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Title: Pr2O3 Supported Nano-layered Ruthenium Catalyzed Acceptorless Dehydrogenative Synthesis of 2-Substituted Quinolines and 1,8-Naphthyridines from 2-Aminoaryl Alcohols and Ketones

Authors: Katsutoshi Nagaoka, Chandan Chaudhari, Katsutoshi Sato, Yuta Ogura, and Shin-ichiro Miayahara

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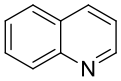
Pr_2O_3 Supported Nano-layered Ruthenium Catalyzed Acceptorless Dehydrogenative Synthesis of 2-Substituted Quinolines and 1,8-Naphthyridines from 2-Aminoaryl Alcohols and Ketones

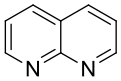
Chandan Chaudhari,*[a] Katsutoshi Sato,[a] Yuta Ogura,[a] Shin-ichiro Miayahara,[a] and Katsutoshi Nagaoka*[a]

Abstract: Pr_2O_3 supported Ru nanolayers and Ru nanoparticles catalysts were examined for the synthesis of quinolines. The Ru nanolayer was most active catalyst and showed a broad substrate scope. Structure-activity relationship demonstrated that the metallic state and morphology of Ru as well as the basic site of Pr_2O_3 were indispensable factors of this catalytic system.

Quinolines and 1,8-naphthyridines are important nitrogen-containing heterocyclic compounds which exist in numerous natural products.[1] Both classes exhibit a wide range of biological activities such as antibacterial,[2] anti-inflammatory,[3] antihypertensive,[4] and antiplatelet activities.[5]Although these compounds are structurally similar to each other, the additional nitrogen atom in 1,8-naphthyridines can impart different chemical properties and require different synthetic methods.



Quinoline



Naphthyridine

Traditionally, quinolines and 1,8-naphthyridines were synthesized by using Friedländer method which involves the condensation of 2–aminoaromaticaldehydes and ketones.[6] However, the limited availability and poor stability of 2-aminoaromaticaldehydes, makes them unfavorable as reactant for the synthesis of quinolines and 1,8-naphthyridines. Quinolines have also been synthesized from 2-aminobenzyl alcohols, which are relatively stable. Using 2-aminobenzyl alcohol, Ru and Cu catalysts were reported for the synthesis of quinolines in the presence of a sacrificial hydrogen acceptor.[7] However, dehydrogenation of 2-aminobenzyl alcohol in the absence of an acceptor would be more desirable in terms of atom economy.

[a] Dr. C. Chaudhari, Dr. K. Sato, Dr. Y. Ogura, S. Miyahara, Prof. Dr. K. Nagaoka
Department of Chemical Systems Engineering,
Graduate school of Engineering, Nagoya University
Furo-cho, Chikusa-ku, Nagoya-464-8603, Japan
E-mail: nagaoka.katsutoshi@material.nagoya-u.ac.jp
E-mail: chaudhari.chandan.subhash@d.mbox.nagoya-u.ac.jp
[b] Dr. K. Sato
Elements Strategy Initiative for Catalysts and Batteries,
Kyoto University, 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245, Japan
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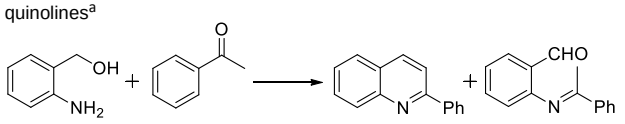
Acceptorless dehydrogenation of alcohols has gained much of attention of researchers for the direct synthesis of chemicals.[8] The only byproducts of this atom-economical and environmentally friendly reaction are water and hydrogen. Several catalytic acceptorless dehydrogenative syntheses of quinolines from 2-aminobenzyl alcohols and alcohols and/or ketones have been reported.[9] For example, homogeneous Ru, Pd, Ir, Cu, Ni, and Co catalysts have been explored for similar transformations under basic conditions,[9a–l] and the use of recyclable Pd and Pd-Ag catalysts in the presence of KOH has also been investigated.[9m,n] However, these methods require high catalyst loading and a basic additive (Table S1). To the best of our knowledge, acceptorless dehydrogenative synthesis of 2-substituted 1,8-naphthyridines has not been reported.

Praseodymium oxide is an important rare earth oxide as adsorbent, catalysts, promoter and high electricity materials.[10] Despite praseodymium oxides have interesting unique structure and phases, it is much less explored as support for noble metal loading.[11] Recently, we developed Pr_2O_3 supported low-crystalline Ru nanolayers catalysts by using $Ru_3(CO)_{12}$ precursor.[12] Interestingly, this catalyst showed excellent activity for ammonia synthesis, better than that of MgO supported Ru nanoparticles catalyst. The synergistic combination of strong basic support (Pr_2O_3) and unique Ru structure could play a vital role in acceptorless dehydrogenative synthesis of heterocycles in absence of basic additives. We herein report that we have successfully developed the first general method for acceptorless dehydrogenative synthesis of 2-substituted quinolines and 1,8-naphthyridines under neutral conditions.

To optimize reaction conditions for the synthesis of 2-phenylquinoline, we performed the reaction of 2-aminobenzyl alcohol (**1**) and acetophenone (**2**) as a model reactions (Table 1). Ru_{CO}/Pr_2O_3 and Ru_{AC}/Pr_2O_3 catalysts were prepared by using $Ru_3(CO)_{12}$ and $Ru(acac)_3$ respectively. Among the tested Pr_2O_3 supported metals (Ru, Rh, Ir and Re), Ru was found to be the most active metal for the synthesis of 2-phenylquinoline (entries 1-6). Interestingly, Ru_{CO}/Pr_2O_3 catalyst demonstrated higher activity than Ru_{AC}/Pr_2O_3 catalyst. 13 % yield of byproduct (Dibenzo[b,f] [1,5]diazocine) was obtained when Ru_{AC}/Pr_2O_3 was used as catalyst (entry 3). Pr_2O_3 was found to be optimal support leading to excellent yield (entries 7-10). Low yield of 2-sustituted quinoline was obtained in the presence of Pr_2O_3 support (entry 12).

To elucidate the dependence of the catalytic activity on the Ru structure, we measured the X-ray absorption near-edge structure (XANES) and X-ray absorption fine structure (EXAFS) spectra of Ru_{CO}/Pr_2O_3-red, Ru_{CO}/Pr_2O_3-unred, and Ru_{AC}/Pr_2O_3-red, as well as Ru powder as a reference compound (Fig. 1; the results of EXAFS curve-fitting analysis are listed in Table S2).

Table 1. Optimization of reaction conditions for the synthesis of 2-phenyl quinolines[a]



1 2 3 4

Entry	Catalyst	Conv. (%)	Yield[b] (%) 3	Yield[b] (%) 4
1	Ru_{CO}/Pr_2O_3	99	95	0
2[c]	Ru_{CO}/Pr_2O_3	71	57	0
3[d]	Ru_{AC}/Pr_2O_3	99	83	0
4	Ir/Pr_2O_3	99	76	0
5	Rh/Pr_3O_3	99	80	2
6	Re/Pr_3O_3	50	48	2
7	Ru/MgO	88	67	0
8	Ru/CeO_2	99	36	0
9	Ru/La_2O_3	58	52	1
10	Ru/γ-Al_2O_3	66	66	2
11	Ru_3CO_{12}	65	5	0
12	Pr_2O_3	36	15	0

a] Reaction conditions: **1** (1 mmol), **2** (1.5 mmol), mesitylene (1.2 mL), catalyst (2 mol% of Ru), 170°C ºC, 24 h, Ar. [b] GC yield. [c] Without reduction. [d] Dibenzo[b,f][1,5]diazocine was obtained as a byproduct.

The designation "red" indicates that the catalyst was reduced at 500 °C for 0.5 h prior to analysis. The EXAFS spectrum of species with a Ru–Ru bond length of 2.66 Å and a coordination number of 10.5. Similarly, the EXAFS of spectrum of Ru_{AC}/Pr_2O_3-red indicated a Ru–Ru bond length of 2.64 Å and a coordination number of 7.9. The coordination numbers for Ru_{CO}/Pr_2O_3-red and Ru_{AC}/Pr_2O_3-red were smaller than that of the Ru powder (12). The XANES spectra of Ru_{CO}/Pr_2O_3-red and Ru_{AC}/Pr_2O_3-red catalyst were identical to that of Ru powder which indicated the state of Ru was made of metallic state. The EXAFS spectrum of the unreduced catalyst (Ru_{CO}/Pr_2O_3-unred) indicated the presence of a Ru–O species (coordination number, 5.5;bond length, 1.99Å). The XANES spectrum of this catalyst had a slightly higher white line intensity, indicating that the Ru had been partially oxidized by exposure to air after catalyst synthesis from $Ru_3(CO)_{12}$.

We also examined the morphology of Ru using scanning transmission electron micrograph (STEM) and energy dispersive X-ray (EDX) (Fig.S1-S4). The reconstructed overlaying image of Ru_{CO}/Pr_2O_3-red catalyst showed that metallic Ru was highly dispersed on the surface of Pr_2O_3 in the form of nanolayers (Fig. S1). In contrast, Ru nanoparticles were observed in reconstructed overlaying image when Ru precursor was changed from $Ru_3(CO)_{12}$ to ruthenium (III) acetylacetonate (Fig. S3 & S4).

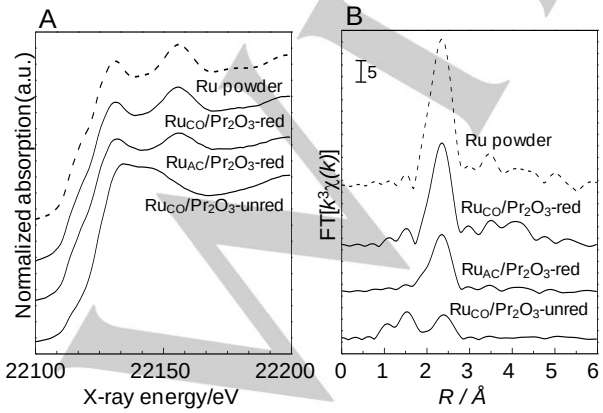
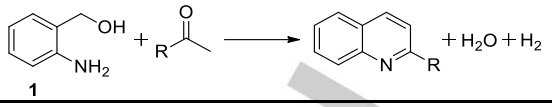
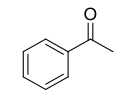
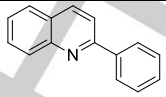
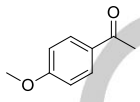
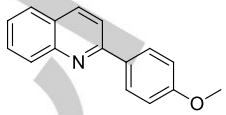
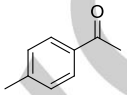
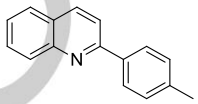
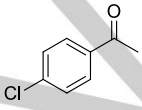
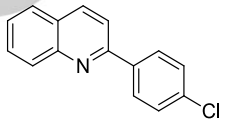
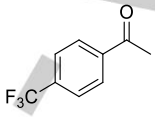
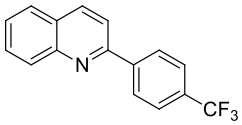
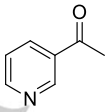
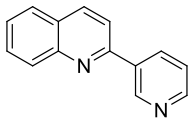
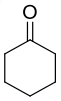
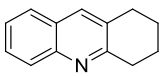
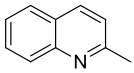
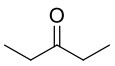
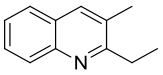
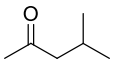
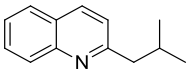
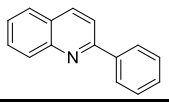


Figure 1. (A) XANES spectra and (B) EXAFS Fourier transforms at Ru K-edge for Ru catalysts and a reference compound (Ru powder)

Table 2. Synthesis of 2-substituted quinoline from 2-aminobenzyl alcohol and ketone[a]



1

Entry	Ketones	Products	Yield[b] (%)
1			95
2			90
3			96
4			87
5			80
6			92
7			51
8			86
9			71
10			85
11[c]			62

[a] Reaction conditions: **1** (1 mmol), ketones (1.5 mmol), mesitylene (1.2 mL), Ru_{CO}/Pr_2O_3 (2 mol% of Ru), 170 ºC, 24 h, Ar. [b] Isolated yield. [c] 48.

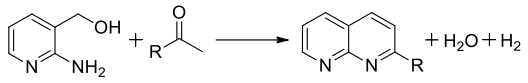
With a combination of structural results and Table 1, it is concluded that metallic and morphology of Ru were key factors for the synthesis of quinolines.

Next, we studied the general applicability of Ru_{CO}/Pr_2O_3 catalyst for the synthesis of quinoline from 2-aminobenzyl alcohol and various ketones under optimized conditions (Table 2). Acetophenone bearing electron-donating group (OCH3 andCH_3) were converted to corresponding quinolines with excellent yield (Table 3, entry 2 and 3). The catalyst was tolerable to electron-withdrawing group and transformed acetophenenone bearing electron-withdrawing to quinolines. Heteroaryl (methyl) ketone, cyclic ketone, methyl ketone and nonmethyl ketone proceeded smoothly to desired products (entries 7-10). Interestingly, this method was applicable not only to ketones but also alcohol. The

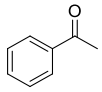
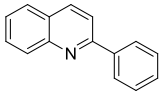
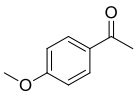
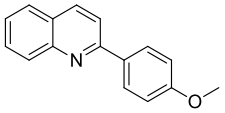
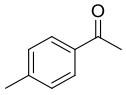
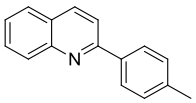
reaction of 2-aminobenzyl alcohol and phenyl ethanol resulted in moderate yield of quinoline (entry 11).

Encouraged by quinoline results, we examined the synthesis of 1,8-naphthyridines from (2-aminopyridin-3-yl)methanol (**5**) and acetophenone (Table 3). The catalyst was also tolerable *N*-containing heterocyclic alcohol and converted electron-rich acetophenone to corresponding naphthyridines products with moderate-good yield (Table 4, entries 2 and 3).

Table 3. Synthesis of 2-substituted 1,8-naphthyridine from and ketones[a]



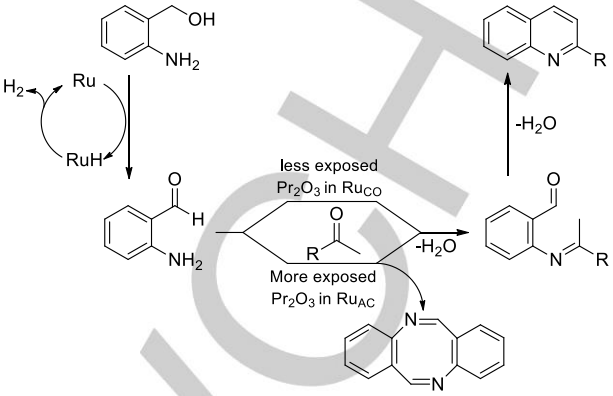
5

Entry	Ketones	Products	Yield[b] (%)
1			95
2			90
3			96

[a] Reaction conditions: 5 (1 mmol), ketones (1.5 mmol), mesitylene (1.2 mL), Ru_{CO}/Pr_2O_3 (2 mol% of Ru), 170 °C, 24 h, Ar. [b] Isolated yield.

The recyclability of Ru_{CO}/Pr_2O_3 was investigated for the synthesis of quinolines from 2-aminobenzyl alcohol and acetophenone (Fig. S5). After the first cycle, the catalyst was washed by acetone and centrifuged followed by drying at 50°C for 12 h under vacuum. The recovered catalyst was reduced at 500 °C for 0.5 h and used for the second cycle. Without significant change in yield of product, the catalyst was reused for cycle number 2 and 3.

In mechanistic studies, we carried out time-yield profile for the reaction of **1** with acetophenone which showed a consecutive reaction mechanism via intermediate (2-aminobenzaldehyde). The yield of the intermediate was increased with time and then decreased accompanying increase in yield of the final product (Fig S6). Furthermore, we confirmed the hydrogen evolution by using gas chromatography in absence of ketones or in presence of ketone (eq. S1 and S2). From these results, we proposed a plausible mechanism for the synthesis of 2-substituted quinolines from 1 and ketones (Scheme 1). The reaction begins with Ru catalyzed acceptorless dehydrogenation of 2-aminobenzyl alcohol to 2-aminobenzaldehyde and hydrogen. Then, Pr_2O_3-promoted condensation of 2-aminobenzaldehyde and ketone leads to cyclised final product. The stability of 2-aminobenzaldehyde over strongly basic Pr_2O_3 support was a crucial factor. In comparison to Ru nanoparticles, Ru nanolayers contain less exposed Pr_2O_3 surface which was confirmed by H_2 chemisorptions (Table S3). It provides more stability for 2-aminobenzaldehyde and converted to quinoline selectively. In contrast, 2-aminobezaldehyde undergo self-condensation over relatively more exposed Pr_2O_3 surface of Ru nanoparticles catalyst and formed (dibenzo[b,f][1,5]diazocine) as byproduct.



Scheme 1. Plausible mechanism for the synthesis of quinoline from 2-aminobenzyl alcohol and acetophenone.

In conclusion, we have developed a general method for the synthesis of 2-substituted quinolines and 1,8-naphthyridines by Ru nanolayers catalyst under acceptor-free and additive-free conditions. Pr_2O_3 supported Ru nanolayers catalyst showed superiority over conventional Pr_2O_3 supported Ru nanoparticles catayst for synthesis of 2-substituted quinolines from 2-aminobenzyl alcohol and ketones. Ru nanolayers catalyst was reused and tolerant to different functional groups of acetopheneone.

Experimental Section

General

Commercially available chemicals (from Tokyo Chemical Industry, Wako Pure Chemical Industries, FURUYA METAL Co., Ltd.) were used without further purifications.

Catalyst preparation

Pr_2O_3 support was prepared by precipitating $Pr(NO_3)_3.6H_2O$ with 25 wt% NH_3 aqueous solution. The obtained light green suspension was kept in solution overnight with constant stirring, followed by filtration of precipitate, washing with distilled water, drying at 70°C for 12 h. Then, the solid was calcined at 700°C in static air for 5 h. MgO, CeO_2 and La_2O_3 supports were prepared by precipitation method using $Mg(NO_3)_2{\cdot}6H_2O$ (Wako) $La(NO_3)_3{\cdot}6H_2O$ (Wako) and $Ce(NO_3)_3{\cdot}6H_2O$ (Kanto Chemical, Japan) precursor respectively and calcined at 700°C for 5 h. γ-Al_2O_3 was supplied by Sumitomo Chemical Company Ltd. Pr_2O_3 supported Ru nanolayers (named, Ru_{CO}/Pr_2O_3) catalyst with 5 wt% metal loading was prepared by an impregnation method; a mixture of Pr_6O_{11} and $Ru_3(CO)_{12}$ dissolved in tetrahydrofuran (THF) was evaporated at 50°C, followed by drying at 70 °C for 12h, and heated at 350°C for 5 h under a flow of He flow to remove CO ligand from $Ru_3(CO)_{12}$ precursor. Similarly, Pr_2O_3 supported Ru nanoparticles (named, Ru_{AC}/Pr_2O_3) catalyst was prepared by using ruthenium (III) acetylacetonate precursor. A mixture of support and precursor dissolved in THF was evaporated

and dried at 70 °C for 12h. Then, the catalyst was calcined at 350°C for 5 h in air. M/Pr_2O_3 (M = Ir, Re, Rh) catalysts were prepared using corresponding metal carbonyl precursor method. Ru/M_xO_y (M_xO_y= MgO, CeO_2, La_2O_3, Al_2O_3) catalysts were prepared by using $Ru_3(CO)_{12}$ precursor.[12,13] Before each catalytic experiment, a pre-reduced catalyst was prepared by in situ pre-reduction of the precursor in a Pyrex tube under a flow of H_2 (30 cm^3 min^{-1}) at 500°C for 0.5 h.

Catalyst characterization

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and EDX elemental mappings were obtained on a JEM-ARM200F electron microscope (JEOL, Japan) operated at 120 kV. The samples were prepared by dispersing in ethanol followed by dropping onto a carbon-coated copper grid, and drying under vacuum at ambient temperature for 24 h. X-ray absorption near-edge structures (XANES) and X-ray absorption fine structure (EXAFS) at Ru K-edge were measured at the BL01B1 in the SPring-8 with the approval of Japan Synchrotron Radiation Research institute. A Si (111) two-crystal was used to obtain both absorption edges. The EXAFS analysis was performed using the Athena. The parameters for the Ru–O and Ru–Ru shells were provided by Artemis programs (ver. 0.9.25) included in the Demeter package. The specific surface areas of Ru_{CO}/Pr_2O_3 and Ru_{AC}/Pr_2O_3 were calculated after N_2 treatment at 300°C by using Brunauer–Emmett–Teller method and BEL-mini instrument (BEL Japan Inc., Japan). H_2 chemisorption of Ru_{CO}/Pr_2O_3 and Ru_{AC}/Pr_2O_3 catalysts was measured to estimate number of exposed Ru atoms. The sample kept in H_2 flow (60 NmL min^{-1}), followed by increasing the temperature from room temperature to 500 °C. The temperature was maintained for 1 h and then sample was purged by Ar flow for 30 min, cooled to −78 °C, and flushed with Ar for 60 min. After this pretreatment, H_2 chemisorption analysis was carried out at −78 °C in an Ar stream (60 NmL min^{-1}) by a pulsed-chemisorption technique. Energy dispersive X-ray fluorescence analyses were carried out using an EDXL 300 (Rigaku).

Typical procedures for the synthesis of 2-substituted quinoline and 1,8 naphthyridine

After pre-reduction, the catalytic activity of Ru/Pr_2O_3 was examined without exposing the catalyst to air. Typically, the mixture 2-aminoaryl alcohol (1.0 mmol) and ketone (1.5 mmol) in mesitylene (1 g) was injected to the pre-reduced catalyst inside the reactor (cylindrical glass tube) through a septum inlet, followed by filling Ar. Then, the reaction mixture was stirred for 24 h under reflux condition. After finishing the reaction, the reaction mixture was cooled and catalyst was separated from reaction mixture using syringe micro-filter. The conversion of 2-aminoaryl alcohol and yield of product were determined by GC using n-dodecane as an internal standard. The product was confirmed by GCMS and purified by flash column chromatography using hexane-ethyl acetate mixture (90:10).

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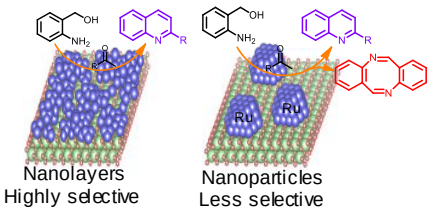

Acceptorless dehydrogenative synthesis and Ru nanolayers: Ru nanolayers were efficient catalyst for acceptorless dehydrogenative synthesis of quinolines. This catalyst was reused and applicable for the synthesis of 1,8-naphthyridine.