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Ruthenium-catalyzed intramolecular hydroamination of aminoalkynes

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Abstract

Low-valent ruthenium complexes with a π-acidic ligand, such as $Ru(\eta^6\text{-cot})(dmfm)_2$ [cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate] and $Ru_3(CO)_{12}$, showed high catalytic activity for the intramolecular hydroamination of aminoalkynes. The reaction is highly regioselective, in which a nitrogen atom is selectively attached to an internal carbon of alkynes to give five-, six-, and seven-membered nitrogen heterocycles as well as indoles in good to high yields.

Keywords: Ruthenium catalyst; Aminoalkynes; Hydroamination; Cyclization

1. Introduction

Among the various addition reactions across C–C multiple bonds, the direct addition of N–H bonds in amines to alkenes and/or alkynes mediated and catalyzed by transition metal complexes is of fundamental importance in organic chemistry, and is both a challenging and highly desirable transformation [1]. To catalyze the hydroamination of alkenes and/or alkynes, two basic approaches have been used; i.e. activation of either the amine by low-valent transition metal complexes or the unsaturated bond by high-valent complexes [2]. In comparison to the intermolecular hydroamination reaction [3], intramolecular hydroamination, especially of aminoalkynes, has been considerably developed using several transition metal catalysts [4–7] as well as lanthanide catalysts [8], since this reaction is a direct and easy way to preparation of various biologically important nitrogen heterocycles. However, the catalyst systems reported so far have serious drawbacks: the catalysts (generally air- and moisture-sensitive) are unwieldy and short catalyst lifetimes lead to low turnover frequencies. As for the ruthenium complex catalyst, Müller et al. have first used $Ru_3(CO)_{12}$ as a catalyst for intramolecular hydroamination of 6-aminohex-1-yne, however, the yield of the product, 2-methyl-1,2-dehydropiperidine, was only 21% [9]. Therefore, there is a considerable interest in new catalytic approaches as well as reinvestigation of the catalytic activity of the ruthenium catalyst. In the course of our study on ruthenium catalysis [10], we previously found the first ruthenium-catalyzed intermolecular hydroamination of alkynes with *N*-aryl-substituted amides via catalytic activation of N–H bond, which offers a novel synthesis of enamides [11a]. Further study on the synthesis of novel amine-coordinated zero-valent ruthenium complexes [12] prompted us to investigate the catalytic activity of low-valent ruthenium complexes for the intramolecular hydroamination reaction via N–H bond activation. We report here the practically useful ruthenium-catalyzed intramolecular hydroamination of aminoalkynes.

2. Results and discussion

Recently, we reported the synthesis of novel zero-valent ruthenium mono- [12a] and bidentate [12b] amine complexes by reacting $Ru(\eta^6\text{-cot})(dmfm)_2$ [cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate] [13] with the corresponding amines. As expected, $Ru(\eta^6$-

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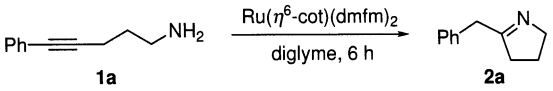
Table 1
Effect of the reaction temperature on Ru(η^6-cot)(dmfm)$_2$-catalyzed intramolecular hydroamination of **1a** to **2a** [a]



1a **2a**

Run	Temperature (°C)	Conversion of **1a** (%) [b]	Yield of **2a** (%) [b]
1	150	100	88
2	140	88	65
3	130	80	55
4	120	35	35

[a] Compound **1a** (2.5 mmol), Ru(η^6-cot)(dmfm)$_2$ (0.1 mmol), diglyme (4.0 ml) for 6 h under an argon atmosphere.
[b] Determined by GLC.

Table 2
Effect of the solvent on Ru(η^6-cot)(dmfm)$_2$-catalyzed intramolecular hydroamination of **la** to **2a** [a]

Run	Solvent	Conversion of **la** (%) [b]	Yield of **2a** (%) [b]
1	Diglyme	100	83
2	Benzonitrile	88	46
3	Nitrobenzene	100	20
4	Mesitylene	63	37
5	Decane	23	23

[a] Compound **la** (2.5 mmol), Ru(η^6-cot)(dmfm)$_2$ (0.10 mmol), solvent (4.0 mL) at 150°C for 4 h under an argon atmosphere.
[b] Determined by GLC.

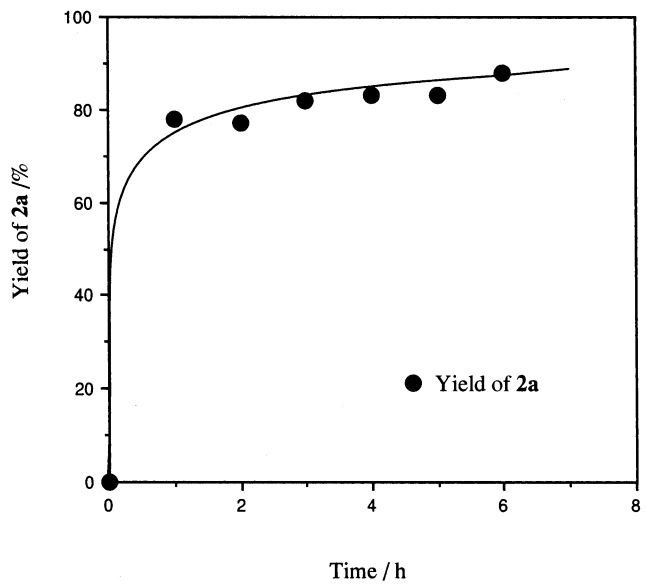
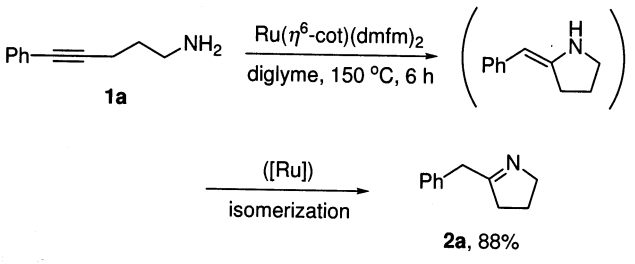


Fig. 1. The time-dependence of Ru(η^6-cot)(dmfm)$_2$-catalyzed intramolecular hydroamination of **1a** to **2a**.

cot)(dmfm)$_2$ showed high catalytic activity for the facile intramolecular hydroamination of general aminoalkynes. For example, treatment of 5-phenyl-4-pentynyl-1-amine (**1a**) with 4.0 mol% Ru(η^6-cot)(dmfm)$_2$ in diglyme at 150°C for 6 h under an argon atmosphere gave 2-benzyl-1-pyrroline (**2a**) in 88% yield without any byproducts which can be detected by GLC (Eq (1)).



1a

(1)

The effects of the reaction temperature and the solvent are summarized in Tables 1 and 2. A reaction temperature over 150°C was required for completion of the present reaction. The highest selectivity of **2a** was observed at 150°C, and the selectivity of **2a** decreased at lower reaction temperatures (Runs 1–3 in Table 1). As for the solvent, benzonitrile and nitrobenzene drastically decreased the yield of **2a**, while the conversion of **1a** was high, due to the polymerization of **1a** to generate highly viscous intractable mixtures. On the other hand, both the conversion of **1a** and the yield of **2a** were decreased in mesitylene and decane without polymerization. Among the solvents examined, diglyme gave the best result.

The time–dependence of the reaction is shown in Fig. 1. Most of **1a** is consumed at the early stage of the reaction, and the reaction is almost complete within 1 h.

Several low-valent ruthenium complexes bearing a π-acidic ligand showed good to high catalytic activity for the transformation of **1a** to **2a** (Table 3). Judging from the results reported by Müller et al. [9], $Ru_3(CO)_{12}$ was expected to show low catalytic activity. However, when $Ru_3(CO)_{12}$ was employed under our optimized reaction conditions, extremely high catalytic activity was observed. Other ruthenium complexes, such as (η^3-C_3H_5)RuBr(CO)$_3$, [$RuCl_2(CO)_3]_2$, and Ru(CO)$_3$-(PPh_3)$_2$, also showed good catalytic activity. On the other hand, the catalytic activities of zero- and divalent ruthenium complexes without a π-acidic ligand, such as Ru(η^4-cod)(η^6-cot) [cod = 1,5-cyclooctadiene], Ru(η^5-cyclooctadienyl)$_2$, Cp*RuCl(cod) [Cp* = pentamethylcyclopentadienyl], [Ru(η^6-C_6H_6)$Cl_2]_2$, $RuCl_2(PPh_3)_3$, and $RuH_2(PPh_3)_4$, were moderate to low.

Since $Ru_3(CO)_{12}$ is commercially available and has a high catalytic activity superior to other ruthenium catalysts, it was used as a catalyst in the following intramolecular hydroamination of several aminoalkynes (**1a**–**g**) (Table 4). The present process regioselectively

Table 3
Catalytic activity of several ruthenium complexes on the intramolecular hydroamination of **la** to **2a** [a]

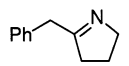
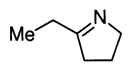
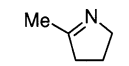
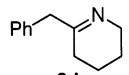
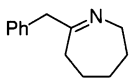
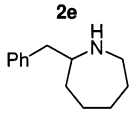
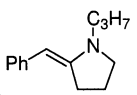
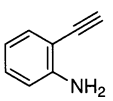
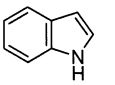
Run	Ruthenium complex	Conversion of **la** (%) [b]	Yield of **2a** (%) [b]
1	$Ru(\eta^6\text{-cot})(dmfm)_2$	100	83
2	$Ru_3(CO)_{12}$	100	>99
3	$(\eta^3\text{-}C_3H_5)$ $RuBr(CO)_3$	100	>99
4	$[RuCl_2(CO)_3]_2$	100	93
5	$Ru(CO)_3(PPh_3)_2$	100	85
6	$Ru(\eta^4\text{-cod})(\eta^6\text{-cot})$	66	30
7	$Ru(\eta^5\text{-cyclooctadienyl})_2$	53	40
8	$[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$	84	46
9	Cp*RuCl(cod)	100	45
10	$RuCl_2(PPh_3)_3$	45	22
11	$RuH_2(PPh_3)_4$	70	13

[a] Compound **la** (2.5 mmol), ruthenium complex (0.10 mmol as Ru atom), diglyme (4.0 mL) at 150°C for 4 h under an argon atmosphere.
[b] Determined by GLC.

gave five-, six-, and seven-membered heterocycles, while the present ring-size dependence of cyclization rates and the product yields is $5 > 6 \gg 7$, consistent with those observed in the lanthanide-catalyzed intramolecular hydroamination of aminoalkynes [8f,h]. Furthermore, in the formation of seven-membered heterocycles such as **2e**, a considerable amount of the saturated heterocycles such as **2e′** was obtained by ruthenium-catalyzed hydrogen-transfer reaction [14]. The marked substituent effects of alkynes fall in the order $Ph > H > Me \gg Me_3Si$, which is completely different from that observed in the lanthanide catalysis [8f,h]. In particular, no reaction occurred with Me_3Si-substituted aminoalkynes, such as 5-trimethylsilyl-4-pentynyl-1-amine. This result suggests that the mechanism of the present reaction may be different from that of a lanthanide-catalyzed reaction. Although a mechanism involving σ-bond metathesis can not be ruled out completely, the present ruthenium-catalyzed intramolecular hydroamination of aminoalkynes would proceed via N–H bond activation [15]. The substituent effects would strongly influence the insertion of an alkyne into the generated Ru–N bond. The present hydroamination reaction is not limited to primary amines, and secondary amines, such as **1f**, also undergo rapid cyclization to give the corresponding enamines in an isolated yield of 72%. $Ru_3(CO)_{12}$ also catalyzes the formation of indoles from 2-alkynylanilines. Specifically, 2-ethynylaniline (**1g**) is converted into indole (**2g**) in an isolated yield of 54%.

One viable mechanism involves the oxidative addition of an amine functionality in aminoalkynes to a coordinatively unsaturated active ruthenium center in a low oxidation state [3c,15,16]. Ru(II) precursors, such as $(\eta^3\text{-}C_3H_5)RuBr(CO)_3$ and $[RuCl_2(CO)_3]_2$, should be reduced first to low-valent catalytically active Ru(0) species under the present reaction conditions. The reaction produces a (hydrido)(amido)ruthenium intermediate. Subsequently, the reaction can take place either at the Ru–N or Ru–H bond. Insertion of an alkyne moiety into the Ru–N bond, followed by reductive elimination/isomerization gives the corresponding cyclic imine with regeneration of an active ruthenium species. Alternatively, the (hydrido)(amido)ruthenium complex might insert the alkyne moiety into the Ru–H bond. However, there is evidence that this type of reaction is unfavorable in comparison with insertion into the Ru–N bond. It has been reported that (hydrido)(amido)complexes $LnMH(NR_2)$ ($M = Pd$, Pt) prefer the insertion of an alkene into the M–N bond [17]. In addition, reductive eliminations involving carbon-heteroatom bond formation are generally less common [18] and probably disfavored relative to carbon–carbon and carbon–hydrogen bond formation.

Table 4
$Ru_3(CO)_{12}$-catalyzed intramolecular hydroamination of aminoalkynes[a]

Run	Aminoalkyne	Temp. (°C)	Product (%)[b]
1	Ph—≡—$(CH_2)_3$—NH_2 **1a**	110	 **2a** >99 (84)
2[c]	Me—≡—$(CH_2)_3$—NH_2 **1b**	110	 **2b** 60
3[c]	H—≡—$(CH_2)_3$—NH_2 **1c**	110	 **2c** 78
4[d]	Ph—≡—$(CH_2)_4$—NH_2 **1d**	120	 **2d** 77
5	Ph—≡—$(CH_2)_5$—NH_2 **1e**	140	 **2e** (21)  **2e'** (13)
6	Ph—≡—$(CH_2)_3$-NH-C_3H_7 **1f**	110	 **2f** (72)
7	 **1g**	110	 **2g** (54)

[a] Aminoalkyne (2.5 mmol), $Ru_3(CO)_{12}$ (0.033 mmol), diglyme (4.0 mL) for 4 h under an argon atmosphere. [b] GLC yield (isolated yield). [c] $(BuOCH_2CH_2)_2O$ was used as a solvent. [d] For 6 h.

In conclusion, we developed the first practically useful ruthenium-catalyzed intramolecular hydroamination of aminoalkynes. These results demonstrate that organoruthenium centers are suitable for the efficient activation of N–H bond, followed by regioselective insertion of an alkyne into the Ru–N bond. These processes provide an effective method for the catalytic synthesis of nitrogen heterocycles such as pyrrole and indole derivatives.

3. Experimental

3.1. General

GLC analyses were performed on a Shimadzu GC-8A gas chromatograph with a glass column (3.2 mm i.d. × 3 m) packed with Silicone OV-17 (2% on Chromosorb W(AW-DMCS), 80–100 mesh) and a Shimadzu GC-14A gas chromatograph with a capillary column (Shimadzu capillary column HiCap-CBP10-M25-025: 0.22 mm i.d. × 25 m). Almost all of the products were isolated by Kugelrohr distillation, and further purification, if needed, was performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., model LC-908) equipped with JAIGEL-1H and 2H columns (GPC) using THF or toluene as an eluent. The ^{1}H (400 MHz) and ^{13}C-NMR spectra (100 MHz) were obtained on a JEOL EX-400 spectrometer. Samples were analyzed in $CDCl_3$, and the chemical shift values are expressed relative to Me_4Si as an internal standard. IR spectra were obtained on a Nicolet Impact 410 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

3.2. Materials

The reagents used in this study were dried and purified before use by standard procedures. $Ru_3(CO)_{12}$ and $[RuCl_2(CO)_3]_2$ were obtained commercially, and used without further purification. Ru(η^6-cot)(dmfm)$_2$ [13], (η^3-C_3H_5)RuBr(CO)$_3$ [19], Ru(CO)$_3$(PPh$_3$)$_2$ [20], Ru(η^4-cod)(η^6-cot) [21], Ru(η^5-cyclooctadienyl)$_2$ [22], [Ru(η^6-C_6H_6)Cl$_2$]$_2$ [23], Cp*RuCl(cod) [24], $RuCl_2(PPh_3)_3$ [25], and $RuH_2(PPh_3)_4$ [26] were prepared as described in the literature. Aminoalkynes (**1a**–**e**) were prepared as reported previously [8h], and **1f** was prepared as described in the literature with some modification. 2-Ethynylaniline (**1g**) was prepared as reported previously [27]. Compounds **1a**–**e** [8h], **2a**–**e** [8h], and **1g** [27] have already been reported. The spectral and analytical data of **2g** were fully consistent with those of an authentic sample. Characterization data of **1f**, **2e′**, and **2f** are given below.

3.3. General procedure for ruthenium-catalyzed intramolecular hydroamination of aminoalkynes

A mixture of aminoalkyne (2.5 mmol), ruthenium catalyst (0.10 mmol as Ru atom), and solvent (4.0 ml) was placed in a two-necked 20 ml Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under an argon atmosphere. The mixture was then magnetically stirred at 110–150°C for 4–6 h. After cooling, the reaction mixture was analyzed by GLC, and the products were isolated by Kugelrohr distillation and/or recycling preparative HPLC.

3.4. Characterization of products

3.4.1. N-Propyl-5-phenyl-4-pentynyl-1-amine (**1f**)

Colorless liquid: b.p. 130°C (2 mmHg, Kugelrohr). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.96 (t, $J = 7.32$ Hz, 3H, CH_3), 1.29 (br s, 1H, NH), 1.54 (septet, $J = 7.32$ Hz, 2H, CH_2CH_3), 1.82 (quintet, $J = 6.83$ Hz, 2H, $NCH_2CH_2CH_2CC$), 2.51 (t, $J = 6.84$ Hz, 2H, CH_2CC), 2.62 (t, $J = 7.32$ Hz, 2H, $CH_2CH_2CH_3$), 2.80 (t, $J = 6.84$ Hz, CH_2N), 7.28–7.44 (m, 5H, Ph). ^{13}C-NMR (100 MHz) δ 11.7, 17.3, 23.1, 28.9, 48.8, 51.7, 80.8, 89.6, 123.8, 127.4, 128.1, 131.4. MS (EI) m/z 200 (M^+–H). Anal. Calc. for $C_{14}H_{19}N$: C, 83.53; H, 9.51. Found: C, 83.55; H, 9.65%.

3.4.2. 2-Benzylhexahydroazepine (**2e′**)

Colorless liquid: b.p. 120°C (1 mmHg, Kugelrohr). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 1.32–1.44 (m, 2H, $CHHCH_2N$, $CHHCHN$), 1.53–1.61 (m, 4H, $2CH_2$), 1.72–1.76 (m, 2H, $CHHCH_2N$, $CHHCHN$), 2.52–2.69 (m, 3H, $CHHN$, CH_2Ph), 2.82–2.92 (m, 3H, $CHHN$, CH, NH), 7.11–7.24 (m, 5H, Ph). ^{13}C-NMR (100 MHz) δ 25.3, 27.0, 30.0, 36.0, 43.6, 47.4, 60.8, 126.2, 128.2, 129.2, 139.5. MS (EI) m/z 189 (M^+). Anal. Calc. for $C_{13}H_{19}N$: C, 82.48; H, 10.12. Found: C, 82.10; H, 10.00%.

3.4.3. 2-Benzylidene-1-propylpyrrolidine (**2f**)

Colorless liquid: b.p. 120°C (1 mmHg, Kugelrohr). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 0.84 (t, $J = 7.33$ Hz, 3H, CH_3),, 1.52 (septet, $J = 7.32$ Hz, 2H, $NCH_2CH_2CH_3$), 1.78 (quintet, $J = 6.83$ Hz, 2H, CH_2), 2.72 (t, $J = 7.32$ Hz, 2H, CH_2CN), 2.99 (t, $J = 7.32$ Hz, 2H, $NCH_2CH_2CH_3$), 3.10 (t, $J = 6.83$ Hz, 2H, CH_2N), 4.97 (s, 1H, CHPh), 6.79–7.14 (m, 5H, Ph). ^{13}C-NMR (100 MHz) δ 12.0, 20.0, 22.1, 31.4, 48.8, 51.6, 90.5, 122.1, 126.0, 128.3, 141.1, 149.9. MS (EI) m/z 201 (M^+). Anal. Calc. for $C_{14}H_{19}N$: C, 83.53; H, 9.51. Found: C, 83.71; H, 9.63%.

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