57.0, 58.7, 58.9, 69.5, 69.8, 70.7, 73.3, 81.3, 108.3, 110.9, 124.8, 125.3, 126.6, 127.1, 128.3, 128.4, 131.3, 142.7, 144.1, 151.9, 173.7, 191.9.

3: M.p. >300 °C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 0.57$ (d, $J = 10.6$ Hz, 1 H), 0.98 (d, $J = 6.8$ Hz, 6 H), 1.30 (d, $J = 12.0$ Hz, 1 H), 1.68 (d, $J = 8.7$ Hz, 2 H), 1.93 (d, $J = 12.0$ Hz, 1 H), 2.00 (d, $J = 8.7$ Hz, 2 H), 2.19 (d, $J = 10.6$ Hz, 1 H), 2.34 (s, 2 H), 2.39 (s, 2 H), 2.44 (s, 2 H), 2.46 (s, 2 H), 2.47 (s, 2 H), 2.60 (d, $J = 9.0$ Hz, 2 H), 2.79 (s, 2 H), 2.87 (d, $J = 9.0$ Hz, 2 H), 3.04 (s, 2 H), 3.16 (s, 6 H), 3.29 (s, 6 H), 3.33 (s, 6 H), 3.59 (d, $J = 9.0$ Hz, 2 H), 3.68 (d, $J = 9.0$ Hz, 2 H), 4.10 (sept, $J = 6.8$ Hz, 1 H), 4.79 (s, 2 H), 4.83 (s, 2 H), 6.53 (s, 2 H), 7.33 (t, $J = 7.1$ Hz, 2 H), 7.43 (t, $J = 7.1$ Hz, 4 H), 7.80 (d, $J = 7.1$ Hz, 4 H); ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta = 0.93$, 17.79, 21.69, 31.36, 33.51, 38.60, 40.10, 40.26, 43.31, 44.57, 44.82, 45.44, 48.92, 51.00, 52.94, 56.46, 58.69, 58.88, 69.57, 70.29, 73.66, 81.63, 81.91, 90.32, 110.93, 113.21, 126.89, 127.09, 128.23, 137.11, 138.36, 147.15, 173.84, 191.59.

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[13] Diphenyldimethoxynaphthalene: E_{ox}(CH$_2$Cl$_2$) = 0.99 eV, $E_{00} = 3.4$ eV. Dimethoxybenzene: E_{ox}(CH$_3$CN) = 1.33 eV, $E_{00} = 3.95$ eV. DCV: E_{red}(CH$_3$CN) = −1.7 eV. From these data, the driving forces for photoinduced ET from locally excited aromatic donor to DCV acceptor in **2** and **3** are estimated to be 0.8 and 0.9 eV, respectively.

[14] The fluorescence quantum yields for **2** and **3** were obtained relative to appropriate model systems lacking the DCV acceptor group.

Ruthenium-Catalyzed Intermolecular Hydroamination of Terminal Alkynes with Anilines: A Practical Synthesis of Aromatic Ketimines**

Makoto Tokunaga, Markus Eckert, and Yasuo Wakatsuki*

Aromatic ketimines are an important class of compounds widely used for the preparation of a variety of nitrogen-containing chemicals, such as tertiary[1a] or secondary amines,[1b–d] nitrogen heterocycles,[1e, 2e,g] carboxylic amides,[1f, 2f] β-enamino esters,[1g] amino alcohols,[1h] α-sulfinyl ketimines,[1i] and many others.[1j–l] Although the condensation of ketones with primary amines is a textbook route to ketimines, the procedure is sometimes not practical for the synthesis of *aromatic* ketimines because aromatic ketones react much more slowly than aliphtic ketones or aldehydes, and methyl ketones are sensitive to aldol-type side reactions.[2a] Therefore synthesis of imines from acetophenone often gives unsatisfactory results (for example, 40–55 % maximum yields from reactions with aniline[2b,d–f, 3]). Another practical route to aromatic ketimines is therefore desired to supplement the classical ketone–amine condensation pathway.

We thought that the hydroamination of phenylacetylene and its derivatives should be a convenient way to synthesize the compounds, and it deserved special attention in terms of its efficiency of atom utilization since it avoids the formation of stoichiometric amounts of by-products.[4] Compared to *intra*molecular cyclizations,[5] however, the *inter*molecular hydroaminations of alkynes[6] is more difficult, and only a few approaches exist.[4] Besides the established stoichiometric aminomercuration/reduction method,[7] the only catalytic reactions known are those with mercury or thallium,[6a,b] and metallocenes of zirconium,[6c] lanthanide,[6d,f] and actinide.[6e] These catalysts or precursors, though interesting in their own right, have problems associated with environmental protection, low activity, and/or air and moisture sensitivity.

Herein we disclose an efficient synthesis of aromatic ketimines based on the regioselective hydroamination of terminal alkynes with anilines using a ruthenium carbonyl catalyst. The incorporation of late transition metals in catalysts have an advantage over early transition metals, lanthanide, and actinide metals in that their low oxophilicity permits the use of many substrates for catalysis that are excluded in the systems with highly oxophilic metals. Yet, to the best of our knowledge, *inter*molecular hydroamination of alkynes by late transition metals other than mercury has not appeared in the literature. This situation is probably because of their very low activity (and small turnover numbers

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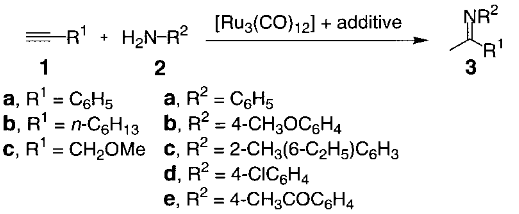
(TON)).[8] The present breakthrough constitutes the effect of a small amount of additive in the catalytic system on attaining a very high activity of the ruthenium catalyst: in many cases 0.1 mol% of the catalyst concentration may be employed. Furthermore, the reaction can be carried out in the open air under solvent-free conditions, and does not require an inert gas atmosphere or strict anhydrous conditions.

We started to explore a practical catalyst system for the hydroamination using the addition of aniline (**2a**) to phenylacetylene (**1a**) as the standard reaction (Scheme 1). Ruthenium phosphane complexes that had been successfully employed for anti-Markovnikov hydration[9a] or homodimerization[9b] of alkynes, and dehydrogenative silylation of alkenes[9c] showed poor activity. Only slightly better results were obtained with the ruthenium carbonyl cluster [$Ru_3(CO)_{12}$].[10] However, we found a dramatic rate enhancement when the cluster was used in the presence of a small amount of acid or its ammonium salt. For example, the reaction was completed in 12 h at 100 °C with only 0.1 mol% [$Ru_3(CO)_{12}$] and 0.3 mol% NH_4PF_6 and gave a 84% yield (GC) of the product **3**, while only a 2.6% yield of the product was obtained under the same conditions but without the additive. The effect of the additives as judged by the GC yields of **3** is compared in Table 1.



Scheme 1. Ruthenium-catalyzed hydroaminaton of terminal alkynes with anilines.

Table 1. Hydroamination of **1a** with **2a** catalyzed by [$Ru_3(CO)_{12}$] and additives.[a]

Additive ([mol%])	Yield [%][b]	Additive ([mol%])	Yield [%][b]
–	1.6	NH_4BF_4 (0.3)	56
$NH_4(CF_3SO_3)$ (0.3)	44	$BF_3 \cdot OEt_2$ (0.3)	71
aq HPF_6 (0.3)	78	$H_2SO_4 \cdot 2PhNH_2$ (0.15)	14
NH_4PF_6[c] (0.1)	19	NH_4I (0.3)	4.2
NH_4PF_6[c] (0.2)	53	aq HCl (0.3)	9.6
NH_4PF_6[c] (0.3)	52	aq HCl (3.0)	4.2
NH_4PF_6[c] (0.3)	84[d]	NH_4Cl (0.3)	9.3
NH_4PF_6[c] (0.3)	92[e]	$HCl \cdot PhNH_2$ (0.3)	7.7
NH_4PF_6[c] (0.6)	50	$MeSO_3H$ (0.3)	48
NH_4PF_6[c] (1.5)	53	CF_3COOH (0.3)	26
NH_4PF_6[c] (3.0)	49	$ClCH_2COOH$ (0.3)	17
KPF_6 (0.3)	1.5	NH_4F (0.3)	4.5
NMe_4PF_6 (0.3)	1.5	$HF \cdot PhNH_2$ (0.3)	29
$NMe_4PF_6 + HCl$ (0.3)	19	aq HF (0.3)	11
aq HBF_4 (0.1)	24	aq HF (excess)	46
aq HBF_4 (0.2)	64	PhCOOH (0.3)	2.7
aq HBF_4 (0.3)	67		

[a] Reactions were carried out with 1 g of **1a**, 1.1 equivalents of **2a**, 0.1 mol% [$Ru_3(CO)_{12}$], and additives in CH_3OH (1 mL) at 100 °C. [b] GC yield after 3 h, unless otherwise stated. [c] Reference experiment with NH_4PF_6 in the absence of [$Ru_3(CO)_{12}$] yielded no detectable product. [d] After 12 h. [e] Yield of the isolated product from a 50-g scale reaction without solvent, see Experimental Section.

The strong acids HPF_6 and HBF_4 and their ammonium salts were the most effective additives,[11] and the reactions with them gave 50–78% yields in 3 h at 100 °C. A decrease in the effect was observed with a decrease in the acidity of the additives: $MeSO_3H$, CF_3COOH, $ClCH_2COOH$, and PhCOOH gave yields of 48, 26, 17, and 2.7%, respectively. However, the effect of the additives is not a simple function of their acidity since aqueous HCl, NH_4Cl, and NH_4I showed only a very small rate enhancement. Moreover, although NH_4F accelerated the reaction only slightly as a consequence of its poor solubility, the effect of hydrogen fluoride and its salts is larger than that for the chloride and iodide. Interestingly, KPF_6 and NMe_4PF_6 gave no effect at all. Addition of HCl to NMe_4PF_6 restored the effect and afforded a better result than those obtained by each additive alone.

The effect of the amount of additives on the reaction yield was examined with NH_4PF_6 and HBF_4. As shown in Table 1, only 0.2 mol% of additive and 0.1 mol% of [$Ru_3(CO)_{12}$] was necessary to achieve the maximum rate; a further addition of these additives did not lead to any further improvement.

In regard to the solvent, the reactions in methanol, 2-propanol, toluene, and THF all gave similar results. It was found that the solvent-free system exhibited the highest reaction rate. It appears that the use of a small excess of **1a** (1.2 equiv) to **2a** often gives better results than a strictly equivalent ratio. We also found that it did not matter whether the reaction was carried out under argon or in air.

On the basis of these findings, a 50-g-scale reaction was carried out to test the practicability of the present system. Neat substrates, 0.1 mol% [$Ru_3(CO)_{12}$], and 0.3 mol% NH_4PF_6 were placed in an open 100-mL one-necked flask. After the mixture had stirred for 3 h at 100 °C, the product **3** was simply distilled directly from the same flask to give the imine of > 99% purity in 92% yield (TON 300 per Ru atom).

The present hydroamination system was also found to be applicable to the reactions of substituted anilines with phenylacetylene (Table 2, entries 1–4).[12] Aniline (**2b**), with an electron-donating substituent, reacts smoothly, but a sterically hindered aniline (**2c**), or one with electron-withdrawing substituents (**2d**, **e**) requires higher loadings of the

Table 2. Hydroamination of **1** with **2** catalyzed by [$Ru_3(CO)_{12}$] and additives.

Entry	Alkyne ([mmol])	Amine ([mmol])	Catalyst ([mol%]) additive ([mol%])	Solvent ([mL])	T [°C] t [h]	Yield [%]
1	**1a** (12)	**2b** (10)	[$Ru_3(CO)_{12}$] (0.1) NH_4PF_6 (0.3)	–	100 3	95[b]
2	**1a** (28)	**2c** (20)	[$Ru_3(CO)_{12}$] (0.7) HBF_4/OEt_2 (2.1)	–	100 12	89[a]
3	**1a** (24)	**2d** (20)	[$Ru_3(CO)_{12}$] (0.2) NH_4PF_6 (0.6)	–	100 3	88[a]
4	**1a** (15)	**2e** (5)	[$Ru_3(CO)_{12}$] (1.0) HBF_4/OEt_2 (3.0)	–	100 12	80[c,d]
5	**1b** (30)	**2a** (20)	[$Ru_3(CO)_{12}$] (0.5) NH_4PF_6 (1.5)	MeOH (3.0)	100 12	63[a]
6	**1c** (10)	**2c** (5)	[$Ru_3(CO)_{12}$] (1.0) HBF_4/OEt_2 (3.0)	toluene (0.7)	100 12	41[c]

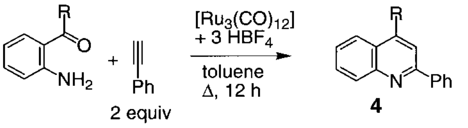
[a] Isolated by distillation. [b] Isolated by recrystalization. [c] Determined by GC analysis. [d] 3:2 mixture of geometrical isomers: ^1H NMR ($CDCl_3$): $\delta = 1.77, 2.47$ (s, 1.2 H), 2.16, 2.51 (s, 1.8 H); ^{13}C NMR ($CDCl_3$): $\delta = 165.4, 167.0, 196.8, 196.9$.

1433-7851/99/3821-3223 $ 17.50+.50/0

catalyst. It is noteworthy that the aromatic imine prepared here from **1a** and **2e** is apparently difficult to synthesize by the ordinary dehydrative condensation of acetophenone and **2e**; a self-condensation of **2e** to form a polymer occurs.

The preparation of nonaromatic ketimines by use of aliphatic 1-alkynes was moderately successful (Table 2, entries 5, 6). The aliphatic acetylenes **1b**, **c** were found to be less reactive than **1a** towards aniline and prolonged reaction times resulted in the partial decomposition of the imine formed. Nevertheless, the utility was demonstrated for the preparation of the imine from **1c** and **2c** (Table 2, entry 6), which is a synthetic intermediate of Metolachlor,[13] one of the most intensively used herbicides.

As an application of the present catalytic system to form aromatic ketimines, a new two-component synthesis of quinolines (Scheme 2) was examined. The quinoline nucleus is present in a variety of natural products, pharmaceuticals, and dyes,[14a] and the synthesis of this important structure has been a steady topic.[14b] The 2,4-disubsitituted quinolines **4** were formed in good to quantitative yields by the reaction of *o*-benzoyl- (**2f**) or *o*-acetylaniline (**2g**) with two equivalents of **1a**. The yields obtained by this method (Scheme 2) are superior to the corresponding Friedländer synthesis, which uses *o*-acylanilines and ketones.[15]



2f, R = C_6H_5
2g, R = CH_3

2 [mmol]	cat. [mol%]	Yield [%]
f (5)	0.7	>99
g (10)	1.5	89

Scheme 2. Ruthenium-catalyzed two-component synthesis of 2,4-disubsituted quinolines.

The reaction mechanism of the present hydroamination reaction, in particular the reason for the remarkable enhancement effect of the additives, remains to be clarified. The observation that NH_4PF_6 and aqueous HPF_6 are quite efficient additives while NMe_4PF_6 is totally ineffective suggests that protons play an important role. However, the conjugated base must also be important since aqueous HCl has only a very small acceleration effect. It has been reported by Lavigne et al. that halides and related salts can promote substituion reactions of $[Ru_3(CO)_{12}]$.[16]

Experimental Section

Special care does not need to be taken with the catalytic reaction to remove air and moisture from the system.

Acetophenone-*N*-phenylimine: A mixture of phenylacetylene (36.8 g, 0.360 mol), aniline (27.9 g, 0.300 mol), $[Ru_3(CO)_{12}]$ (0.192 g, 0.300 mmol), and NH_4PF_6 (0.147 g, 0.900 mmol) was stirred at 100 °C for 3 h, then distilled under reduced pressure[17] to give the imine (bp. 90–95 °C, 0.1 Torr; 53.7 g, 0.275 mol, 92 %).

2,4-Diphenylquinoline: A mixture of phenylacetylene (1.02 g, 10.0 mmol), 2-aminobenzophenone (0.986 g, 5.00 mmol), $[Ru_3(CO)_{12}]$ (22.4 mg, 0.035 mmol), 48 % aqueous HBF_4 (14 µL, 0.105 mmol), and toluene (3 mL) was stirred at 160 °C for 12 h. Water was removed by azeotropic dehydration. The products were separated by column chromatography on silica gel (hexane/CH_2Cl_2 3/1) to give 2,4-diphenylquinoline (1.41 g, 5.00 mmol, >99 %).

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Chemically Triggered Assembly of Chiral Triangular Metallomacrocycles**

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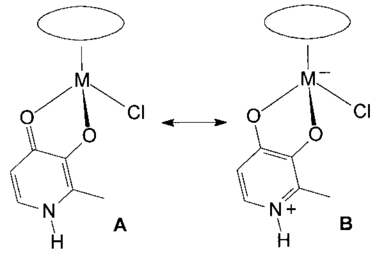
Dedicated to Professor Theodore Severin on the occasion of his 70th birthday

Self-assembly processes that are based on interactions between transition metals and ligands are among the most elegant methods for the construction of large macrocyclic compounds. In recent years a variety of amazingly complex structures have been built in this way.[1] The focus of interest has been on two-dimensional polygons such as squares and rectangles, but three-dimensional polyhedra[2] and possible applications are now beginning to be explored.[1, 3] In comparison with rectangular assemblies there have been relatively few reports on triangular metallomacrocycles.[4–6] This is especially true for complexes with rigid heterocyclic ligands, a class of compounds that was very successfully employed for the construction of other polynuclear assemblies. A possible explanation, as suggested by Stang et al.,[1b] is the fact that the required 60° turning angle is quite uncommon in transition metal chemistry.[7]

Herein we describe the synthesis and crystal structure of two chiral, triangular macrocycles in which half-sandwich complexes of iridium(III) and ruthenium(II) occupy the corner positions. The heterocyclic bridging ligand is the dianion of 3-hydroxy-2-methyl-4(1*H*)-pyridone. This ligand[8] as well as *N*-substituted derivatives[9] are easily synthesized from commercially available 3-hydroxy-2-methyl-4-pyrone (maltol). These ligands have received considerable attention since they are good chelators of various metal ions, especially iron(III).[10] Recently, we reported the first examples of organometallic complexes with *N*-alkyl and *N*-aryl pyridones.[11] During the course of the work we realized that the nonsubstituted 3-hydroxy-2-methyl-4(1*H*)-pyridone should be an ideal candidate for the synthesis of well defined oligonuclear transition metal assemblies. The starting point of our investigations was the chiral pentamethylcyclopentadienyl (Cp*) iridium(III) complex **1**. This compound was obtained as a racemic mixture from $[\{Cp^*IrCl_2\}_2]$ and 3-hydroxy-2-methyl-4(1*H*)-pyridone in the presence of one equivalent of base.

In accordance with previous studies on transition metal pyridone complexes it was assumed that the mesomeric form B (Figure 1) contributes significantly to the electronic structure of **1**.[11, 12] We therefore anticipated that the proton bound at the nitrogen atom should be acidic. Simultaneously the chloride ligand was expected to be labile. Combining these two characteristics should allow a base-induced oligomerization of **1**. In fact, if **1** was stirred with one equivalent of NaOMe (or NEt_3) in methanol the yellow complex **2** was obtained in quantitative yield (Scheme 1).[13] Alternatively, **2** can be prepared directly from $[\{Cp^*IrCl_2\}_2]$, the pyridone ligand, and NaOMe (molar ratio 1:2:4).



1 $ML_n = Cp^*Ir$
3 $ML_n = (\eta^6\text{-cymene})Ru$

Figure 1. Mesomeric forms that contribute to the electronic structure of **1** and **3**.

The ^1H NMR spectrum of **2** was indicative of a highly symmetrical structure: only one signal was observed for the Cp* protons and only one set of signals was detected for the pyridone protons. It is known that the symmetry of supramolecular assemblies based on metal–ligand interactions is strongly biased by the geometric requirements of the ligand as well as the transition metal.[1a,b] The geometry of half-sandwich complexes can be described as pseudo-octahedral with angles between the three "piano-stool legs" approaching 90° (for example, Cl-Ir-(μ-Cl) = 88.49° in $[\{Cp^*IrCl_2\}_2]$[14]). Since the heterocyclic ligand is nearly planar our initial guess

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