{1}$.

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