Supporting Information

Title : A New Solvent System for Recycling Catalysts for A Chelation-Assisted Hydroacylation of Olefins with Primary Alcohols

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General Remarks. NMR spectra were recorded in CDCl₃ on Bruker Avance DPX 250 spectrometer (¹H NMR, 250 MHz; ¹³C NMR, 62.5 MHz) spectrometer, and the chemical shift was expressed in ppm relative to TMS. IR spectra were recorded on Nicolet Impact 400 spectrometer. GC analyses were conducted using Donam DS 2000 Gas Chromatography. Mass spectra were obtained using G1800A GCD System. ICP-MS analyses were obtained from National Center for Inter-University Facilities, Seoul National University, Seoul, Korea, using Perkin Elmer SCIEX ELAN 6100. All the materials used in experiments were purchased from commercial sources except [(C₈H₁₄)₂RhCl]₂ (**4**), which was prepared as described in the literature.¹ Alcohols (**1**) were dried over CaSO₄ and distilled prior to use. Olefins (**2**) were distilled over sodium, and 4,4'-dipyridyl was recrystallized from ethanol and stored in glove box. 4-diphenylphosphinobenzoic acid (**4a**), triphenylphosphine (**4b**), 2-amino-4-picoline (**5**), and phenol were purchased from Aldrich Co., and used as received. Ionic liquids, [BMIM]PF₆ (BMIM = 1-butyl-3-methylimidazolium) and [BMIM]BF₄, were purchased from Chirogene, and used as received. All experiments were conducted in glove box under Ar atmosphere.

Typical Procedures for Catalyst Recycling. The Reaction of Benzyl Alcohol (1a) and 1-Hexene (2a). (Table 1, entry 1) A screw-capped pressure vial (1 mL) was charged with 34.6 mg (0.320 mmol) of benzyl alcohol (**1a**), 134.4 mg (1.600 mmol) of 1-hexene (**2a**), 5.7 mg (0.016 mmol) of [(C₈H₁₄)₂RhCl]₂ (**3**), 19.6 mg (0.064 mmol) of 4-

¹ Osborn, J. A.; Wilkinson, G. In *Reagents for Transition Metal Complex and Organometallic Synthesis*;

diphenylphosphinobenzoic acid (**4a**), 34.6 mg (0.320 mmol) of 2-amino-4-picoline (**5**), 25.0 mg (0.160 mmol) of 4,4'-dipyridyl, and 100 mg of phenol. The reaction mixture was stirred in an oil bath that was preheated at 150 °C for 6h. After cooling to room temperature, the reaction mixture formed two phases. The upper layer was decanted, after centrifuging (10 min), washed with 0.8 mL of n-pentane (three times), and purified by column chromatography (SiO₂, *n*-hexane : ethyl acetate = 5 : 2) to afford 53.5 mg (88%) of heptanophenone (**6a**). To the remaining lower layer were added 34.6 mg (0.320 mmol) of benzyl alcohol (**1a**), and 134.4 mg (1.600 mmol) of 1-hexene (**2a**) for the next reaction.

Among the products, a commercially available compound such as **6a** was identified by comparison with authentic specimens. Other ketones such as 4,4-dimethyl-1-phenylpentanone (**6b**),² 1-phenylnonanone (**6c**),² 1-phenylundecanone (**6d**),³ 4,4-dimethyl-1-(4- α,α,α -trifluoromethylphenyl)-1-pentanone (**6e**)⁴, 1-(4-methoxyphenyl)-heptanone (**6f**),² 4,4-dimethyl-1-(4-methoxyphenyl)pentanone (**6g**),⁵ and have already been reported, and were identified by ¹H NMR, ¹³C NMR, IR, and MS spectra.

Angelich, R., Ed.; Wiley: New York, 1989; Vol. 28, pp 90-91.

² Jun, C.-H.; Lee, D.-Y.; Lee, H.; Hong, J.-B. *Angew. Chem. Int. Ed.* **2000**, *39*, 3070.

³ Loupy, A.; Chatti, S.; Delamare, S.; Lee, D.-Y.; Chung, J.-H.; Jun, C.-H. *J. Chem. Soc., perkin Trans 1* **2002**, 1280

⁴ Jun, C.-H.; Lee, D.-Y.; Kim, Y.-H.; Lee, H. *Organometallics* **2001**, *20*, 2928.

⁵ Russell, G. A.; Shi, B. *Synlett* **1993**, 701

The extent of a leaching of rhodium catalyst was estimated by ICP-MS analyses of the upper layer. For ICP-MS analyses, the reaction of benzyl alcohol (**1a**) and 1-hexene (**2a**) was performed according to the procedure described above. After the reaction, the upper layer was decanted, after centrifuging (10 min), washed with 1.0 mL of *n*-pentane (three times). The combined solution was evaporated under reduced pressure, concentrated *in vacuo*, then the content of rhodium was determined by ICP-MS analyses. To the remaining lower layer were added benzyl alcohol and 1-hexene for the next reaction, and after the reaction the upper layer was separated by the same method for ICP-MS analyses.

In order to confirm that a ketone is clearly separated from the polar phase, an experiment measuring the extent of recovery of ketone from the reaction system was carried out as follows. To a mixture consisting 5.7 mg (0.016 mmol) of $[(C_8H_{14})_2RhCl]_2$ (**3**), 19.6 mg (0.064 mmol) of 4-diphenylphosphinobenzoic acid (**4a**), 34.6 mg (0.320 mmol) of 2-amino-4-picoline (**5**), 25.0 mg (0.160 mmol) of 4,4'-dipyridyl, and 100 mg of phenol, was added 56.4 mg (0.320 mmol) of hexanophenone. The upper layer was extracted using 0.8 mL of *n*-pentane after centrifuging (10 min), and it was found that 56.2 mg (99.6%) of hexanophenone was recovered after three decantation (48.8 mg, 5.1 mg, 2.3 mg at each decantation).

In order to examine the extent of a leaching of 2-amino-4-picoline, the following experiment was carried out. A screw-capped pressure vial (1 mL) was charged with 34.6 mg (0.320 mmol) of 2-amino-4-picoline (**5**), 25.0 mg of 4,4'-dipyridyl, 100 mg of phenol, and 134.4 mg (1.600 mmol) of 1-hexene (**2a**). The reaction mixture was stirred in an oil bath that was preheated at 150 °C for 15 min, then cooled to room temperature to form two phases. The upper layer was extracted using 0.8 mL of *n*-pentane after centrifuging (10 min). The GC analysis revealed that 1.9 mg of **5** (5% based on the initial amount of **5**) was found in the combined upper layer after three decantation.

The Reaction of Benzyl Alcohol (1a) and 1-Hexene (2a) Varying the Amount of 2-Amino-4-picoline (5). The reaction was carried out following the same procedure described above (Table 1, entry 1) varying the amount of **5** from 20 mol% to 120 mol% (based on the amount of **1a**). After the reaction, the reaction mixture was diluted by adding 3 mL of CH₂Cl₂, and the yield of **6a** was determined by GC analysis. The results are summarized in Table S1.

Table S1. The Hydroacylation of 1-Hexene (2a) with Benzyl Alcohol (1a) Varying the Amount of 2-Amino-4-picoline

entry	The amount of 2-amino-4-picoline (5) ^a	Yield of 6a (GC yield)
1	20 mol%	70
2	40 mol%	95
3	60 mol%	99
4	80 mol%	100
5	100 mol%	100
6	120 mol%	100

^a Based on the amount of **1a**.

Reaction of Benzyl Alcohol (1a) and 1-Hexene (2a) using Ionic Liquids as Reaction Medium (eq S1). A screw-capped pressure vial (1 mL) was charged with 34.6 mg (0.320 mmol) of benzyl alcohol (**1a**), 134.4 mg (1.600 mmol) of 1-hexene (**2a**), 5.7 mg (0.016 mmol) of $[(C_8H_{14})_2RhCl]_2$ (**3**), 34.6 mg (0.320 mmol) of 2-amino-4-picoline (**5**), and 100 mg of ionic liquid (1-*n*-buthyl-3-methylimidazolium hexafluorophosphate or 1-*n*-buthyl-3-methylimidazolium tetrafluoroborate). As an external ligand, 0.064 mmol (20 mol% based on **1a**) of 4-diphenylphosphinobenzoic acid (**4a**) or triphenylphosphine (**4b**) was used. The reaction mixture was stirred in an oil bath, which was preheated at 150 °C, for 6h. After cooling to room temperature, the upper organic layer was decanted, washed with *n*-pentane,

and purified by column chromatography (SiO₂, *n*-hexane : ethyl acetate = 5 : 2) to afford heptanophenone (**6a**). The remaining ionic liquid layer was reused for the next reaction by addition of substrates, **1a** and **2a**. The results are summarized in Table S2.

In all cases, the yields of **6a** were low maybe due to heterogeneity derived from the limited solubility of a substrate (1-hexene). Especially, when the reactions were conducted using PPh₃ as a ligand, the yield of **6a** dropped at the 2nd reaction. It was observed that the large amount of PPh₃ was found in the upper organic layer.

Table S2. The Hydroacylation of 1-Hexene (2a**) with Benzyl Alcohol (**1a**) using Ionic Liquids (eq S1)**

entry	Ionic liquid	Phosphine	Isolated yield of 6a (%)			
			1	2	3	4
1	[BMIM]BF ₄	PPh ₃	34	(7) ^b	-	-
2	[BMIM]PF ₆	PPh ₃	27	(7) ^b	-	-
3	[BMIM]BF ₄	4-PBA	56	43	47	33
4	[BMIM]PF ₆	4-PBA	49	32	41	52

^a BMIM = 1-*n*-butyl-3-methylimidazolium. ^b The yields in parenthesis are GC yield.