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ONE-STEP SYNTHESIS OF VINYL CARBAMATES CATALYZED BY MONONUCLEAR RUTHENIUM COMPLEXES VIA ADDITION OF CARBON DIOXIDE AND AMINE TO TERMINAL ALKYNES

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Summary. Terminal alkynes with secondary amines (dimethylamine, diethylamine, piperidine, morpholine) and CO_2 in the presence of mononuclear ruthenium catalysts, afford the vinyl carbamates $R^1CH{=}CH{-}O{-}CONR_2$. The reaction studies suggest, as the active catalytic species, a ruthenium-vinylidene intermediate.

Vinyl carbamates have been shown to be useful intermediates for the access to agricultural and pharmaceutical chemicals or to transparent polymers[1]. However, the formation of these enol carbamates, which results from halogenoalkyl carbamates[2] or vinyl chloroformates[3], is not straitghforward and always involves a multi-step synthesis starting from phosgene. We have shown recently that $Ru_3(CO)_{12}$ could catalyze the formation of vinyl carbamates[4] from alkyne and diethylamine in moderate yields. We now wish to report that mononuclear ruthenium complexes appear to be better catalysts for the activation of terminal alkynes toward ammonium carbamates, arising directly from CO_2 and a variety of secondary amines, to afford vinyl carbamates in one step. The related studies strongly suggest the involvement of a ruthenium-vinylidene intermediate as the active catalytic species ; and although the (η^2-alkyne)-metal $\longrightarrow$ (η^1-alkylidene)-metal rearrangement is now well established[5,6], evidence of the latter intermediate in the catalytic addition of CO_2, or of a CO_2-adduct has, never been reported before.

Scheme I

$$\text{R-C}{\equiv}\text{CH} + CO_2 + \text{HNR}'_2 \xrightarrow{(Ru)} \text{R-CH=CH-O-C(=O)-NR}'_2 + \text{R-CH=CH-C}{\equiv}\text{C-R}$$

1: R=Ph | **3**: R=Ph
2: R=nBu | **5-9** | **4**: R=nBu

(R; $-NR'_2$) : **5** (nBu; $-NEt_2$); **6** (Ph; $-NEt_2$); **7** (Ph; $-NMe_2$); **8** (Ph; -N ); **9** (Ph; -N  O

Table 1 - Synthesis of vinyl carbamates from phenylacetylene[a]

Amine	T°C	% Yields [b]
Et_2NH	100	**6** : 53 (Z) , 10 (E) ; **3** : 9
Me_2NH	140	**7** : 16 (Z) , 4 (E) ; **3** : traces
	100	**8** : 15 (Z) , ; **3** : 22
	100	**9** : 16 (Z) , ; **3** : traces

a) general conditions : 10 mmol of alkyne, 20 mmol of amine, 0.2 mmol of $RuCl_3.xH_2O$ in 10 mL of THF, initial Pressure of CO_2 : 50 bar ; 20 hours ; b) yields (%) are based on the starting alkyne.

Phenylacetylene **1**, 2 equivalents of diethylamine and 0.02 equivalent of $RuCl_3.3H_2O$ in THF were placed in an autoclave under 50 bar of carbon dioxide and heated at 100°C for 20 hours. The Z and E vinyl carbamate isomers **6** were obtained in an overall yield of 63% with a small amount (9%) of the E isomer of **3**, a dimer of **1** (Scheme 1, Table I). Under similar conditions, hex-1-yne **2** led to 10% yield of both Z and E isomers of **5** with 7% of both isomers of **4**. Phenylacetylene **1** with secondary amines such as dimethylamine, piperidine and morpholine led respectively to the formation of the vinyl carbamates **7**, **8**, and **9** (Table I). The Z isomer of the vinyl carbamates is always the major product and is accompanied by the E isomer of **3**. The conversion of the alkyne is high (70-90 %) but besides the vinyl carbamates and dimers **3** or **4** the red polyphenylacetylene is always formed.

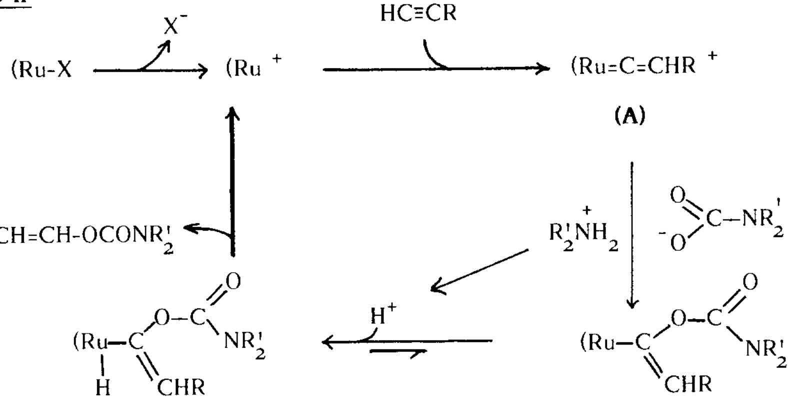
The formation of vinyl carbamates is also catalyzed by a variety of mononuclear ruthenium(II) precursors $RuCl_2(CH_3CN)$(p-cymene), $[RuCl(CH_3CN)_2(\text{p-cymene})]^+ BF_4^-$, $RuCl_2$-(PMe_3)(p-cymene), $RuCl_2(py)_2$(norbonadiene) and $RuCl_2(PMe_3)(C_6Me_6)$ catalyze the transformation of **1** into **6** in 26, 41, 58, 64 and 67 % yield respectively in acetonitrile at 125°C. Under similar conditions $Ru_3(CO)_{12}$ catalyzed the transformation of **2** into **6** in 10-17 % yields[4].

The catalytic reaction can be performed in a variety of solvents such as diethylether, THF or acetonitrile, but not in halogenated solvents. For any set of conditions, two equivalents of amine per alkyne are required in order to get the better yields in vinyl carbamates. This is consistent with the in situ formation of ammonium carbamate, according to equation(1), which is expected to add to an active form of the alkyne.

$$2R_2NH + CO_2 \rightleftharpoons R_2NCO_2^-, H_2\overset{+}{N}R_2 \quad (1)$$

The formation of vinyl carbamates does not occur with disubstituted acetylenes such as diphenylacetylene, even under drastic conditions, but only with terminal alkynes. This observation, the regioselective addition of the carbamate to the terminal alkyne carbon and the facile formation of ruthenium-vinylidene complexes from halogeno-ruthenium(II) derivatives[6], suggest that the addition of carbamate to the alkyne may proceed via a ruthenium-vinylidene intermediate according to Scheme II rather than via a bimetallic intermediate with insertion of the C=C bond, into the

Scheme II



(Ru-O(carbamate) bond, as for the addition of carboxylic acids to alkynes in the presence of $Ru_3(CO)_{12}$ [7]. Several observations support the ruthenium-vinylidene catalytic species of type **(A)** (Scheme II). The addition of a small amount (0.2 mmol) of NEt_3 decreases the yield significantly and it is known that intermediate of type **(A)** are easily deprotonated by NEt_3[6]. The formation of vinyl carbamates is always accompanied by polymerization of the alkyne 1 or 2, and tungsten-vinylidene intermediates have just been reported to be efficient catalysts for polymerization of terminal alkynes[8]. Thus polymerization and addition of carbamate appear to be competitive reactions from intermediate **(A)**. Finally, if ruthenium-vinylidene species could not be characterized under the reaction conditions (autoclave) or isolated from the studied ruthenium(II) precursors, one of these has been trapped with methanol: the reaction of $C_6Me_6(Me_3P)RuCl_2$ with 1 in the presence of $NaPF_6$ in methanol affords the carbene-ruthenium complex[9] $[(C_6Me_6)(Me_3P)ClRu{=}C(OMe)CH_2Ph]^+PF_6^-$, the addition product of methanol to a vinylidene-metal intermediate, such as intermediate **(A)**.

This synthesis of vinyl carbamates corresponds to the formal addition of carbamic acid to terminal alkynes and illustrates a novel use of CO_2 as a reagent instead of a multi-step reaction involving phosgene[2,3]. Our present results, and the evidence of tungsten-vinylidene species in the polymerization of alkynes[8], suggest that metal-vinylidene should be considered as possible catalytic species for reactions involving terminal alkynes.

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