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Co-catalyst dependent cycloisomerization or ring closing metathesis of α,ω-dienes catalyzed by arene ruthenium complex with side-arm alcohol

Yoshiharu Miyaki, Takafumi Onishi, Sensuke Ogoshi, Hideo Kurosawa *

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

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Abstract

Cycloisomerization and ring closing metathesis of some α,ω-dienes were catalyzed by a cationic arene ruthenium chelate complex [Ru{η^6:η^1-Ph$(CH_2)_3$OH}(PCy_3)Cl]BF_4 (**1a**) in the presence of triethylamine and phenylacetylene, respectively, as co-catalysts. Analogous catalyst systems employing arene ruthenium cations without the side arm alcohol functional group showed lower efficiencies.

Keywords: Cycloisomerization; RCM; Arene ruthenium complexes

1. Introduction

Recently, we reported synthesis of ruthenium(II) complexes containing an oxygen, nitrogen, and phosphorous donor atoms tethered to a η^6-arene ring [1]. Among these were alcohol chelate complexes with tertiary phosphines or *N*,*N*′-chelate ligands (Scheme 1) which exhibited a hemilabile behavior in solution. Although the alcohol complex with *N*,*N*′-chelates **2** afforded, on treatment with base, alkoxy chelate complexes **3** which are inert to β-hydrogen elimination, the similar treatment of the alcohol chelates having tertiary phosphines led to the decomposition of complexes. It is presumed that in the latter case a much more labile hydride complex was formed by β-hydrogen elimination of an alkoxy chelate complex [2]. It occurred to us that this active hydride complex, generated in situ, could be potentially applied to catalysts of some organic reactions.

We report here catalytic cycloisomerization of α,ω-dienes using an alcohol chelate complex [Ru{η^6:η^1-Ph$(CH_2)_3$OH}(PCy_3)Cl]BF_4 (**1a**) as the catalyst precursor and amine as the co-catalyst. We also found that the combination of **1a** and phenylacetylene, instead of the amine, led to the change of the catalytic course of the transformation of the same α,ω-dienes to the ring closing metathesis (RCM).

2. Results and discussion

Cycloisomerization of α,ω-dienes has attracted attention as the useful and facile construction methods of medium-membered ring. This reaction was promoted by catalytic amounts of palladium [3], nickel [4], yttrium [5], and ruthenium [6] complexes. RCM of the analogous dienes has been already used as an effective strategy in the synthesis of complex molecules with multiple functionality [7], and ruthenium complexes were mainly used as catalysts of RCM.

We found that in the presence of 5 mol% of [Ru{η^6:η^1-Ph$(CH_2)_3$OH}(PCy_3)Cl]BF_4 (**1a**) and triethylamine in refluxing CH_2Cl_2 for 64 h, tosylated diallylamine (**4a**) gave *exo*-methylene pyrrolidine (**5a**) in excellent yield (Scheme 2). A small amount of 2*H*-pyrroline (**6a**) was also detected in the reaction mixture. On the other hand, in the presence of 5 mol%, each of

* Corresponding author. Tel.: +81-6-8797392; fax: +81-6-8797394.

E-mail address: kurosawa@ap.chem.eng.osaka-u.ac.jp (H. Kurosawa).

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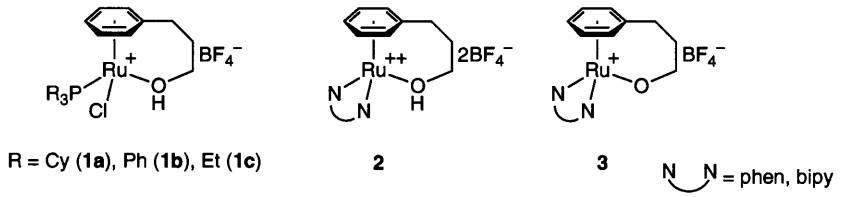
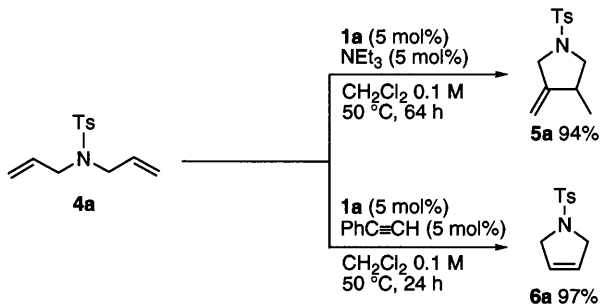


Scheme 1.

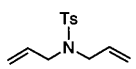
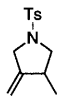
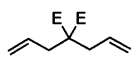
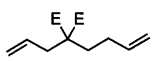
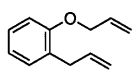
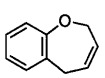
1a and phenylacetylene in refluxing CH_2Cl_2 for 24 h, RCM of **4a** occurred to give 2*H*-pyrroline (**6a**) in excellent yield. Results are summarized in Table 1. The cycloisomerization also proceeded in refluxing THF with the use of only 1% amount of **1a**. Diallyl malonate (**4b**) also underwent co-catalyst dependent cycloisomerization or RCM to give **5b** or **6b**, respectively. The cycloisomerization of allyl-homoallyl malonate (**4c**) was unsuccessful and isomerization to allyl-crotyl malonate only occurred (**4c**:allyl-crotyl malonate = 5:1), while RCM of **4c** proceeded to give cyclohexene derivative in good yield. Although RCM of **4d** occurred to give **6d** in good yield as well, even any double bond shift did not occur in an attempt of cycloisomerization of **4d**. The nature of the phosphine ligand affected the catalytic activity. Triphenylphosphine (**1b**) and triethylphosphine (**1c**) analogs of **1a** did not show catalytic activity for cycloisomerization and RCM of **4a**.



Scheme 2.

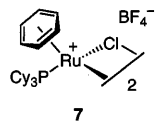
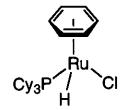
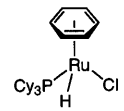
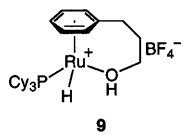
The existence of the side-arm alcohol group appears advantageous to the catalytic efficiency. Thus, in com-

Table 1
Cycloisomerization and RCM reaction catalyzed by ruthenium(II) complex **1a** and co-catalyst

Entry	Substrate	Cyclioisomerization[a]	RCM[b]
1	 **4a**	 **5a** 1) In CH_2Cl_2, 50 °C, 64 h, 94% 2) In THF, 75 °C, 69 h, 88%[c]	 **6a** 97%, 24 h
2	 **4b** E = CO_2Et	 **5b** In THF, 75 °C, 48 h, 83%[d]	 **6b** 79%[e], 24 h
3	 **4c** E = CO_2Et	No cyclization	 **6c** 76%, 24 h
4	 **4d**	No cyclization	 **6d** 74%[e], 48 h

[a] Reaction condition: 5 mol% of both **1a** and NEt_3, $[substrate]_0 = 0.1$ M. Yield was determined by GC.
[b] Reaction condition: 5 mol% of both **1a** and PhC≡CH, $[substrate]_0 = 0.1$ M in CH_2Cl_2, 50 °C. Yield was determined by NMR.
[c] 1 mol% of both **1a** and NEt_3.
[d] Yield was determined by NMR.
[e] 25 mol% of PhC≡CG.

Table 2
Cycloisomerization of **4a** using some ruthenium(II) complexes

Entry	Ruthenium complex/condition[a]	Additive	GC yield of **5a**
1	 **7** 5 mol%, 66 h, CH_2Cl_2, 50 °C	NEt_3 5 mol%, ^iPrOH 25 mol%	26%
2	 **8** 5 mol%, 39 h, CH_2Cl_2, 50 °C	none	trace
3	 **8** 5 mol%, 39 h, CH_2Cl_2, 50 °C	$AgBF_4$ 5 mol%	24%
	1 mol%, 18 h, THF, 75 °C	$AgBF_4$ 1 mol%	20%
4	 **9** 1 mol%, 18 h, THF, 75 °C	none	61%

[a] $[substrate]_0 = 0.1$ M

parison to the catalytic efficiency of **1a** shown in Table 1, a cationic benzene complex without a side-arm alcohol (**7**) and triethylamine, catalyzed the cycloisomerization of **4a** much less efficiently even in the presence of 5 equivalents of ^{i}PrOH as a potential hydride source (Table 2, entry 1). Moreover, **7** (5 mol%) in the presence of phenylacetylene (5 mol%) in CH_2Cl_2 at 50°C catalyzed RCM of **4a** with less efficiency (57% yield, 24 h) than using **1a** as the catalyst precursor.

Two mechanisms of the ruthenium-catalyzed cycloisomerization have been so far considered [6]: (i) ruthenium hydride intermediate plays a key role; and (ii) oxidative coupling of dienes at the ruthenium center triggers the catalytic cycle. Itoh et al. mentioned that some isolable η^5-cyclopentadienyl ruthenium(II) hydrides, e.g. $CpRuH(PPh_3)_2$ and $Cp^*RuH_3(PPh_3)$, failed to catalyze cycloisomerization of the 1,6-diene in refluxing 1,2-dichloroethane [6]. We tried to confirm the generation of ruthenium hydride species in the reaction of **1a** with one equivalent of triethylamine in CD_2Cl_2 by low temperature NMR spectroscopy. Upon addition of the amine to **1a** at -70°C, a new broad ^{31}P peak (δ 36.1) replaced the peak due to **1a** (δ 34.9) almost completely. It is speculated that this new peak is due to an alkoxy complex, e.g. $[Ru\{\eta^6{:}\eta^1\text{-}C_6H_5(CH_2)_3O\}(PCy_3)Cl]$. When the temperature was raised gradually, the peak at δ 36.1 decreased and another peak (δ 62.5) grew up. It is notable that this considerably lower field peak is in the range of the ^{31}P peak of the arene–ruthenium hydride complexes, $[Ru(\eta^6\text{-}C_6H_6)(PCy_3)HCl]$ (**8**) and $[Ru\{\eta^6{:}\eta^1\text{-}Ph(CH_2)_3OH\}(PCy_3)H]BF_4$ (**9**) which were newly prepared in this study, as described below. In ^{1}H-NMR spectra at -30°C, we observed two resonances at the ruthenium hydride regions (δ -6.55 and -7.96). These resonances were split into doublets (J = 47.3 and 49.7 Hz) probably due to coupling with PCy_3. Again these chemical shifts and J values are similar to those of **8** and **9**. However, we found no resonances ascribable to an aldehyde hydrogen at very low fields [8]. Moreover, we could not isolate and characterize distinct hydride species because of their instability.

Next we prepared some arene ruthenium hydride complexes **8** and **9** and tested their catalytic efficiency. These complexes were prepared by using formate as the hydride source under a milder condition than that of the previous method for analogous complexes, which involved refluxing a 2-propanol solution of the arene ruthenium halides with sodium carbonate [9]. Complex **9** is a rare example in which the hydride and alcohol ligand are bonding to the same transition metal center. The neutral complex **6** alone was not active for the cycloisomerization of **4a** (entry 2). A small improvement in the catalytic activity was observed with the combination of **8** and $AgBF_4$ (entry 3), suggesting a requirement of a weakly coordinated ligand. The cycloisomerization of **4a** in refluxing THF by the use of 1 mol% of **7** proceeded with the higher efficiently (entry

4). It is suggested again that the existence of the hemilabile side-arm alcohol appears to play a key role. When **9** was treated with ethylene (1 atm) in CD_2Cl_2 at room temperature for 3 min, a new ^{31}P peak (δ 65.6) completely replaced that of **9** (δ 61.8) and a new hydridic peak (δ −9.56, $J_{PH} = 32.4$ Hz) and two new broad peaks for ethylene (δ 2.2–2.4) were detected in ^1H-NMR spectra. This new species seems to be a hydride ethylene complex with the side-arm alcohol set free; cf. $\delta(CH_2O)$ 3.60 for the new complex with $\delta(CH_2O)$ 3.05 and 3.52 for **9**. Further transformations (e.g. insertion of ethylene) of this complex did not take place when the CD_2Cl_2 solution was heated for 17 h.

In conclusion, cycloisomerization and RCM of α,ω-dienes proceeded with the same catalyst precursor **1a** by choosing the appropriate co-catalyst. The amine co-catalyst may assist generation of a hydride species, while phenylacetylene would react with **1a** to give a vinylidene ruthenium species, which is responsible for the RCM reactions. It is well known that the reaction of coordinately unsaturated ruthenium complexes with terminal alkynes afforded vinylidene complexes [10], though not detected in the present system, and that some vinylidene or allenylidene ruthenium complexes act as catalysts for RCM [11]. The exact functions of the side arm alcohol during the present catalyses cannot be specified at this moment, except for a possible role as a source of the hydride ligand in the cycloisomerization. It is also speculated that the hemilabile nature of the side arm alcohol ligand or an aldehyde one, if formed by β-hydrogen transfer from alkoxy group to ruthenium, could help to prevent, via weak coordination, decomposition of an otherwise unstable, coordinately unsaturated active intermediate.

3. Experimental

3.1. General remarks

Most of the commercially available reagents were used without further purification. Solvents were dried by standard methods and distilled prior to use. ^1H- and ^{31}P-NMR spectra were recorded with a JEOL GSX-270 spectrometer. Gas chromatographic analyses were performed on a HITACHI G-3000 equipped with a SHIMAZU CBP-10 capillary column (25 m × 0.25 mm) with helium as carrier gas.

3.2. Starting materials

Compound **4a** was prepared from diallylamine and tosyl chloride in CH_2Cl_2. Compounds **4b** and **4c** were prepared from diethylallyl malonate and allyl bromide (**4b**) or homoallyl bromide (**4c**) in THF containing sodium hydride. Compound **4d** was prepared from *o*-allylphenol and allyl bromide in DMSO containing KOH. The complexes $[Ru(\eta^6\text{-}C_6H_6)(PCy_3)Cl_2]$ and $[Ru(\eta^6\text{-}C_6H_6)(PCy_3)Cl_2](BF_4)_2$ were synthesized in manners similar to those [12,13] for analogous complexes.

3.3. Typical procedure for cycloisomerization of α,ω-dienes

To a solution of **4a** (251 mg, 1.0 mmol) and triethylamine (7.0 μl, 0.05 mmol) in CH_2C1_2 (10 ml) was added **1a** (32 mg, 0.05 mmol). The reaction mixture was refluxed at 50°C for 64 h. The yield of the products was calculated by GC using *n*-pentadecane as an internal standard. Cycloisomerization products **5a** [4] and **5b** [14] were known compounds.

3.4. Typical procedure for RCM of α,ω-dienes

To a solution of **4a** (251 mg, 1.0 mmol) containing phenylacetylene (5.5 μl, 0.05 mmol) in CH_2Cl_2 (10 ml) was added **1a** (32 mg, 0.05 mmol). The reaction mixture was refluxed at 50°C for 24 h. The yield of products was calculated by NMR using nitromethane as an internal standard. RCM products **6a** [15], **6b** [16], **6c** [17], and **6d** [18] were known compounds.

3.5. Synthesis of alcohol chelate ruthenium complex $[Ru\{\eta^6\text{:}\eta^1\text{-}Ph(CH_2)_3OH\}(PCy_3)Cl]BF_4$ (**1a**)

This was prepared similarly to the literature method [1b]. ^1H-NMR ($CDCl_3$): δ 1.18–2.21 (m, 35H), 2.82 (brs, 2H), 3.80 (brs, 2H), 4.69 (brs, 1H), 5.38 (brt, 1H), 5.98 (brs, 3H). ^{31}P-NMR ($CDCl_3$): δ 36.95 (s). Anal. Calc. for $C_{27}H_4BClF_4OPRu$: C, 50.68; H, 7.09. Found: C, 50.31; H, 6.99%.

3.6. Synthesis of ruthenium hydride complex $[Ru(\eta^6\text{-}C_6H_6)(PCy_3)HCl]$ (**8**)

The treatment of $[Ru(\eta^6\text{-}C_6H_6)(PCy_3)Cl_2]$ (93 mg, 0.175 mmol) with one equivalent of sodium formate in MeOH (10 ml) for 1 h gave a black–yellow suspension. This was filtered off with celite and the filtrate was evaporated under N_2. Recrystallization from benzene–hexane gave fine yellow powders (58%). ^1H-NMR (C_6D_6): δ −7.04 (d, $^2J_{PH} = 51.0$ Hz, 1H), 1.11–2.12 (m, 33H), 4.99 (s, 6H). ^{31}P-NMR (C_6D_6): δ 62.94 (s). Anal. Calc. for $C_{28}H_{48}ClPRu$: C, 58.11; H, 8.13. Found: C, 57.88; H, 8.17%.

3.7. Synthesis of cationic ruthenium hydride complex $[Ru\{\eta^6\text{:}\eta^1\text{-}Ph(CH_2)_3OH\}(PCy_3)H]BF_4$ (**9**)

The treatment of **1a** (337 mg, 0.527 mmol) with one equivalent of $AgBF_4$ and sodium formate in MeOH (10 ml) for 1 h gave a yellow suspension. This was filtered

off and the filtrate was evaporated under N_2. Recrystallization from THF–hexane gave fine yellow powders (35%). ^{1}H-NMR (CD_2Cl_2): δ −6.22 (d, $^2J_{PH}$ = 47.0 Hz, 1H), 1.17–1.96 (m, 35H), 2.38–2.48 (m, 1H), 2.68–2.78 (m, 1H), 3.03–3.07 (m, 1H), 3.52 (m, 2H), 3.99 (dd, $^3J_{HH}$ = 7.02, 4.59, 1H), 5.58–5.63 (m, 1H), 5.86 (d, $^3J_{HH}$ = 5.40, 1H), 5.95 (t, $^3J_{HH}$ = 5.40, 1H), 6.16 (d, $^3J_{HH}$ = 5.40, 1H). ^{31}P-NMR (CD_2Cl_2) δ 61.74 (s). Anal. Calc. for $C_{27}H_{46}BF_4OPRu$: C, 53.56; H, 7.66. Found: C, 53.42; H, 7.55%.

Acknowledgements

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