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Preliminary communication

Synthesis of methacrylate monomers from alkynes and arenealkenylruthenium(II) catalyst ☆

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Abstract

The alkenyl derivatives [$(C_6Me_6)(PMe_3)ClRu$-C(OMe)=CHR] **IIIa** (R = Me) and **IIIb** (R = Ph) have been prepared by deprotonation of the corresponding carbene complexes [$(C_6Me_6)(PMe_3)ClRu$=C(OMe)CH_2R][PF_6-] **II** with Me_3COK. Complexes **III** can be used as efficient catalysts for the addition of functional carboxylic acids to terminal alkynes to give dioxolanone **4**, from R(-)mandelic acid, or methacrylates of the type CH_2=C(Me)CO–OY: Y = C(=CH_2)^{n}Bu, **6**, $CH_2CH_2C≡CH$, **8**, or C(=CH_2)$CH_2CH_2CH_2CH_2$C(=CH_2)OCOC(Me)=CH_2, **10**.

Keywords: Arene complexes; Alkenyl complexes; Ruthenium; Methacrylate monomers; Synthesis

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1. Introduction

Enol esters derivatives of unsaturated acids are useful reagents, for the mild acylation of fragile substrates because they avoid the release of strong acids from acyl halides or the activation of classical esters by strong bases [1,2], and are of interest as polymer precursors. One of the best ways to prepare enol esters is the simple catalyzed addition of carboxylic acids to terminal alkynes such as hex-1-yne **1** in the presence of an areneruthenium(II) catalyst [$RuCl_2(PR_3)$(arene)], **I**, that allows the regioselective addition of the carboxylate on carbon C(2) [3], as shown in Eq. 1. However, catalysts of type **I** failed to promote the addition of hydroxy or unsaturated carboxylic acids, especially acrylic derivatives, to alkynes.

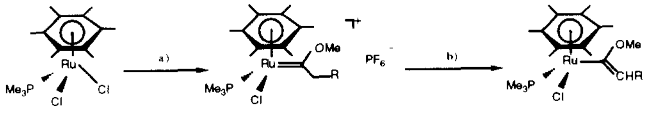
(1)

We now report that easily available alkenylruthenium(II) complexes are efficient catalyst precursors for the regioselective addition of functional carboxylic acids to terminal alkyne carbon C(2) and that this reaction can be directed to the large-scale synthesis of methacrylate monomers.

2. Discussion

The yellow alkenylruthenium catalysts **III** have been prepared by simple deprotonation of the corresponding carbene complexes [Ru=C(OMe)CH_2R(Cl)(PMe_3)(η^6-C_6Me_6)][PF_6] **II** [4] resulting from the one-step reaction of **I** with terminal alkynes and MeOH [5]. Thus, the treatment of **IIa** and **IIb** with one equivalent of Me_3COK at 0°C in THF leads to **IIIa** and the stable **IIIb**, in 32% and 70% yields, respectively (Scheme 1).

Evidence for the high catalytic activity of complexes **IIIa** and **IIIb** for the activation of terminal alkynes was revealed by a comparative study of complexes **I** and **III** as catalysts for the enol benzoate synthesis [6,7] (Eq. 1). Monitoring the reaction using gas chromatography shows that the reaction is much faster with complexes **III**. When 4×10^{-5} mole of ruthenium complex was used with 10 mmol of benzoic acid and a slight excess of hex-1-yne **1** at 80°C in toluene, the transformation was complete in less than 2 h with either of the equally



I **IIa** (R = Me), **IIb** (R = Ph) **IIIa** (R = Me) **IIIb** (R = Ph)

Scheme 1. (a) RC≡CH, MeOH, Na[PF_6], rt; (b) tBuOK, THF, 0°C.

☆ Dedicated to Professor Fausto Calderazzo on the occasion of his 65th birthday.

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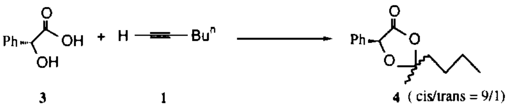
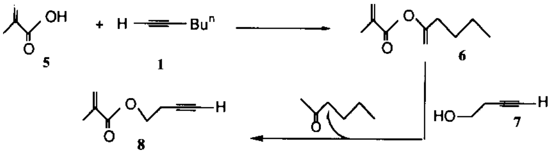
active **IIIa** or **IIIb** catalysts, but required 15 h with precursor **I**. Derivative **2** was isolated in 95% yield. The related carbene complex **IIb** showed a very weak activity for this reaction. This proves that the catalytically active species does not correspond to the product of the reversible protonation by the carboxylic acid of **IIIb** to give **IIb**. It suggests that a coordinatively unsaturated ruthenium species is produced by reductive elimination of the alkenyl from the protonated ruthenium species, although the resulting alkene could not be identified.

This higher catalytic efficiency prompted us to attempt the activation of hex-1-yne in the presence of **III** towards functional substrates for which complexes **I** appeared inefficient [1]. Thus, the addition of R(-)-mandelic acid **3** (10 mmol) to hex-1-yne in the presence of 6×10^{-5} mol of catalyst **IIIb** (15 h at 100°C) gave 84% of dioxolanones **4** [8] with good diastereoselectivity (*cis* : *trans* = 9 : 1) (Eq. 2).



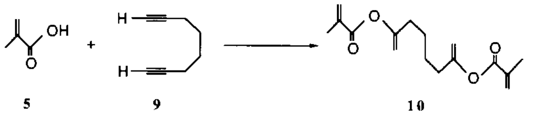
(2)

As functional methacrylate derivatives are of importance for new co-polymers, the reaction of methacrylic acid **5** (71 mmol) with hex-1-yne was carried out in the presence of 0.1 mol% of **IIIb**, *without solvent*, at 80°C for 16 h, and the enol methacrylate **6** was obtained in a 10 g scale in 98% yield (Eq. 3). The methacrylate **6** was used as an acylating reagent of homopropargylic alcohol **7** to produce, the methacrylate **8** (68% yield) containing a terminal alkyne group (Eq. 3) after 18 h at room temperature and subsequent distillation. Derivative **8** is a key monomer for co-polymers with methyl methacrylate [9].



(3)

Bifunctional molecules containing polymerizable ends can be used as building blocks for cross-linked polymers and we have considered the possibility of producing a bifunctional enol methacrylate. Oct-1,7-diyne **9** reacts with two equivalents of **5** (17 mmol) and catalyst **IIIb** (0.04 mmol) at 80°C for 15 h, affording, via two regioselective O–C(2) bond formation reactions, only derivative **10**, which was purified by vacuum transfer and isolated in 86% yield (Eq. 4).



(4)

Compounds **6**, **8** and **10** are key derivatives for the formation of oligomers [10] by reaction with diamines.

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