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Ruthenium-Catalyzed Allenyl Carbamate Formation from Propargyl Alcohols and Isocyanates

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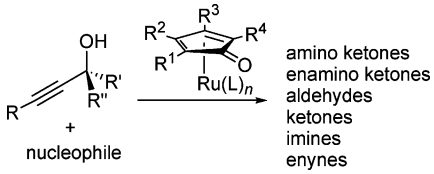
Ruthenium complexes of redox-coupled cyclopentadienone ligands catalyze the formation of allenyl carbamates from propargyl alcohols and isocyanates. This efficient and atom-economical process represents the first catalytic access to allenyl carbamates, compounds of high synthetic potential. The reaction needs an acidic co-catalyst and can be performed at room temperature. In addition, new (cyclopentadienone)iron and -ruthenium complexes were synthesized, and mechanistic aspects regarding catalytic transformations of propargyl systems with ruthenium catalysts are obtained.

Introduction

The development of new flexible reactions to obtain useful products with added value from simple and cheap materials is of high interest. The homogeneous transition metal catalysis delivers various processes and a broad range of new mechanisms to this field.[1] Our aim is the development of transition metal catalyzed processes using complexes of redox-coupled ligands, mainly (cyclopentadienone)ruthenium derivatives, to obtain relevant, especially nitrogen-containing, compounds. This type of catalyst, which is already known from hydrogen transfer reactions,[2] provides unique features towards catalytic transformations of bifunctional substrates, like propargyl alcohols, due to the electronic coupling of the dienone ligand and its basic coordination site. According to this concept, the range of selective catalytic transformations of propargyl alcohols with ruthenium catalysts[3] could recently be extended. With (cyclopentadienone)ruthenium catalysts α- or β-amino ketones, enamino ketones, aldehydes, ketones, imines, enynes or alkenes are accessible from propargyl alcohols (Scheme 1).[4]



Scheme 1. Catalytic transformations of propargyl alcohols.

Results and Discussion

In extension of previous work,[4b] several donor- and acceptor-substituted carbonyl(cyclopentadienone)ruthenium and -iron complexes were synthesized, and their catalytic activities towards propargyl alcohols – focused on amination reactions – were investigated. Four major groups of catalysts differing in the ligand's substitution pattern were investigated. Series **1** is acceptor-substituted, while the complexes of series **2**–**4** carry nitrogen donors in the 3- and 4-position. The complexes of series **3** and **4** contain additional acceptors, whereas the compounds of series **4** are hydrogen-bonded (Figure 1, Table 1).

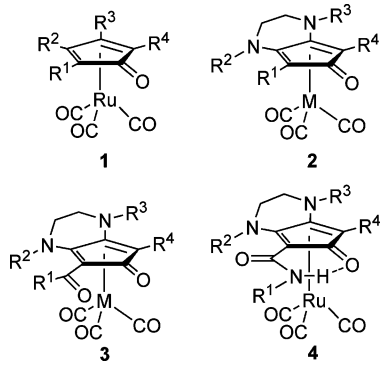


Figure 1. Substituted (cyclopentadienone)ruthenium and -iron complexes.

It had previously been shown that the substituents of the cyclopentadienone ligand determine the mode of activation of propargyl alcohols by the ruthenium complexes leading to different catalytic cycles. Acceptor-substituted catalysts of series **1** form alkenyl complexes **5** with terminal or internal secondary propargyl alcohols, while tertiary propargyl alcohols are not reactive. The diamino-substituted ana-

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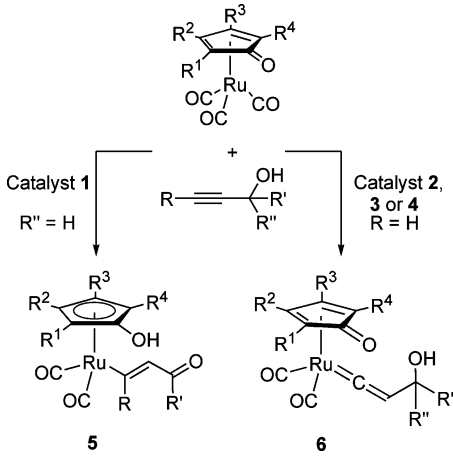
Table 1. Substitution pattern of catalysts **1**–**4**.

Catalyst	R^1	R^2	R^3	R^4
1a[4b]	Ph	Ph	Ph	Ph
1b[4b]	Me	Ph	Ph	Me
1c[4b]	CO_2Me	Ph	Ph	CO_2Me
2a[4b] (M = Ru)	Ph	Ph	Ph	Ph
2b[4b] (M = Ru)	Ph	Me	Me	Ph
2b-Fe (M = Fe)	Ph	Me	Me	Ph
2c[4b] (M = Ru)	H	Me	Me	Ph
2d (M = Ru)	H	Me	Me	Me
2e[4b] (M = Ru)	Ph	CH_2CH_2OH	CH_2CH_2OH	Ph
3a[4b] (M = Ru)	Ph	Me	Me	Ph
3b (M = Ru)	Ph	Me	Me	Me
3c (M = Ru)	Me	Me	Me	Me
3d (M = Ru)	Me	CH_2CH_2OAc	CH_2CH_2OAc	Me
3d-Fe (M = Fe)	Me	CH_2CH_2OAc	CH_2CH_2OAc	Me
3e[4b] (M = Ru)	Ph	CH_2CH_2OBz	CH_2CH_2OBz	Ph
3f[4b] (M = Ru)	OEt	Me	Me	H
3g[4b] (M = Ru)	OEt	Me	Me	CO_2Et
4a[4b]	Ph	Me	Me	Ph
4b[4b]	naphthyl	Me	Me	Ph
4c[4b]	cyclohexyl	Me	Me	Ph

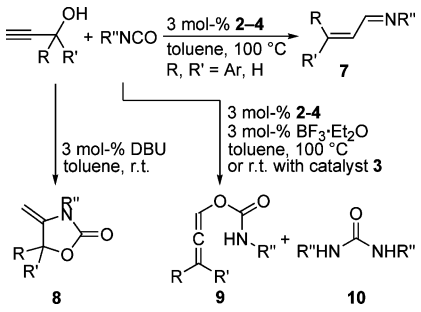
logues of series **2**–**4** seem to generate γ-hydroxyvinylidene species **6** from terminal propargyl alcohols, while internal propargyl alcohols are not reactive (Scheme 2).[4b] The corresponding iron complexes **2b-Fe** and **2d-Fe** are catalytically inactive under similar reaction conditions.



Scheme 2. Different modes of propargyl alcohol activation.

Due to these different intermediates several selective transformations of propargyl alcohols could be achieved.[4a,4b] As one example, complexes of series **2**–**4** catalyze the formation of α,β-unsaturated imines **7** from aryl-substituted propargyl alcohols and isocyanates under neutral conditions.[4b] Propargyl carbamates that derived from aryl-substituted propargyl alcohols and isocyanates behave similarly, while aliphatic propargyl carbamates are not transformed under neutral reaction conditions. Herein, new results obtained by further investigations of the latter reaction and leading to the first catalytic access to allenyl carbamates are reported. The synthetic potential of this class of compounds, including the only stoichiometric method to obtain allenyl carbamates previously published, has impressively been demonstrated by Hoppe et al.[5]

The fact that aliphatic propargyl carbamates are not transformed by catalysts **2**–**4** under neutral reaction conditions led us to investigate the effect of basic or acidic additives on the latter reaction. In the presence of a catalytic amount of an amine base like DBU or DABCO, the well-known 5-*exo*-dig cyclization of the initially formed propargyl carbamate leading to 5-methylene-1,3-oxazolidin-2-ones **8** was observed.[6] This cyclization does not need the metal catalyst and occurs in some cases already at room temperature. In the presence of acidic additives like $BF_3{\cdot}Et_2O$, $Sc(OTf)_3$, HBF_4 or NH_4PF_6 allenyl carbamates **9** are formed accompanied by symmetrical urea derivatives **10** as by-products. The formation of symmetrical ureas from carbon dioxide and amines in the presence of ruthenium complexes and terminal propargyl alcohols has already been described by Dixneuf et al.[3k] The best results regarding the formation of **9** were obtained with $BF_3{\cdot}Et_2O$ as additive, while the use of NH_4PF_6 leads to Rupe rearrangement[7] as an undesired side reaction (Scheme 3). Conversion of compound **8** in the presence of the ruthenium catalyst and a Lewis acid was not observed.



Scheme 3. Catalytic transformations of propargyl alcohols with isocyanates.

Catalysts of series **2** and **3** give the highest yields, while those of series **4** show lower activity. If the reaction is performed without a metal catalyst or with catalysts of series **1**, with the analogues iron complexes **2b-Fe** and **2d-Fe** or without a Lewis acid the corresponding propargyl carbamate **11** was quantitatively recovered (Table 2, Entries 1, 4, 5, 6, 9, 13, 21); the use of $Ru_3(CO)_{12}$ or $RuCl_2(PPh_3)_3$, however, leads to the corresponding urea derivatives in high yields (Table 2, Entries 2, 3).

Various propargyl alcohols and isocyanates are suitable substrates for this reaction but secondary propargyl alcohols react slowly (Table 3, Entries 1–13). Propargyl carbamates derived from aliphatic propargyl alcohols and isocyanates behave similarly, while aryl-substituted propargyl carbamates form symmetric urea derivatives in high yields. In case of labile substrates, the reaction can be performed at room temperature with complexes of series **3** due to the stronger coordination of the Lewis acid and better solubility of the resulting adduct (Table 3, Entries 14–17).

A plausible mechanism starts with the initial formation of a vinylidene species that is attacked in α-position. By

Table 2. Allenyl carbamate formation from 3-methyl-1-pentyn-3-ol and phenyl isocyanate with various catalysts.[a]

Entry	Catalyst	Additive	Yield[b] **9e** [%]	Yield[b] **10** [%]	Recovered[b] **11** [%]
1	–	$BF_3{\cdot}Et_2O$	–	–	99
2	$RuCl_2(PPh_3)_3$	$BF_3{\cdot}Et_2O$	–	55	40
3	$Ru_3(CO)_{12}$	$BF_3{\cdot}Et_2O$	–	91	–
4	**1a**	$BF_3{\cdot}Et_2O$	–	–	90
5	**1b**	$BF_3{\cdot}Et_2O$	–	–	92
6	**1c**	$BF_3{\cdot}Et_2O$	–	–	91
7	**2a**	$BF_3{\cdot}Et_2O$	57	15	10
8	**2b**	$BF_3{\cdot}Et_2O$	65	16	5
9	**2b**	–	–	–	98
10	**2b**	$Sc(OTf)_3$	31	10	45
11	**2b**	HBF_4	55	19	9
12	**2b**	NH_4PF_6	39	9	18
13	**2b-Fe**	$BF_3{\cdot}Et_2O$	–	–	97
14	**2c**	$BF_3{\cdot}Et_2O$	59	16	6
15	**2d**	$BF_3{\cdot}Et_2O$	57	14	8
16	**2e**	$BF_3{\cdot}Et_2O$	55	14	7
17	**3a**	$BF_3{\cdot}Et_2O$	52	12	12
18	**3b**	$BF_3{\cdot}Et_2O$	58	15	7
19	**3c**	$BF_3{\cdot}Et_2O$	58	17	7
20	**3d**	$BF_3{\cdot}Et_2O$	60	17	5
21	**3d-Fe**	$BF_3{\cdot}Et_2O$	–	–	98
22	**4a**	$BF_3{\cdot}Et_2O$	29	12	44

[a] Reaction conditions: 0.5 mL of toluene, 3 mol-% of catalyst, 3 mol-% of additive, 1 mmol of 3-methyl-1-pentyn-3-ol, 1 mmol of phenyl isocyanate, 100 °C, 3 h. [b] Isolated yield (based on isocyanate).

Table 3. Allenyl carbamate formation from various propargyl alcohols and isocyanates.

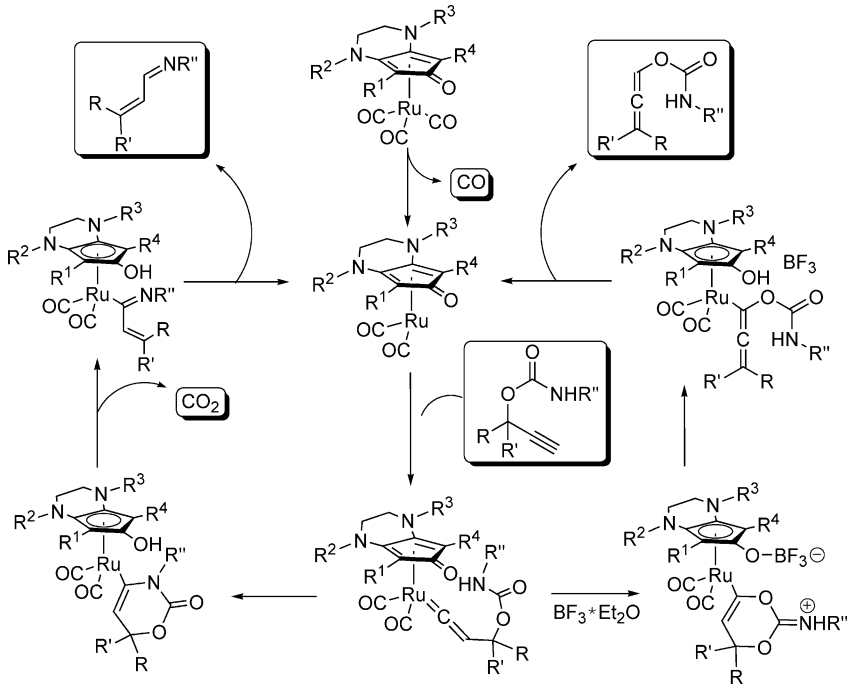
Entry	R	R′	R′′	Cat.	Yield[d] **9** [%]	Yield[d] **10** [%]	Recovered[d] **11** [%]
1[a]	Me	Me	Ph	**2b**	50 (**9a**)	20	8
2[a]	Me	Me	Bn	**2b**	43 (**9b**)	17	14
3[a]	Me	Me	Cy	**2b**	45 (**9c**)	18	12
4[a]	Me	Me	allyl	**2b**	43 (**9d**)	18	15
5[a]	Me	Et	Ph	**2b**	65 (**9e**)	16	5
6[a]	Me	Et	Bn	**2b**	74 (**9f**)	15	2
7[a]	Me	Et	Cy	**2b**	48 (**9g**)	13	21
8[a]	Me	Et	allyl	**2b**	69 (**9h**)	19	2
9[a]	C_5H_{10}		Ph	**2b**	62 (**9i**)	12	7
10[a]	C_5H_{10}		Bn	**2b**	68 (**9j**)	13	8
11[a]	C_5H_{10}		Cy	**2b**	59 (**9k**)	12	14
12[a]	C_5H_{10}		allyl	**2b**	71 (**9l**)	18	2
13[b]	H	Me	Ph	**2c**	50 (**9m**)	26	18
14[c]	Me	Et	Ph	**2b**	15 (**9e**)	10	69
15[c]	Me	Et	Ph	**3b**	49 (**9e**)	11	28
16[c]	Me	Et	Ph	**3c**	45 (**9e**)	10	31
17[c]	H	Me	Ph	**3b**	24 (**9m**)	14	55

[a] Reaction conditions: 0.5 mL of toluene, 3 mol-% of catalyst, 3 mol-% of $BF_3{\cdot}Et_2O$, 1 mmol of ropargyl alcohol, 1 mmol of isocyanate, 100 °C, 3 h. [b] Reaction conditions: 0.5 mL of toluene, 3 mol-% of catalyst, 3 mol-% of $BF_3{\cdot}Et_2O$, 1 mmol of propargyl alcohol, 1 mmol of isocyanate, 100 °C, 8 h. [c] Reaction conditions: 0.5 mL of toluene, 3 mol-% of catalyst, 3 mol-% of $BF_3{\cdot}Et_2O$, 1 mmol of propargyl alcohol, 1 mmol of isocyanate, r. t., 3 d. [d] Isolated yield (based on isocyanate).

using an isocyanate that forms a propargyl carbamate with the propargyl alcohol this nucleophilic attack occurs intramolecularly. Under neutral conditions the nitrogen atom acts as nucleophile, while under acidic conditions the carbonyl oxygen atom attacks. The unsaturated system is reductively eliminated after elimination of the leaving group in β-position (Scheme 4).

Conclusions

The first catalytic access to allenyl carbamates has been reported. The new procedure using redox-coupled (cyclopentadienone)ruthenium complexes as catalysts represents a simple selective, efficient and atom-economical method starting from readily available propargyl alcohols and isocy-



Scheme 4. Postulated catalytic cycle.

anates and delivers new mechanistical aspects regarding catalytic transformations of propargyl systems with ruthenium catalysts. An asymmetric variant of the new catalytic process using enantiomerically enriched samples of the axial-chiral complexes **2c**–**d**, **3a**–**g**, **4a**–**c** as catalysts is currently under investigation.

Experimental Section

General Procedure: 3 mol-% of catalyst **2**–**4** was dissolved in 0.5 mL of toluene; 3 mol-% of BF_3·Et_2O diluted in toluene, 1 mmol of the propargyl alcohol and 1 mmol of the isocyanate were subsequently added. The mixture was stirred under argon at 100 °C for 3 h (for **9m**: 8 h) or at room temperature for 3 d. Evaporation of the solvent and chromatography of the residue on silica furnished the allenyl carbamates **9**.

Supporting Information (see footnote on the first page of this article): Experimental procedures and full characterizations.

Acknowledgments

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