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Well-Defined N-Heterocyclic Carbene Based Ruthenium Catalysts for Direct Amide Synthesis from Alcohols and Amines

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Well-defined N-heterocyclic carbene based ruthenium complexes were developed as highly active catalysts for direct amide synthesis from alcohols and amines. A catalytic amount of a base such as KO^tBu was essential to initiate the catalytic cycle. Activity of the Ru complexes was comparable with the reported *in situ* Ru catalysts. These catalysts provided mechanistic insight suggesting a Ru hydride species as an active catalytic intermediate. The generation of the Ru hydride was critical for the amidation of free aldehydes.

Introduction

The amide bond is a key functional group in organic and biological chemistry.[1] Several groups have reported direct amide synthesis from alcohols and amines by liberating two molecules of hydrogen using Ru-,[2−5] Rh-,[6] and Ag-based[7] catalyst systems. Milstein and co-workers developed a Ru catalyst, **1**, for the amide synthesis using a hemilabile PNN pincer ligand (Figure 1).[2] *In situ* generated catalysts using a commercially available ruthenium source and supporting ligands with[3] or without[4,5] hydrogen acceptors have also been reported. The direct acylation of amines with alcohols is a highly atom economical transformation that evolves hydrogen as a sole byproduct with less waste than traditional amide synthesis, often producing toxic chemical waste with tedious procedures.[2−7]

However, there are many challenges in this reaction. All reported ruthenium catalyst systems require elevated temperature under toluene reflux and give lower yields for sterically hindered substrates and less basic aryl amines such as aniline. It has also been shown that simpler *in situ* generated catalyst systems from readily available materials have lower TON.[5] To improve current catalyst systems, it is essential to understand the identity of catalytic intermediates and mechanisms.

Our group recently developed phosphine-free *in situ* generated N-hetercocyclic carbene (NHC) based ruthenium catalysts from imidazolium salts, a base, pyridine, and $[Ru(p\text{-cymene})Cl_2]_2$.[5] The result indicated that the NHC-based ruthenium complexes synthesized from $[Ru(p\text{-cymene})Cl_2]_2$ such as **2**,[8a] **3**, and **4**[8b] might be real catalytic intermediates for the direct amide synthesis (Figure 1). Identifying well-defined catalysts from *in situ* generated catalysts is important to investigate the mechanism and improve the activity further by rational design of catalysts. Herein, we report the catalytic activity of the well-defined NHC-based ruthenium complexes and the study of catalytic intermediates.

Results and Discussion

Catalytic Activity of 2−4. On the basis of the reports showing the high activity of 1,3-diisopropylimidazolium bromide (**5**) on *in situ* generated ruthenium catalyst systems,[4,5] we synthesized complex **3** modifying the reported procedure by using a Ag carbene.[8] The structure was confirmed by X-ray crystallography (Figure 2). The structure of **3** is similar to that of the reported **4**. To our surprise, when complexes **2**−**4** were initially screened with 2-phenylethanol (**6**) and benzylamine (**7**), they did not show any activity. Mimicking the reported *in situ* conditions, bases such as NaH and KO^tBu were found necessary for catalytic activity (Table 1). Weaker bases such as K_2CO_3 were not as effective as NaH and KO^tBu (entry 11, Table 1). Further optimization demonstrated that only a catalytic amount of a base, 15−20 mol %, is ideal for the catalysis (Table 1). The major role of these bases was previously considered for *in situ* generation of NHCs from imidazolium salts. However, the current results with well-defined precatalysts indicated that the role of bases is more than generation of NHC and is related to activation of the Ru complexes. To our delight, supporting

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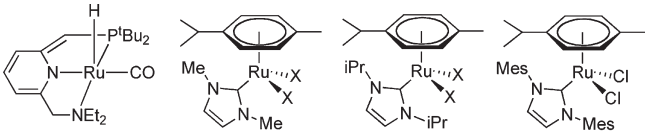

1 2 X = Cl 2-I X = I 3 X = Cl 3-I X = I 4

Figure 1. Ru complexes for amide synthesis from alcohols.

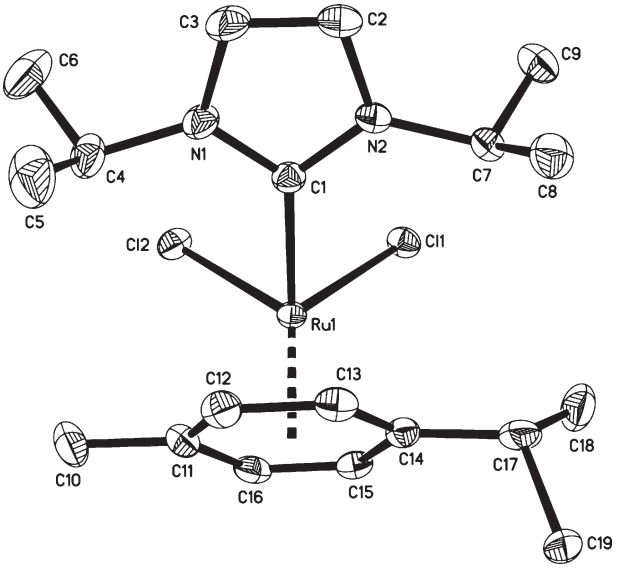

Figure 2. Crystal structure of **3** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Ru1−C1 2.0828(14), Ru1−Cl1 2.4439(4), Ru1−C13 2.1701(14). Selected bond angles (deg): C1−Ru1−C13 89.55(5), C1−Ru1−Cl1 89.87(4), Cl1−Ru1−Cl2 83.006(13).

ligands such as pyridine, acetonitrile, and phosphines, which were required for improving activity of *in situ* generated catalysts, were not necessary for the well-defined complexes **2**−**4**.

Interestingly, even though NHC precursors that have isopropyl wingtip groups such as **5** were reported to be significantly superior than 1,3-dimethylimidazolium salt in *in situ* catalyst systems,[4,5] **2** and **3** showed comparable activity. The reason is not clear, but we think that there might be less efficiency of NHC−Ru bond formation in *in situ* generation with 1,3-dimethylimidazolium iodide (**9**).[9,10] To improve the activity, we tried to exchange the chloride ligands with bromide and iodide. However, complexes **2-I** and **3-I** also did not show any improvement over **2** and **3**.[11] The use of silver salts such as $AgBF_4$ to abstract chloride ligands did not show any improvement either.

(9) It is reported that the NHC of **5** (pK_a ~22, in DMSO) is a little more basic than that of **9** (pK_a ~21, in DMSO). See: Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717.

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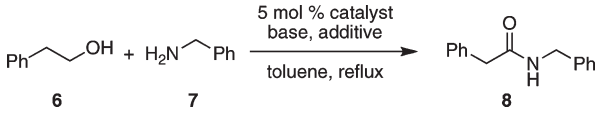
(11) Synthesis of **2-Br** was attempted; however, mixtures of mono- and disubstituted bromo complexes were observed even in the presence of excess (~30 equiv) NaBr.

Table 1. Optimization of Conditions[a]



6 7 8

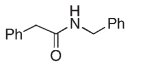
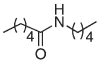
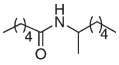
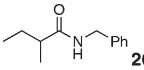
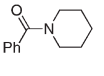
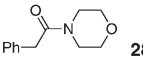
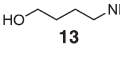
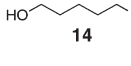
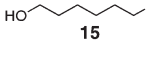
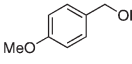
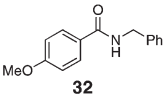
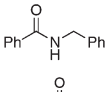
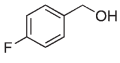
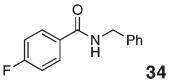
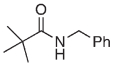
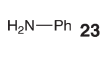
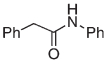
		base		additive		
entry	Ru complex	base	mol %	additive	mol %	yield[b] (%)
1	**3**					0
2	**3**	KO^{t}Bu	5			7
3	**3**	KO^{t}Bu	10			82
4	**3**	KO^{t}Bu	15			93
5	**3-I**	KO^{t}Bu	15			93
6	**3**	KO^{t}Bu	20			89
7	**3**	KO^{t}Bu	40			60
8	**3**	KO^{t}Bu	60			50
9	**3**	KO^{t}Bu	100			10
10	**3**	NaH	20			93
11	**3**	K_2CO_3	20			0
12	**2**	KO^{t}Bu	15			97
13	**2-I**	KO^{t}Bu	15			89
14	**4**	KO^{t}Bu	15			72
15	**2**	KO^{t}Bu	20			46[c]
16	**2**	KO^{t}Bu	20	NaBr	100	44[c]
17	**2**	KO^{t}Bu	20	NaI	100	42[c]
18	**2**	KO^{t}Bu	20	KBr	100	46[c]

[a] 5 mol % catalyst, toluene, reflux, 24 h unless otherwise noted. [b] Determined by GC using dodecane as an internal standard. [c] 80 °C, 24 h.

Substrate Scope. Complex **2**, with smaller wingtip groups of NHC, was chosen to expand the substrate scope, expecting improvement for challenging sterically hindered substrates. A range of amides were synthesized with good to excellent yields with precatalyst **2** (Table 2). Excellent yields were obtained for sterically nonhindered substrates (entries 1, 2). Modestly hindered substrates worked reasonably well (entries 3, 4). Cyclic secondary amines such as **21** and **22** also reacted smoothly, producing the corresponding amides with good yields (entries 5, 6). In particular, five- to seven-membered cyclic lactams, **29**, **30**, and **31**, were synthesized efficiently from α,ω-amino alcohols (entries 7−9). We studied the electronic effect on alcohols using benzyl alcohol derivatives. Slighlty reduced yields were observed with electron-deficient substrates (entries 10−12). However, rather disappointingly, it also showed a similar limitation on sterically bulky substrates and less basic aniline, demonstrating challenges in this area (entries 13, 14).[2−5]

Catalytic Intermediates. With the benefit of the structurally well-defined complex **2**, we attempted to reveal the mechanism and catalytic intermediates during catalysis. 1-Hexanol (**10**) and 1-pentylamine (**19**) were chosen for the study, because the corresponding amide product **24** is completely soluble in toluene-d_8 during catalysis. We first tried an NMR reaction with the same catalytic conditions (5 mol % **2**, 15 mol % K^{t}OBu) in toluene-d_8 to investigate catalytic intermediates during catalytic reactions. Several interesting features were observed. Even though complex **2** itself did not have high solubility in toluene, it was immediately solubilized by the addition of substrates in the presence of a base with characteristic peaks of π-bound *p*-cymene, which shows characteristic upfield shifts near 5 ppm in the ^{1}H NMR spectrum. This observation indicated that exchange of chloride with alkoxide is a rapid initiation step. Concurrent

Table 2. Direct Amide Synthesis Catalyzed by 2[a]

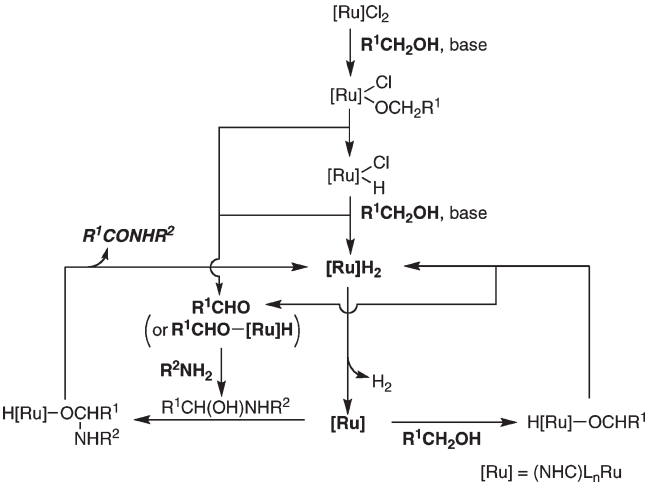
entry	alcohol	amine	amide	yield[b] (%)
1				93
2	 **10**	 **19**	 **24**	95
3		 **20**	 **25**	56[c]
4	 **11**		 **26**	70
5	 **12**	 **21**	 **27**	83
6		 **22**	 **28**	65[c]
7	 **13**		 **29**	68
8	 **14**		 **30**	88
9	 **15**		 **31**	53
10	 **16**		 **32**	85
11			 **33**	81
12	 **17**		 **34**	66
13	 **18**		 **35**	10
14		 **23**	 **36**	34[d]

[a] Catalyst **2** (5 mol %), KO[t]Bu (15 mol %), toluene, reflux, 24 h unless otherwise noted. [b] Isolated yields, average of two runs. [c] 20 mol % KOtBu. [d] Mesitylene, 163 °C.

formation of ruthenium hydrides as singlets, shown at δ −6.6 ppm (major) and −7.7 ppm (minor) by ^{1}H NMR spectroscopy, was observed immediately after the addition of substrates with KO[t]Bu at ambient temperature. When the reaction mixture was heated at 115 °C and the amide started to form, two hydridic peaks disappeared and a major hydride peak at δ −9.8 ppm was observed, along with many trace weak hydridic peaks at about δ −10 to −20 ppm.[12]

Encouraged by the observations, we tried an NMR tube reaction in toluene-d_8 with a 1:3:3 ratio reaction of **2**, **10**, and KO[t]Bu. At room temperature, a major hydride peak was observed at the same position observed in catalytic reactions at δ −6.6 ppm. However upon heating to 115 °C, the hydride peak disappeared and a new singlet at δ −9.8 ppm was observed.[12] With prolonged heating, 2−3 h, the peak disappeared along with many trace hydridic peaks, implying decomposition of catalysts.[12] Peaks from π-bound cymene near 5−6 ppm also disappeared after a few hour heating. With **2** and **10** without a base, no reaction was observed, suggesting a base is required to generate the Ru hydride complex. These observations strongly indicated that a ruthenium hydride species is an active catalytic intermediate.

Scheme 1. Proposed Mechanism



Proposed Mechanism. On the basis of the studies, it is proposed that the role of a catalytic amount (at least 2 equiv vs precatalyst) of a base is to stimulate the generation of the ruthenium alkoxide species (Scheme 1). Subsequent β-hydrogen elimination can generate the Ru(II) dihydride species. The generation of $[Ru]H_2$ from $[Ru]Cl_2$ with the help of a base and the Ru(0)/Ru(II) cycle have been suggested in catalytic alcohol dehydrogenation,[13] N-alkylation of amines with alcohols,[14] and esterification of alcohols.[15] In addition, synthesis of the $[(p\text{-cymene})RuH_2(PCy_3)]$ complex from $[(p\text{-cymene})RuCl_2(PCy_3)]$ with methanol and K_2CO_3 has been reported.[16] However, attempts to synthesize $[(p\text{-cymene})RuH_2(IMe)]$ **2-H$_2$** under the same conditions were not successful, limiting clear characterization of the observed Ru-H intermediate. Diminished catalytic activity from increased amount of a base from 20 mol % also supported the role of a base and implied that deprotonation of all alcohols is not necessary for alcohols to react with a catalytically active intermediate.

(12) The ^{1}H NMR spectra were obtained at ambient temperature, after the NMR tube was heated at 115 °C in an oil bath for the specified time.

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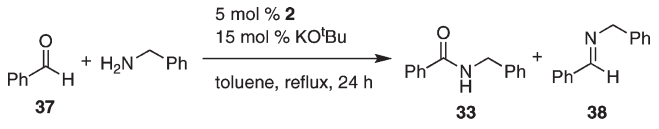
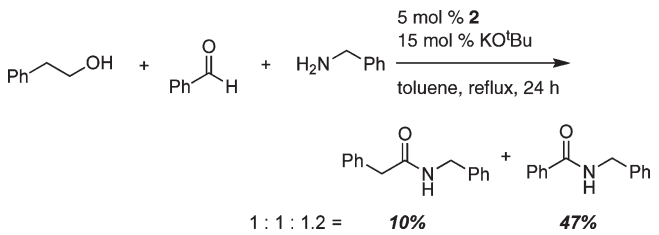
Scheme 2. Amidation of Aldehyde[a]



[a] Determined by GC using dodecane as an internal standard, average of two runs.

Scheme 3. Reactions of a Mixture of an Alcohol and an Aldehyde[a]



[a] Determined by GC using dodecane as an internal standard, average of two runs.

The proposed mechanism is similar to the mechanism proposed for the Ru-catalyzed alkylation of amine using the "borrowing hydrogen" methodology.[14] We think that the critical point is whether a hemiaminal intermediate would be further oxidized to a corresponding amide or would form an imine, which could be subsequently hydrogenated to an amine by elimination of water. On the basis of the reports on the alkylation of amine done with similar Ru complexes with supporting phosphine ligands and the essential role of NHC ligands on the amide formation,[4,5,14] we believe that the more σ-donating NHC ligand has a critical role to facilitate the oxidation over the elimination of water.

It was reported that *in situ* generated NHC-based Ru was not active[4] or was much less active[5] in the amide formation of aldehydes with amines, forming imines as major products, even though aldehydes were proposed as intermediates formed by dehydrogenation of alcohols. To rationalize the results, it was proposed that Ru coordination on the generated aldehyde would be essential for the catalytic cycle.[4,5] Indeed, we could not observe any free aldehyde during the NMR studies, suggesting the short lifetime of free aldehyde, if it is even generated.

However, our study on the catalytic intermediate indicated that there might be another possible reason for the limited activity of the aldehyde. It would be less efficient to form active [Ru]H_2 from [Ru]Cl_2 and an aldehyde without the help of primary alcohols. To see whether primary alcohols are essential for the catalysis, we ran two reactions of the amidation of an aldehyde with and without a primary alcohol (Scheme 2). Aldehyde itself did not efficiently produce an amide from benzaldehyde (**37**) with benzylamine (**7**) under the same reaction conditions using complex **2**. However, when we added 10 mol % of the primary alcohol **6** as an additive, the reaction smoothly generated the corresponding amide, *N*-benzylbenzamide (**33**), demonstrating that formation of a catalytically active species by an alcohol is necessary for the amidation of aldehydes. However, the observation of 9% of **38** that was sometimes observed in trace amounts, less than 3%, in the reaction of benzyl alcohol and benzyl amine, and no observation of free aldehyde during the discussed NMR studies, implied that the direct amide formation from alcohol might occur through Ru-bound aldehyde-like species, instead of free aldehyde. A recent mechanistic study with a heterogeneous Ag catalyst on the same transformation indicated that the reaction proceeded through metal-bound aldehyde-like species, not through a free aldehyde.[7]

To investigate further, we ran a reaction with a mixture of **6**, **37**, and **7** (1:1:1.2 ratio). The corresponding amides **8** and **33** were obtained in 10% and 47% yields, respectively, suggesting that once a catalytically active species is generated, aldehydes could generate amides more favorably than alcohols (Scheme 3). Although it is still not conclusive whether a free aldehyde is generated during the amidation of primary alcohols or not, our study clearly indicated that generation of a ruthenium hydride is essential for the formation of amides from either alcohol or aldehyde.

Conclusions

In conclusion, we have shown that well-defined N-heterocyclic carbene based ruthenium complexes are active for the direct amide synthesis of alcohols with a catalytic amount of a base. The Ru complexes enabled us to approach a facile mechanistic investigation, suggesting that formation of a Ru hydride catalytic intermediate by alcohols and a catalytic amount of a base is necessary for catalytic cycles.

Experimental Section

General Considerations. Unless otherwise noted, all reactions were carried out using standard Schlenk techniques or in an argon-filled glovebox. Dichloromethane, diethyl ether, and toluene were dried over a Pure Solv solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories and dried over molecular sieves. NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or toluene-d_8 using a Bruker DPX300, AMX400, JEOL ECA400, or JEOL ECA400SL spectrometer, and TMS (tetramethylsilane) was used as a reference. Chemical shifts were reported in ppm and coupling constants in Hz. Elemental analyses were performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University. GC analyses were carried out with a 7980A GC system from Agilent Technologies, equipped with an HP-5 column. 1,3-Dimethylimidazolium iodide (**9**),[17] (1,3-dimethylimidazol-2-ylidene)silver(I) iodide,[18] 1,3-diisopropylimidazolium bromide (**5**),[19] and compound **4**[8b] were prepared by literature procedures. Other chemicals were purchased from commercial suppliers and used as received without further purification.

Synthesis of 2. A mixture of (1,3-dimethylimidazol-2-ylidene)silver(I) iodide (148.9 mg, 0.45 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (137.8 mg, 0.23 mmol) was stirred in CH_2Cl_2 at room temperature for 6 h. The white precipitate (AgI) was then filtered through Celite. After removal of the solvent under vacuum, analytically pure product **2** was obtained by washing the crude product with diethyl ether (3 × 5 mL). Yield: 93% (168.3 mg, 0.42 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.03 (s, 2H, CH_{imid}), 5.39 (d, J = 5.96 Hz, 2H, CH_{pcym}), 5.06 (d, J = 5.96 Hz, 2H, CH_{pcym}), 3.96 (s, 6H, NCH_3), 2.93 (septet, J = 6.88 Hz, 1H, $CH_{isop\ pcym}$), 1.98 (s, 3H, CH_{3pcym}), 1.25 (d, J = 6.84 Hz, 6H, $CH_{3isop\ pcym}$). The formation of complex **2** was confirmed

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by comparing the chemical shifts of ^{1}H NMR with reported values.[8a]

Synthesis of 2-I. A Schlenk tube was charged with complex **2** (67.7 mg, 0.17 mmol), NaI (509.7 mg, 3.4 mmol), and 5 mL of THF. The reaction mixture was stirred at room temperature for 8 h. The solvent was removed under vacuum. The residue was dissolved in toluene, and the resulting suspension was passed through a plug of Celite. All the volatiles were removed, and the residue was washed with diethyl ether (3 × 5 mL) to give **2-I** as a dark red powder. Yield: 70% (69.8 mg, 0.12 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.08 (s, 2H, CH_{imid}), 5.59 (d, J = 5.60 Hz, 2H, CH_{pcym}), 5.18 (d, J = 5.56 Hz, 2H, CH_{pcym}), 4.04 (s, 6H, CH_{3imid}), 3.15 (septet, J = 6.88 Hz, 1H, $CH_{isop\ pcym}$), 1.96 (s, 3H, CH_{3pcym}), 1.23 (d, J = 6.88 Hz, 6H, $CH_{3isop\ pcym}$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 170.4 (C-Ru), 124.4 (CH_{imid}), 110.0 (Cq_{pcym}), 99.9 (Cq_{pcym}), 86.6 (CH_{pcym}), 83.0 (CH_{pcym}), 44.9 (CH_{3imid}), 32.0 ($CH_{isop\ pcym}$), 23.0 ($CH_{3isop\ pcym}$), 19.2 (CH_{3pcym}). Anal. Calcd for $C_{16}H_{24}Cl_2I_2N_2Ru$ (**2-I**·CH_2Cl_2, 670.2): C, 28.68; H, 3.61; N, 4.18. Found: C, 28.41; H, 3.89; N, 4.33.

Synthesis of 3. A suspension of 1,3-diisopropylimidazolium bromide (106.4 mg, 0.46 mmol) and Ag_2O (64.0 mg, 0.28 mmol) in CH_2Cl_2 was stirred at room temperature in the dark for 2 h. The mixture was then filtered through a plug of Celite, and to the filtrate was added [Ru(*p*-cymene)Cl_2]$_2$ (139.8 mg, 0.23 mmol). The reaction mixture was stirred at room temperature for 2 h and then filtered through Celite. The solvent was removed under vacuum. Washing the crude product with diethyl ether (3 × 5 mL) can afford **3** as an orange powder. Yield: 90% (189.8 mg, 0.41 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.15 (s, 2H, CH_{imid}), 5.48 (d, J = 5.97 Hz, 2H, CH_{pcym}), 5.34−5.25 (m, 2H, $CH_{isop\ imid}$), 5.06 (d, J = 6.00 Hz, 2H, CH_{pcym}), 2.94 (septet, J = 6.96 Hz, 1H, $CH_{isop\ pcym}$), 2.01 (s, 3H, CH_{3pcym}), 1.42 (br, 12H, $CH_{3isop\ imid}$), 1.31 (d, J = 6.93 Hz, 6H, $CH_{3isop\ pcym}$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 172.2 (C-Ru), 119.5 (CH_{imdi}), 107.4 (Cq_{pcym}), 98.5 (Cq_{pcym}), 86.9 (CH_{pcym}), 82.0 (CH_{pcym}), 52.5 ($CH_{isop\ imid}$), 31.2 ($CH_{isop\ pcym}$), 25.5 ($CH_{3isop\ imid}$), 25.1 ($CH_{3isop\ imid}$), 22.9 ($CH_{3isop\ pcym}$), 19.2 (CH_{3pcym}). Anal. Calcd for $C_{20}H_{32}Cl_4N_2Ru$ (**3**·CH_2Cl_2, 543.4): C, 44.21; H, 5.94; N, 5.16. Found: C,44.68; H, 5.63; N, 5.37.

Synthesis of 3-I. A Schlenk tube was charged with complex **3** (83.4 mg, 0.18 mmol), NaI (539.6 mg, 3.6 mmol), and 5 mL of THF. The reaction mixture was stirred at room temperature for 8 h. All volatiles were removed under vacuum. The residue was dissolved in toluene, and the resulting suspension was passed through a plug of Celite. All the volatiles were removed, and the residue was washed with diethyl ether (3 × 5 mL) to give **3-I** as a dark red powder. Yield: 68% (78.5 mg, 0.12 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.19 (s, 2H, CH_{imid}), 5.69 (d, J = 5.91 Hz, 2H, CH_{pcym}), 5.52 (septet, J = 6.60 Hz, 2H, $CH_{isop\ imid}$), 5.15 (d, J = 5.88 Hz, 2H, CH_{pcym}), 3.29 (septet, J = 6.93 Hz, 1H, $CH_{isop\ pcym}$), 2.01 (s, 3H, CH_{3pcym}), 1.44 (br, 12H, $CH_{3isop\ imid}$), 1.32 (d, J = 6.96 Hz, 6H, $CH_{3isop\ pcym}$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 167.6 (C−Ru), 120.1 (CH_{imid}), 108.4 (Cq_{pcym}), 99.8 (Cq_{pcym}), 87.3 (CH_{pcym}), 82.3 (CH_{pcym}), 55.0 ($CH_{isop\ imid}$), 32.0 ($CH_{isop\ pcym}$), 25.7 ($CH_{3isop\ imid}$), 25.1 ($CH_{3isop\ imid}$), 23.2 ($CH_{3isop\ pcym}$), 19.8 (CH_{3pcym}). Anal. Calcd for $C_{20}H_{32}Cl_2I_2N_2Ru$ (**3-I**·CH_2Cl_2, 726.3): C, 33.08; H, 4.44; N, 3.86. Found: C, 33.46; H, 4.01; N, 4.03.

General Procedure for Amide Synthesis. In an argon-filled glovebox, a 10 mL oven-dried Schlenk tube was charged with complex **2**, **3**, or **4** (0.025 mmol), base (0.075 mmol), and 0.6 mL of toluene. The Schlenk tube was then taken out, and alcohol (0.50 mmol) and amine (0.55 mmol) were added. The reaction mixture was heated to reflux under a flow of argon to facilitate removal of hydrogen for 24 h before being cooled to room temperature. All the volatiles were removed under vacuum. Purification of the crude product by flash chromatography afforded amides. All the amides were identified by spectral comparison with literature data.[3−5]

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of new compounds and X-ray data for complex **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.