Supporting Information

A Ruthenium-Grafted Hydrotalcite as a Multifunctional Catalyst for Direct α -Alkylation of Nitriles with Primary Alcohols

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Synthesis of Ru-grafted hydrotalcite: Hydrotalcite (HT), $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$, was synthesized according to the literature procedure (See: Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 173). The hydrotalcite (1.0 g) was added to 100 mL of a 5.0×10^{-4} M aqueous solution of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$. Then the heterogeneous mixture was stirred at 25 °C for 1 h under air. The solid product was isolated by centrifugation, washed thoroughly with deionized water and dried in vacuo at room temperature, affording Ru/HT as a gray powder (Ru content: 0.5 wt %). X-ray diffraction studies showed the retention of its layered structure with a basal spacing of 7.7 Å. Various ruthenium supported solid base catalysts, such as Ru/MgO, Ru/ Al_2O_3 , Ru/ $\text{Mg}(\text{OH})_2$, and Ru/ $\text{Al}(\text{OH})_3$ were synthesized by the same procedure. MgO, $\text{Mg}(\text{OH})_2$, and $\text{Al}(\text{OH})_3$ were purchased from Wako Pure Chemicals. Ru/ Al_2O_3 was synthesized using γ - Al_2O_3 (JRC-ALO-4).

α -Alkylation of nitriles with alcohols: Into an autoclave (10 mL) were placed the Ru/HT (0.15g, Ru: 0.0075 mmol), ethanol (2 mL), and phenylacetoneitrile (1.0 mmol). The resulting mixture was vigorously stirred at 180 °C under Ar. After 20 h, the catalyst was separated by filtration and the GC analysis of the filtrate showed a 98 % yield of 2-phenylbutyronitrile. The filtrate was evaporated and the crude product was purified by column chromatography using silica to afford a pure product (0.136 g, 94 % isolated yield).

To confirm whether the above α -alkylation occurred on the solid surface, the Ru/HT catalyst was removed by filtration after ca. 50 % conversion of phenylacetoneitrile at the reaction temperature. Further treatment of the filtrate under the identical reaction conditions did not afford any product.

Recycling experiment revealed the Ru/HT catalyst could be reused without any appreciable loss of activity and selectivity; over 92 % yields of phenylacetoneitrile were obtained after the first and second runs at 130 °C for 40 h.

For the large-scale α -alkylation, into an autoclave (10 mL) were placed the Ru/HT (0.8 g, Ru: 0.04 mmol), ethanol (5 mL), and phenylacetoneitrile (20 mmol). The reaction mixture was vigorously stirred at 180 °C under Ar for 30 h. Then, the catalyst was separated by filtration and the GC analysis of the filtrate showed an 82 % yield of 2-phenylbutyronitrile.

Hydrogen transfer reaction of benzyl alcohol with 2-phenylcinnamonitrile: Into an autoclave (10 mL) were placed the Ru/HT (0.15 g, Ru: 0.0075 mmol), toluene (2 mL), benzyl alcohol (1.5 mmol), and (Z)-2-phenylcinnamonitrile (1.0 mmol). The reaction mixture was vigorously stirred at 180 °C under Ar. After 20 h, the catalyst was separated by filtration and the GC analysis of the filtrate showed a 98% yield of 2,3-diphenylpropionitrile together with benzaldehyde.

Aldol condensation of phenylacetonitrile with benzaldehyde: Into an autoclave (10 mL) were placed the parent HT (0.15 g), toluene (2 mL), benzaldehyde (1.5 mmol), and phenylacetonitrile (1.0 mmol). The reaction mixture was vigorously stirred at 180 °C under Ar. After 7 h, the catalyst was separated by filtration and the GC analysis of the filtrate showed a 98 % yield of 2-phenylcinnamionitrile. The Ru/HT also promotes this condensation to afford (Z)-2-phenylcinnamionitrile in 96 % yield.

α -Alkylation using a deuterated alcohol: Into an autoclave (10 mL) were placed the Ru/HT (0.15 g, Ru: 0.15 mmol), toluene (2 mL), benzyl- d_7 alcohol (1.5 mmol), and phenylacetonitrile (1.0 mmol). The reaction mixture was vigorously stirred at 180 °C under Ar. After 20 h, the catalyst was separated by filtration, and the ^1H NMR analysis of the filtrate showed the formation of two deuterated α -alkylated products at a ratio of 4:3.

Synthesis of α,α -dialkyl phenylacetonitriles: Into an autoclave (10 mL) were placed the Ru/HT (0.15g, Ru: 0.0075 mmol), ethanol (2 mL), and phenylacetonitrile (1.0 mmol). The reaction mixture was vigorously stirred at 180 °C under Ar for 20 h. After completion of the alkylation, excess ethanol was evaporated, followed by addition of acrylonitrile (3.0 mmol) and DMF (2 mL) to the same flask and further reaction at 150 °C. After 1 h, the catalyst was separated by filtration, and the GC analysis of the filtrate showed a 93 % yield of 2-ethyl-2-phenylglutarodinitrile based on phenylacetonitrile. For the reactions of methyl acrylate and acryl amide as Michael acceptors, the solvent used was

DMSO instead of DMF (Table 1S).

Table 1S. Ru/HT Catalyzed One-pot Synthesis of α,α -dialkylated phenylacetonitrile^a

$ \begin{array}{c} \text{1a} + \text{2a} \xrightarrow[180\text{ }^{\circ}\text{C, 20 h}]{\text{Ru/HT (0.15 g, 0.75 mol\%)}} \left[\text{Ph}-\text{CH}(\text{Et})-\text{CN} \right] \xrightarrow[150\text{ }^{\circ}\text{C}]{\text{alkene Z, solvent (2 mL)}} \text{Ph}-\text{C}(\text{Et})_2-\text{CH}_2-\text{Z}-\text{CN} \\ \text{(not isolated)} \end{array} $				
entry	alkene Z	solvent	time (h)	overall yield (%) ^b
1	$\text{CH}_2=\text{CHCN}$ 5a	DMF	1	93
2	$\text{CH}_2=\text{CHCOOMe}$ 5b	DMSO	1	82(80)
3 ^c	$\text{CH}_2=\text{CHCONH}_2$ 5c	DMSO	20	84

^a**1a** (1 mmol), **2a** (2 mL). ^bDetermined by GC. Based on phenylacetonitrile. ^cRu/HT (0.3 g; 0.015 mmol). Values in parentheses are isolated yields.

Characterization by Ru K-edge X-ray absorption fine structure (XAFS): X-ray absorption spectra were recorded at the beam line 01B1 station attached to the Si(311) monochromator at SPring-8 for JASRI, Harima, Japan (prop. No. 2003B0944-Uxa-np). The detailed procedures for data analysis are described elsewhere (See: Tanaka, T.; Yamashita, H.; Tsuchitani, R.; Funabiki, T.; Yoshida, S. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 2987). Inverse FT of k^3 -weighted Ru K-edge EXAFS experimental data for the Ru/HT are shown in Figure 1S. The results of curve-fitting analysis are summarized in Table 2S.

Figure 1S. The inverse FTs of the Ru/HT performed in the range of 0.9-2.0 Å (a) and 1.9-3.0 Å (b). The dotted lines in part (a) and (b) show the results of curve-fitting analysis using five Ru-O (a), and one Ru-O, and Ru-Mg (b) shell parameters.

Table 2S. Curve-fitting Results of Ru K-edge EXAFS of the Ru/HT^a

Shell	CN ^a	R ^b (Å)	Δσ ^c (Å ²)
Ru-O(1)	3.0	1.97	0.0022
Ru-O(2)	2.3	2.04	0.0006
Ru-O(3)	0.9	1.82	0.0064
Ru-Mg	1.5	3.18	0.0060

^aCoordination number, ^bInteratomic distance, ^cΔσ is the difference between Debye-Waller factor of the samples and that of the reference sample.

The distance of the shortest Ru-O bond is slightly longer than that of the Ru(IV)=O observed in the Ru complexes with σ-saturated tertiary amine ligands (1.765 Å) (See: Che, C. M.; Lai, T. F.; Wong, K. Y. *Inorg. Chem.* **1987**, 26, 2289), but shorter than the Ru(II)-OH bond in the nitrosylruthenium porphyrin complex (1.956 Å) (See: Miranda, K. M.; Bu, X.; Lorković, I.; Ford, P. C. *J. Am. Chem. Soc.* **1997**, 36, 4838). The Ru-O distance of 2.04 Å is close to that from the Ru cation to the oxygen atom in an aqua ligand (See: (a) Liobet, A.; Hodgson, D. J.; Meyer, T. *Inorg. Chem.* **1990**, 29, 3760 (b) Wilkinson, G.; Gillard, R. D.; MacClevarty, J. A. Eds.; *Comprehensive Coordination Chemistry*; Pergamon: Oxford, 1987, Vol. 4, pp.420-423).

IR measurement: Figure 2S shows the IR spectra of (A) benzyl alcohol, (B) fresh Ru/HT, (C) after treatment of (B) with benzyl alcohol at 80 °C under Ar atmosphere. The signal derived from Ru-H species was detected at 2120 cm^{-1} after treatment of the Ru/HT with benzyl alcohol (B vs. C). In the case of $\text{RuH}_2(\text{PPh}_3)_3$, the $\nu(\text{Ru-H})$ band was observed at 2150 cm^{-1} (See, Dijkman, A.; Marino-González, A.; Payeras, A. M. i; Arends, I. W. C. E.; Sheldon, R. A. *J. Am. Chem. Soc.* **2001**, *123*, 6826).

Figure 2S. IR spectra of the sample (A)-(C)

We have tried to detect Ru-D species after treatment of the Ru/HT catalyst with benzyl- d_7 -alcohol by IR spectroscopy. However, the strong broad absorption due to the HT support did not allow us to detect the Ru-D signal, which may appear at around 1500 cm^{-1} . The signal at 2120 cm^{-1} was not detected after treatment of the Ru/HT with benzyl- d_7 -alcohol.

For IR measurement of the Ru-H species, the solid catalyst was filtered and subjected to the disk with KBr. All the manipulations were carried out under Ar atmosphere.