

Simple RuCl₃-Catalyzed Amide Synthesis from Alcohols and AminesSubhash Chandra Ghosh^[a] and Soon Hyeok Hong^{*[a]}**Keywords:** Amides / N-heterocyclic carbenes / Carbene ligands / Ruthenium / Grubbs catalyst / Amidation

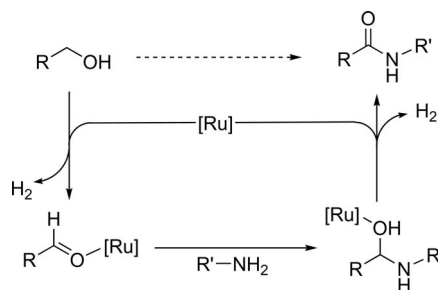
A catalyst for the direct synthesis of amides from amines and alcohols, generated in situ from the economically attractive and readily available RuCl₃, an N-heterocyclic carbene (NHC), and pyridine, was developed. Of the screened NHC precursors, a less bulky one gave better yields for modestly

sterically hindered substrates. In a search for the true catalytic intermediates, Grubbs catalysts were found to be active for the amidation of alcohols under basic conditions, suggesting that an Ru complex supported by an NHC ligand can catalyze the reaction.

Introduction

Syntheses of amides are typically carried out through the coupling of activated carboxylic acid derivatives with amines.^[1] Although the traditional methods give good results, they lack atom economy and often produce toxic chemical waste with tedious associated procedures. Some recent approaches include oxidative amidation of aldehydes with amines^[2,3] and hydrative amide synthesis with alkynes and azides.^[4] However, the development of better methods by which amides can be synthesized from stable and simple starting materials is still required.

Since Naota's and Murahashi's report of Ru-catalyzed intramolecular oxidative amidation reactions from 1,4- and 1,5-amino alcohols to form lactams,^[3] several groups have reported amide formation from alcohols with the aid of Ru,^[5–7] Rh,^[8] and Ag^[9] catalysts. Among them, Ru complexes have been most extensively investigated.^[3,5–7] The strategy is first to oxidize the alcohol to an aldehyde and then further to oxidize the hemiaminal, formed from the aldehyde and the amine, to an amide with evolution of 2 equiv. of hydrogen gas (Scheme 1). The direct acylation of amines with alcohols is a highly desirable, atom-economical transformation in which hydrogen is evolved as the sole by-product with less waste than in the traditional amide synthesis. However, there are still many challenges, such as the costs associated with transition metals, requirements for milder reaction conditions, and limitations in substrate scope, for the developed methodology to find use in natural-products synthesis and the pharmaceutical industry.



Scheme 1. Ru-catalyzed amide formation from alcohols and amines.

Our group has reported on the phosphane-free direct synthesis of amides catalyzed by [Ru(*p*-cymene)Cl₂]₂ or [Ru(benzene)Cl₂]₂ complexes with N-heterocyclic carbenes (NHCs).^[6] In view of the excellent activities of these catalytic systems, generated in situ, and of the hypothesized dissociation of η^6 -bound arenes during catalysis, we became interested in finding a more economical and readily available ruthenium source. Here we report our findings relating to the development of amide synthesis with the use of simple RuCl₃ under phosphane-free conditions.

Results and Discussion

Optimization of RuCl₃ Catalytic System

The reaction between 2-phenylethanol and benzylamine to afford *N*-benzyl-2-phenylacetamide was chosen as a model reaction with which to establish effective conditions (Table 1). The economically attractive and readily available RuCl₃ was selected as a catalyst precursor. Initially, different bases were screened for in situ generation of an active NHC–Ru catalyst. NaH (40 mol-%) was found to give good

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results in terms of amide formation, with a 79% yield. Weaker bases, including K₂CO₃ and even KO^tBu, did not show good activity. Various L-type supporting ligands were then screened to improve the activity. The use of acetonitrile improved the yield to 86%. Replacement of acetonitrile with PPh₃, PCy₃, DPPE, PCy₂Ph, and DPPP led to lower levels of conversion (Entries 3–7). The use of pyridine resulted in the best yield (90%), and it was selected for further screening (Entry 8). We then examined different NHC precursors (Entries 9–15; Figure 1). The NHC precursor **5** showed slightly reduced activity relative to the NHC precursor **1** (Entry 12), but other aryl-substituted NHCs gave lower yields.

Table 1. Screening with different NHCs and ligands.^[a]

$\text{Ph-CH}_2\text{-CH}_2\text{-OH} + \text{H}_2\text{N-CH}_2\text{-Ph} \xrightarrow[\text{40 mol-\% NaH, toluene, reflux}]{\substack{5 \text{ mol-\% [Ru] \\ 5 \text{ mol-\% NHC salt} \\ 5 \text{ mol-\% ligand}}} \text{Ph-CH}_2\text{-CH}_2\text{-C(=O)-NH-CH}_2\text{-Ph}$				
Entry	Catalyst	NHC precursor	Ligand	Yield (%) ^[b]
1	RuCl ₃	1	none	79
2	RuCl ₃	1	CH ₃ CN	86
3	RuCl ₃	1	PPh ₃	83
4	RuCl ₃	1	PCy ₃	77
5	RuCl ₃	1	DPPE	51
6	RuCl ₃	1	PCy ₂ Ph	63
7	RuCl ₃	1	DPPP	63
8	RuCl ₃	1	pyridine	90
9	RuCl ₃	2	pyridine	27
10	RuCl ₃	3	pyridine	28
11	RuCl ₃	4	pyridine	21
12	RuCl ₃	5	pyridine	83
13	RuCl ₃	6	pyridine	45
14	RuCl ₃	7	pyridine	23
15	RuCl ₃	8	pyridine	26
16	RuCl ₃ ·xH ₂ O	1	pyridine	55 ^[c]
17	RuCl ₃	1	pyridine	66 ^[d]

[a] RuCl₃ (5 mol-%), NHC precursor (5 mol-%), NaH (40 mol-%), and ligand (5 mol-%) in toluene at reflux for 24 h, unless otherwise noted. [b] GC yield with dodecane as an internal standard. [c] NaH (50 mol-%). [d] 1 mol-% catalyst loading.

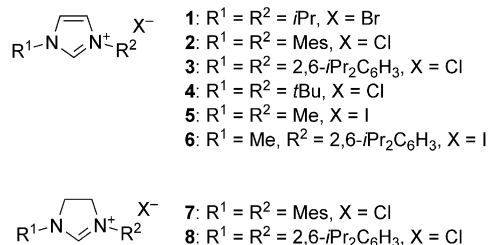


Figure 1. NHC precursors.

Use of the more economical RuCl₃·xH₂O with slightly more NaH (50 mol-%) resulted in a 55% yield of amide (Entry 16). With 1 mol-% catalyst loadings of RuCl₃, a 66% yield of the amide was observed (Entry 17). The presence

of various hydrogen acceptors such as acetone (83%), benzalacetone (84%), and 3-methylbutan-2-one (65%) did not improve the yields. Other solvents, such as THF (55%), benzene (47%), and acetonitrile (0%), under reflux conditions, gave considerably lower or zero yields of the desired product.

Substrate Scope and Limitation

After the optimization of the reaction conditions, the substrate scope of the developed catalytic system was examined (Table 2). Sterically unhindered alcohols and amines were converted into the desired amides in good yields (79–82%, Entries 1–4). The reactions between benzylamine and hex-5-en-1-ol or pent-3-yn-1-ol generated the corresponding amides with concomitant hydrogenation of the double bond and the triple bond (Entries 5 and 6).

Reactions between benzylamine and butane-1,4-diol or benzene-1,2-dimethanol, to afford the cyclic tertiary imides (succinimide and phthalimide derivatives), were attempted. Only limited amounts of the products were obtained, however, with observation of γ -butyrolactone and phthalide.^[10] Interested in this observation, we examined the reaction behavior of butane-1,4-diol and benzene-1,2-dimethanol in the absence of amines. The corresponding γ -butyrolactone and the phthalide were obtained in 59% and 76% yields, respectively, with our catalytic system (Entries 7 and 8). An effective phthalide synthesis from 1,2-benzenedimethanol with Cp^{*}Ru^{II} catalyst systems has previously been reported.^[11]

Formation of a five-membered lactam by intramolecular amidation proceeded smoothly (Entry 9), although in the case of 2-aminophenethyl alcohol, indole was isolated in 84% yield, instead of indolin-2-one (Entry 10). The formation of indole from 2-aminophenethyl alcohol with RuCl₂(PPh₃)₃ as a catalyst was also reported by Watanabe and co-workers.^[12] The introduction of a methoxy group in the molecule did not have any effect on the activity (Entries 11 and 12). When 4-chlorobenzylamine was used, the corresponding amide was obtained in 52% yield along with the dechlorinated amide (12%, Entry 13).

Reactions with cyclic secondary amines also gave the corresponding amides in good yields (Entries 14 and 15). Lower yields, however, were obtained with sterically bulky substrates and the NHC precursor **1** (Entries 16 and 18). When the less bulky NHC precursor **5** was screened, the yields of the amides were increased significantly (Entries 17 and 19). In the case of a sterically highly hindered substrate and the less nucleophilic aniline, limited activity was observed whether **1** or **5** was used, as also observed with other Ru catalytic systems (Entries 22 and 23).^[5,6]

Insight into Catalytic Intermediates

Encouraged by the activity observed with simple RuCl₃, we tried to isolate a catalytically active species, presumably consisting of Ru with an NHC, pyridine, and chlorido li-

Table 2. Direct synthesis of amides from alcohols and amines.^[a]

Entry	Alcohol	Amine	Amide	Yield (%) ^[b]	Entry	Alcohol	Amine	Amide	Yield (%) ^[b]
1				80	13				52
2				79	14				76
3				79	15				80
4				82	16				51
5				70	17				70 ^[e]
6				57	18				34
7				59 ^[c]	19				68 ^[e]
8				76	20				74 ^[e]
9				51	21				74 ^[e,f]
10				84 ^[d]	22				21 ^[e,f]
11				73	23				19 ^[e]
12				79					

[a] RuCl_3 (5 mol-%), NHC precursor **1** (5 mol-%), NaH (40 mol-%), and pyridine (5 mol-%) in toluene at reflux for 24 h, unless otherwise noted. [b] Isolated yields. [c] Butane-1,4-diol (0.2 M) used. [d] Indole was isolated as the major product (84%). [e] NHC precursor **5** used (5 mol-%). [f] In mesitylene at 165 °C.

gands. However, many attempts to isolate and characterize a well-defined Ru complex from the reaction of **5**, NaH, and pyridine with RuCl_3 were unsuccessful. The need for larger amounts (40 mol-%) of NaH in this RuCl_3 system than in the reported Ru^{II} -based catalytic systems (15–20 mol-%)^[6a] was noted. It is proposed that the role of NaH in this RuCl_3 system is both to reduce Ru^{III} to Ru^{II} or Ru^0 and to generate NHC from an imidazolium salt as a base.^[13] Some nonreducing strong bases did not show any activity in the amidation reaction.^[14] A role of NaH as a reducing agent for Ru and Fe complexes has been reported.^[15]

Grubbs and co-workers reported an interesting NHC- and pyridine-based Ru complex – $(\text{H}_2\text{IMes})\text{RuCl}_2(\text{pyridine})_3$ (**10**) – from the decomposition of the Grubbs catalyst **9** (Figure 2).^[16] We suspected that our catalytic intermediate

might have a structure similar to that of the decomposition product **10**. With this as our hypothesis, we tested the readily available Grubbs-type NHC-based catalysts **9**, **11**, and **12** shown in Figure 2 for the alcohol amidation reactions.

The NHC-based olefin metathesis catalysts tested were all catalytically active for amide synthesis under similar basic conditions, which suggests that an Ru complex supported by an NHC ligand can catalyze the amidation reaction (Table 3).^[17] The requirement for a catalytic amount of a base has been reported for other $[\text{Ru}]\text{Cl}_2$ -based catalytic systems.^[5b,6] The proposed role is the generation of a catalytically active $[\text{Ru}]\text{H}_2$ species through the exchange of chloride and alkoxide formed from a primary alcohol and a base,^[6b] as proposed for catalytic alcohol dehydrogenation,^[18] *N*-alkylation of amines with alcohols,^[19] and esterification of alcohols.^[20] Of the three catalysts screened, the

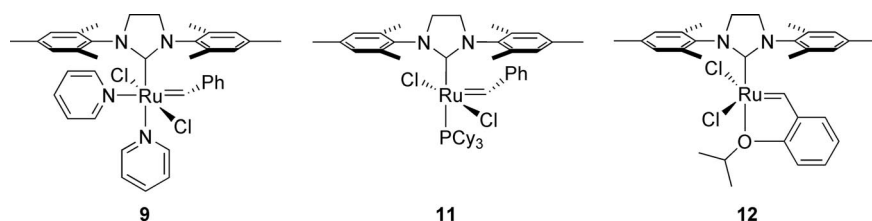


Figure 2. NHC-based Ru olefin-metathesis catalysts.

pyridine-based **9** demonstrated the highest activity, which is consistent with the screened data in Table 1 showing that the pyridine ligand improved the activity. However, the activities of the catalysts **9–12** were less than those of the reported catalytic systems, presumably due to the mesityl-based saturated NHC ligand. It has been reported that the *i*Pr- or Me-based unsaturated NHC precursors **1** and **5** were better activators than aryl-based NHC precursors.^[5b,6]

Table 3. Amide synthesis catalyzed by Grubbs-type catalysts.

$\text{Ph-CH}_2\text{-CH}_2\text{-OH} + \text{H}_2\text{N-CH}_2\text{-Ph} \xrightarrow[\text{toluene, reflux, 24 h}]{[\text{Ru}]}$ $\text{Ph-CH}_2\text{-CH}_2\text{-C(=O)-NH-CH}_2\text{-Ph}$			
Entry	Catalyst (5 mol-%)	NaH (mol-%)	Yield (%) ^[a]
1	9	–	0
2	9	20	62
3	11	20	49
4	12	20	48

[a] GC yield with dodecane as an internal standard.

Conclusions

A catalyst generated in situ from the economically attractive and readily available RuCl₃, an N-heterocyclic carbene, and pyridine was developed for the direct synthesis of amides from amines and alcohols. A less bulky N-heterocyclic carbene gave better yields for sterically modestly hindered substrates. Additionally, NHC-based olefin metathesis catalysts were found to be active for the amidation of alcohols under basic conditions, suggesting that an Ru complex supported by an NHC ligand can catalyze the reaction.

Experimental Section

General Considerations: All reactions were carried out in oven-dried glassware under dry argon or nitrogen. All alcohols, amines, and anhydrous pyridine were obtained from Aldrich or Alfa Aesar and used as received. The imidazolium salts **1**, **5**, and **6** were synthesized according to literature procedures.^[6] Sodium hydride (60% dispersion in mineral oil) was purchased from Aldrich, washed several times with pentane, dried, kept in a glove box, and directly used for the amide synthesis. Toluene was dried with a Pure Solv solvent purification system. Analytical TLC was performed with Merck 60 F254 silica gel plates (0.25 mm thickness). Column chromatography was performed with Merck 60 silica gel (230–400 mesh). NMR spectra were recorded with a JEOL ECA400 (¹H NMR at 400 MHz, ¹³C NMR at 100 MHz) spectrometer. Tetramethylsilane was used as a reference, and the chemical shifts are reported in ppm and the coupling constant in Hz. GC yields were obtained with an Agilent 7890A instrument with an HP-5 column. Mass spectrometry was performed with a Waters Q-ToF Premier Micro-mass instrument, in Electro Spray Ionization (ESI) mode.

General Procedure for Amide Synthesis: RuCl₃ (10.4 mg, 0.05 mmol), the NHC precursor **1** or **5** (0.05 mmol), NaH (9.6 mg, 0.40 mmol), and pyridine (4 µL, 0.05 mmol) in toluene (0.6 mL) were placed in an oven-dried Schlenk tube under an inert gas. After having been heated to reflux for 20 min, the reaction mixture was removed from the oil bath, and the alcohol (1 mmol) and the amine

(1.1 mmol) were added. The mixture was heated to reflux under a flow of argon to facilitate removal of hydrogen for 24 h. After the system had cooled to room temperature, all volatiles were removed under vacuum. The amide product was purified by silica gel column chromatography. All the amides – *N*-benzyl-2-phenylacetamide,^[6] *N*-pentyl-2-phenylacetamide,^[6] *N*-hexyl-2-phenylacetamide,^[6] *N*-pentylhexanamide,^[6] *N*-benzylpentanamide,^[6] *N*-benzylhexanamide,^[6] isobenzofuran-1(3*H*)-one,^[10] pyrrolidin-2-one,^[6] *N*-benzyl-2-methoxyacetamide,^[6] 4-(phenylacetyl)morpholine,^[6] *N*-benzyl-2-methylbutanamide,^[6] *N*-(2-heptyl)-hexanamide,^[6] *N*-benzyl-*N*-methyl-2-phenylacetamide,^[6] *N*-benzylpivalamide,^[6] and *N*,2-diphenylacetamide^[6] – were identified by spectral comparison with literature data.

***N*-Benzyl-2-(4-methoxyphenyl)acetamide:** The title compound was purified by silica gel column chromatography (hexane/ethyl acetate, 2:1; *R*_f = 0.27) to afford a white solid. Isolated yield: 79%. ¹H NMR (CDCl₃): δ = 7.30–7.14 (m, 7 H, Ar-H), 6.87–6.58 (m, 2 H, Ar-H), 5.81 (br. s, 1 H, NH), 4.38 (d, ³*J*_{H,H} = 5.9 Hz, 2 H, NCH₂), 3.77 (s, 3 H, OCH₃), 3.54 (s, 2 H, PhCH₂) ppm. ¹³C NMR (CDCl₃): δ = 171.5, 159.0, 138.4, 130.7, 128.8, 127.6, 127.5, 126.9, 114.6, 55.4, 43.7, 43.0 ppm. HRMS (ESI-TOF): calcd. for C₁₆H₁₈NO₂ 256.1338 [M + H]⁺; found 256.1341.

***N*-(4-Chlorobenzyl)-2-phenylacetamide:** The title compound was purified by silica gel column chromatography (hexane/ethyl acetate, 3:1; *R*_f = 0.20) to afford a white solid. Isolated yield: 52%. ¹H NMR (CDCl₃): δ = 7.36–7.23 (m, 7 H, Ar-H), 7.11–7.08 (m, 2 H, Ar-H), 5.66 (br. s, 1 H, NH), 4.35 (d, ³*J*_{H,H} = 5.96 Hz, 2 H, NCH₂), 3.62 (s, 2 H, PhCH₂) ppm. ¹³C NMR (CDCl₃): δ = 171.2, 136.9, 134.8, 133.3, 129.6, 129.2, 129.0, 128.9, 127.6, 43.9, 43.0 ppm. HRMS (ESI-TOF): calcd. for C₁₅H₁₅ClNO 260.0842 [M + H]⁺; found 260.0847.

1-(Phenylacetyl)piperidine: The title compound was purified by silica gel column chromatography (hexane/ethyl acetate, 3:1; *R*_f = 0.31) to afford a viscous liquid. Isolated yield: 76%. ¹H NMR (CDCl₃): δ = 7.26–7.19 (m, 5 H, Ar-H), 3.68 (s, 2 H, PhCH₂), 3.52 (t, ³*J*_{H,H} = 5.9 Hz, 2 H, piperidinyl-H), 3.31 (t, ³*J*_{H,H} = 5.5 Hz, 2 H, piperidinyl-H), 1.52–1.46 (m, 4 H, piperidinyl-H), 1.30–1.26 (m, 2 H, piperidinyl-H) ppm. ¹³C NMR (CDCl₃): δ = 169.2, 135.4, 128.6, 128.59, 126.6, 47.3, 42.8, 41.2, 26.2, 25.5, 24.4 ppm. HRMS (ESI): calcd. for C₁₃H₁₈NO 204.1388 [M + H]⁺; found 204.1381.

***N*-(2-Heptyl)-2-phenylacetamide:** The title compound was purified by silica gel column chromatography (hexane/ethyl acetate, 3:1; *R*_f = 0.26) to afford a white solid. Isolated yield: 34% (with **1**) and 68% (with **5**). ¹H NMR (CDCl₃): δ = 7.32–7.20 (m, 5 H, Ar-H), 5.38 (d, ³*J*_{H,H} = 7.8 Hz, 1 H, NH), 3.95–3.87 (m, 1 H, NCH), 3.50 (s, 2 H, PhCH₂), 1.29, 1.17 (m, 8 H, CHCH₂CH₂CH₂CH₂CH₃), 1.01 (d, ³*J*_{H,H} = 6.9 Hz, 3 H, CHCH₃), 0.82 (t, ³*J*_{H,H} = 6.8 Hz, 3 H, CH₂CH₃) ppm. ¹³C NMR (CDCl₃): δ = 170.3, 135.4, 129.4, 129.0, 127.3, 45.4, 44.1, 36.7, 31.7, 25.6, 22.6, 20.9, 14.1 ppm. HRMS (ESI): calcd. for C₁₅H₂₄NO 234.1858 [M + H]⁺; found 234.1861.

Supporting Information (see footnote on the first page of this article): ¹H and ¹³C NMR spectra of new compounds and ¹H NMR spectra of reported compounds.

Acknowledgments

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- [1] a) S.-Y. Han, Y.-A. Kim, *Tetrahedron* **2004**, *60*, 2447–2467; b) C. A. G. N. Montalbetti, V. Falque, *Tetrahedron* **2005**, *61*,

- 10827–10852; c) E. Valeur, M. Bradley, *Chem. Soc. Rev.* **2009**, 38, 606–631; d) R. C. Larock, *Comprehensive Organic Transformation*, VCH, New York, **1999**.
- [2] For some examples, see: a) S. Seo, T. J. Marks, *Org. Lett.* **2008**, 10, 317–319; b) Y. Suto, N. Yamagiwa, Y. Torisawa, *Tetrahedron Lett.* **2008**, 49, 5732–5735; c) J. Gao, G.-U. Wang, *J. Org. Chem.* **2008**, 73, 2955–2958; d) W. J. Yoo, C. J. Li, *J. Am. Chem. Soc.* **2006**, 128, 13064–13065; e) A. Tillack, I. Rudloff, M. Beller, *Eur. J. Org. Chem.* **2001**, 523–528.
- [3] T. Naota, S.-I. Murahashi, *Synlett* **1991**, 693–694.
- [4] a) S. Cho, E. Yoo, I. Bae, S. Chang, *J. Am. Chem. Soc.* **2005**, 127, 16046–16047; b) M. P. Cassidy, J. Raushel, V. V. Fokin, *Angew. Chem.* **2006**, 118, 3226–3229; *Angew. Chem. Int. Ed.* **2006**, 45, 3154–3157.
- [5] a) C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, 317, 790–792; b) L. U. Nordström, H. Vogt, R. Madsen, *J. Am. Chem. Soc.* **2008**, 130, 17672–17673; c) A. J. A. Watson, A. C. Maxwell, J. M. J. Williams, *Org. Lett.* **2009**, 11, 2667–2670.
- [6] a) S. C. Ghosh, S. Muthaiah, Y. Zhang, X. Xu, S. H. Hong, *Adv. Synth. Catal.* **2009**, 351, 2643–2649; b) Y. Zhang, C. Chen, S. C. Ghosh, Y. Li, S. H. Hong, *Organometallics* **2010**, 29, 1374–1378; c) S. Muthaiah, S. C. Ghosh, J.-E. Jee, C. Chen, J. Zhang, S. H. Hong, *J. Org. Chem.* **2010**, 75, 3002–3006.
- [7] For reviews on ruthenium in organic synthesis, see: a) S.-I. Murahashi (Ed.), *Ruthenium in Organic Synthesis*, Wiley-VCH, Weinheim, Germany, **2004**; b) T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.* **1998**, 98, 2599–2660.
- [8] a) K.-i. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto, R. Yamaguchi, *Org. Lett.* **2004**, 6, 2785–2788; b) T. Zweifel, J.-V. Naubron, H. Grützmacher, *Angew. Chem.* **2009**, 121, 567–571; *Angew. Chem. Int. Ed.* **2009**, 48, 559–563.
- [9] K.-i. Shimizu, K. Ohshima, A. Satsuma, *Chem. Eur. J.* **2009**, 15, 9977–9980.
- [10] We are currently investigating the use of other Ru catalytic systems to effect imide synthesis from diols.
- [11] M. Ito, A. Osaku, A. Shiibashi, T. Ikariya, *Org. Lett.* **2007**, 9, 1821–1824.
- [12] Y. Tsuji, S. Kotachi, K.-T. Huh, Y. Watanabe, *J. Org. Chem.* **1990**, 55, 580–584.
- [13] An Ru^{II}/Ru⁰ catalytic cycle for this type of transformation has been proposed; see ref.^[6b,6c]
- [14] Strong bases (40 mol-%), such as LDA, LiHMDS, and *n*BuLi, which can generate NHC from **1**, did not produce any amide from the reaction between 2-phenylethanol and benzylamine.
- We thank a reviewer for the suggestion of the possible dual role of NaH both as a reducing agent and as a base.
- [15] For some examples, see: a) W. Gasafi-Martin, G. Obe-rendfellner, K. von Werner, *Can. J. Chem.* **1996**, 74, 1922–1924; b) L. Busetto, F. Marchetti, S. Zucchini, V. Zanotti, *Organometallics* **2006**, 25, 4808–4816; c) J. Scott, I. Vidyaratne, I. Korobkov, S. Gambarotta, P. H. M. Budzelaar, *Inorg. Chem.* **2008**, 47, 896–911; d) A. Zanardi, R. Corberán, J. A. Mata, E. Peris, *Organometallics* **2008**, 27, 3570–3576.
- [16] a) S. H. Hong, A. G. Wenzel, T. T. Salguero, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2007**, 129, 7961–7968; for more references on decomposition of Grubbs catalysts, see: b) S. H. Hong, A. Chlenov, M. W. Day, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2007**, 46, 5148–5151; c) S. H. Hong, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2004**, 126, 7414–7415; d) M. Ulman, R. H. Grubbs, *J. Org. Chem.* **1999**, 64, 7202–7207.
- [17] For recent representative reviews on non-metathetic behavior of Grubbs-type catalysts, see: a) B. Alcaide, P. Almendros, A. Luna, *Chem. Rev.* **2009**, 109, 3817–3858; b) B. Schmidt, *Eur. J. Org. Chem.* **2004**, 1865–1880; c) B. Alcaide, P. Almendros, *Chem. Eur. J.* **2003**, 9, 1258–1262.
- [18] J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg, D. Milstein, *Organometallics* **2004**, 23, 4026–4033.
- [19] a) S.-I. Murahashi, K. Kondo, T. Hakata, *Tetrahedron Lett.* **1982**, 23, 229–232; b) R. Grigg, T. R. B. Mitchell, S. Sutthivai-yakit, N. Tongpenyai, *J. Chem. Soc., Chem. Commun.* **1981**, 611–612; c) Y. Watanabe, Y. Tsuji, H. Ige, Y. Ohsugi, T. Ohta, *J. Org. Chem.* **1984**, 49, 3359–3363; d) Y. Watanabe, Y. Morisaki, T. Kondo, T.-A. Mitsudo, *J. Org. Chem.* **1996**, 61, 4214–4218; e) S. Ganguly, D. M. Roundhill, *Polyhedron* **1990**, 9, 2517–2526; f) K.-T. Huh, Y. Tsuji, M. Kobayashi, F. Okuda, Y. Watanabe, *Chem. Lett.* **1988**, 449–452; g) S. Naskar, M. Bhattacharjee, *Tetrahedron Lett.* **2007**, 48, 3367–3370; h) D. Hollmann, A. Tillack, D. Michalik, R. Jackstell, M. Beller, *Chem. Asian J.* **2007**, 2, 403–410; i) A. Tillack, D. Hollmann, D. Michalik, M. Beller, *Tetrahedron Lett.* **2006**, 47, 8881–8885; j) A. Del Zotto, W. Baratta, M. Sandri, G. Verardo, P. Rigo, *Eur. J. Inorg. Chem.* **2004**, 524–529; k) M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson, J. M. J. Williams, *J. Am. Chem. Soc.* **2009**, 131, 1766–1774, and more references therein.
- [20] a) S.-I. Murahashi, K. Ito, T. Naota, Y. Maeda, *Tetrahedron Lett.* **1981**, 22, 5327–5330; b) S.-I. Murahashi, T. Naota, K. Ito, Y. Maeda, H. Taki, *J. Org. Chem.* **1987**, 52, 4319–4327; c) J. Zhao, J. F. Hartwig, *Organometallics* **2005**, 24, 2441–2446.

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