

Letter

Ruthenium–carbene catalysts for the synthesis of 2,3-dimethylfuran

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Abstract

A variety of neutral arene–ruthenium–carbenes of type (arene)RuCl₂(=C(NR)CH₂CH₂NR) have been used for the catalytic transformation of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran. The catalytic reaction takes place at 80°C with mononuclear complexes **III–V** to afford the furan in ~90% yield. The binuclear catalysts **VIa** and **VIIa** having a linked bis-carbene bridge operate at room temperature to initiate an exothermic reaction offering 90–97% of furan.

Keywords: Ruthenium–carbene catalysts; Activation of *Z*-enynols; Catalytic synthesis of 2,3-dimethylfuran

1. Introduction

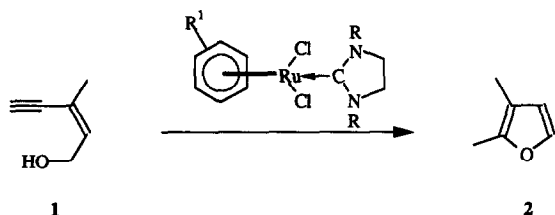
Catalytic transformations of alkynes have a potential for developing new methodologies in organic synthesis [1], via formal selective addition to the C≡C bond to directly afford unsaturated functional molecules with atom economy [2]. In the recent years several ruthenium complexes were revealed as efficient catalysts to create new carbon–carbon bonds with alkynes as in their dimerization into *Z*-enynes [3] and butatriene [4] or their coupling with alkenes leading to dienes [5,6] and butenolides, [7] or with allylic alcohols to generate, according to the nature of the catalyst, either α,β -un-

saturated ketones [8] or γ,δ -unsaturated aldehydes, acetals [9] and ketones [10]. Ruthenium(II) complexes have also been found to promote selective carbon–heteroatom bond formation reactions in the catalytic synthesis of vinyl carbamates [11], enol esters [12a,12b], functional dienes [13] and β -keto esters [14].

Recently, we have found that RuCl₂(PPh₃)-(arene) and [Ru(μ -O₂CH)(CO)₂(PPh₃)₂] complexes could act as catalysts for the activation of (*Z*)-2-en-4-yn-1-ols toward their intramolecular cyclization into furans [15]. The interest of furans in organic synthesis [16] motivated the search for new catalysts favoring this reaction. We now report on the study of a variety of ruthenium–carbene derivatives of type (arene)Cl₂Ru=C(NR)CH₂CH₂NR as catalysts for the transformation of (*Z*)-3-methylpent-2-en-4-yn-

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1-ol **1** into 2,3-dimethylfuran **2** (Eq. (1)) and we show that binuclear biscarbene complexes are so efficient that the catalytic reaction is initiated at room temperature without solvent and is exothermic.

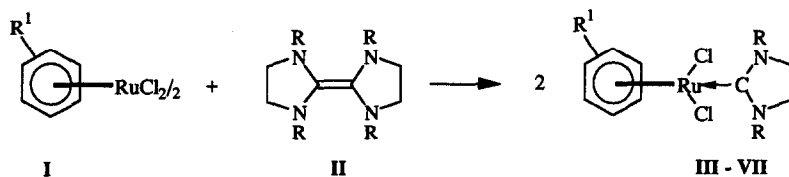


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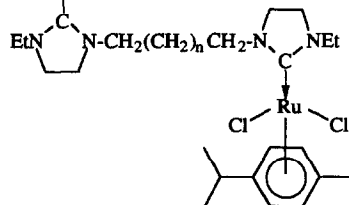
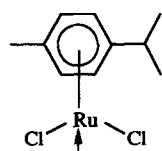
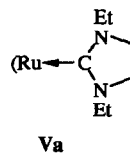
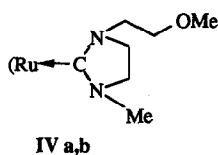
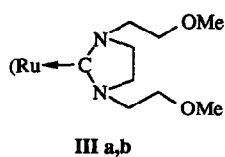
2. Results and discussion

A variety of ruthenium–carbene derivatives **III–VII** have been prepared from [(arene)RuCl₂]₂ dimers **I** (arene = *p*-cymene (**a**), hexamethylbenzene (**b**)), by analogy to the cleavage of the chlorobridges by phosphines [17], by reaction of the enetetramines **II**, that are electron-rich olefins [18]. The reaction was shown to generate the cleavage of the C=C bond [19] and the formation of the neutral ruthenium–carbenes **III–VII** [20] of which the carbene ligand is expected to be a strong σ -donor group [21] (Scheme 1).

(*Z*)-3-methylpent-2-en-4-yn-1-ol **1** (10 mmol) was added in a Schlenk tube to 0.1 mmol of



arene: *p*-Me-C₆H₄-^{*i*}Pr (**a**)
C₆Me₆ (**b**)



Scheme 1.

Table 1
Catalytic synthesis of 2,3-dimethylfuran

Entry	Catalyst	T (°C)	Time (h)	Yield (%) ^{a,b}
1	IIIa	60	1.5	44
2	IIIa	60	2.5	60
3	IIIa	60	16.5	87 (78) ^b
4	IIIb	60	1	60
5	IIIb	60	6.5	83 (75) ^b
6	IIIa	80	1	79
7	IIIa	80	2.25	87
8	IIIa	80	3.7	90 (82) ^b
9	IIIb	80	1	67
10	IIIb	80	3.4	88
11	IIIb	80	3.75	89 (83) ^b
12	IVa	80	1	87
13	IVa	80	2	92 (85) ^b
14	IVb	80	1	80
15	IVb	80	2.25	90 (85) ^b
16	Va	80	1	74
17	Va	80	2	92 (82) ^b
18 ^d	VIa	r.t. ^c	1	49
19 ^d	VIa	r.t. ^c	2	50
20 ^d	VIa	r.t. ^c	6	84
21 ^d	VIa	r.t. ^c	21	95 (83) ^b
22 ^d	VIIa	r.t. ^c	0.2	87
23 ^d	VIIa	r.t. ^c	1	97

Reaction conditions: To 0.1 mmol of ruthenium catalyst **III–V** were added 10 mmol of (*Z*)-3-methylpent-2-en-4-yn-1-ol without additional solvent. The mixture was stirred in an oil bath at 60°C – 80°C for 1–20 h. The reaction with 0.05 mmol of catalysts **VIa** and **VIIa** was performed starting at room temperature.

^a Yield measured using gas chromatography.

^b Isolated yield after distillation.

^c The stirring at 22°C led to an exothermic reaction.

^d 0.05 mmol of complex.

ruthenium complexes **III–V** without any additional solvent and the mixture was stirred at 60–80°C in an oil bath for 1–20 h. The conversion of **1** was monitored by gas chromatography and led to the formation of only one product, the colorless 2,3-dimethylfuran **2** (Eq. (1)) which was identified by spectroscopy [15]. (**2**: ¹H NMR (300 MHz, CDCl₃) δ (ppm): 1.94 and 2.19 (s, Me), 6.14 and 7.19 (d, CH=, ³J_{HH} = 1.8 Hz), IR (film) ν_(C=C) = 1605 cm⁻¹.)

The results are summarized in Table 1. They show that the ruthenium–carbene complexes **III–V** are good catalysts for the transformation of **1** into **2** above 60°C. The best yields were obtained at 80°C for 1–3 h (entries 6 and 9, 10 as compared to entries 1 and 4, respectively). It

is noteworthy that the catalysts **IIIb** and **IVb** containing the hexamethylbenzene ligands are more efficient at 60°C than **IIIa** and **IVa** containing the *p*-cymene group, as the conversion of **1** is faster (entries 4 and 5 as compared to entries 1 and 3). This difference in behavior is no longer worthy to note at 80°C. This is attributed to the easiness of displacement of the arene ligand which is observed by gas chromatography, and is supposed to be the key step generating the active ruthenium species from (arene)RuCl₂(PR₃) [12b].

The comparison of catalysts **III** and **IV** indicates that complexes **IV** containing only one coordinating 'arm' linked to the nitrogen atoms are more efficient (entries: 6, 12 and 9, 14). Complex **Va** bearing no coordinating arms attached to the carbene ligand appeared to be also an efficient catalyst, as 92% yield of **2** were formed (entry 17). Thus, the catalysts **III–V** in an average of 2–3 h at 80°C could afford 90% of furan **2** which was isolated in 80–85% yields after distillation (entries: 8, 11, 13, 15, 17). The catalytic efficiency of complexes **III–V** is comparable to that of RuCl₂(PR₃)(arene) complexes [15] which can even operate at 60°C.

Attempts to carry out the same transformation **1** → **2** with the complexes **VIa** and **VIIa** having their carbene units linked by a N–CH₂CH₂–N (**VIa**) or N–CH₂CH₂CH₂–N bridge (**VIIa**) led to the observation that the reaction did not require any heating. Actually, starting from room temperature, the stirring of 0.05 mmol of the binuclear complex into 10 mmol of the enynol **1** led to an exothermic reaction. With complex **VIa** the stirring at 22°C for 21 h afforded 95% yield of **2** (83% isolated) (entry 21). Under similar conditions, the stirring of catalyst **VIIa** in enynol **1** led to an exothermic reaction bringing the reaction mixture to the boil. The reaction was almost completed after 10 min and a 97% yield of **2** was reached after 1 h (entries 22, 23).

The above reaction represents a new example of metal complexes of N-heterocyclic carbenes in catalysis. The first example has just been

described to promote the Heck reaction in the presence of imidazole derivative carbene–palladium catalysts [22]. No proof can be brought to explain the efficiency of catalysts **VIa** and **VIIa**, which are by far the best catalysts for the formation of furan **2** with respect to complexes **III–V** or $\text{RuCl}_2(\text{PR}_3)(\text{arene})$ [15]. However, the suggestion can be made that their *p*-cymene ligand can be lost, as observed by gas chromatography, much more easily than from the mononuclear complexes, thus generating an active coordinatively unsaturated ruthenium species able to activate the triple bond of the enynol.

Acknowledgements

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