

Activation of alkynes with ruthenium complexes

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Abstract - Mononuclear ruthenium complexes, especially $\text{RuCl}_2(\text{PR}_3)(\text{arene})$ complexes, activate terminal alkynes in catalytic regioselective syntheses of vinylcarbamates from monosubstituted alkynes or acetylene with carbon dioxide and secondary amines, enol esters via addition of carboxylic acids and N-protected aminoacids to alkynes, and O- β -oxopropyl carbamates and esters directly from propargyl alcohols. The stoichiometric interaction of $\text{RuCl}_2(\text{PR}_3)(\eta^6\text{-C}_6\text{Me}_6)$ with terminal alkynes in alcohol and in the presence of NaPF_6 provides a general route to arene-ruthenium-carbene complexes via reactive ruthenium-vinylidene intermediates. Propargyl alcohol derivatives allow the access to vinyl arene-ruthenium-vinylcarbene complexes via ruthenium-allenylidene species.

INTRODUCTION

Acetylenic derivatives are potentially useful starting chemicals for the access to vinyl derivatives which are able to display specific properties. The direct addition to alkynes usually requires the activation of the carbon-carbon triple bond. Selected transition metal complexes can make this activation not only possible but also catalytic. Examples of transformations of alkynes catalysed by transition metal complexes are now classical. More than 60 years after the discovery nickel tetracarbonyl by L. Mond et al. (ref. 1) this simple complex was found by W. Reppe (ref. 2) to be an excellent catalyst precursor for the alcoxycarbonylation of alkynes and the formation of acrylic acids or esters. The key-step of this reaction is the insertion of the carbon-carbon triple bond of the alkyne into the Ni-H bond resulting from the protonation of nickel(0) species. More recently, new methods for the synthesis of furanones have been found by carbonylation of alkynes (ref. 3). The reaction is performed under water gas shift conditions, catalysed by rhodium carbonyl clusters (ref. 4) and involves the insertion of the alkyne into an alcoxycarbonyl carbon-rhodium bond.

An important contribution to the synthesis of vinyl derivatives has appeared to be the cross-coupling reaction (ref. 5). The coupling of unsaturated halides with main group organometallic compounds is catalysed mainly by nickel(0) or palladium(0) complexes and leads to the regio- and stereoselective formation of carbon-carbon bonds. The determining step concerns the oxidative addition of the unsaturated hydrocarbon halide to the low-valent metal center. This reaction has been used extensively for the synthesis of functional olefins. However, this type of cross-coupling reaction is not efficient for the formation of heteroatom-carbon bond in the synthesis of olefins. We have considered the possibility to produce functional olefinic compounds with vinylcarbon-heteroatom bond simply by adding nucleophiles to activated alkynes.

Acetic acid is known to add to acetylene itself to produce vinyl acetate. The industry process requires catalysis by Zn(II) salts between 170-250°C. It has been advantageously replaced by oxidative addition of acetic acid to ethylene catalysed by Pd(II) salts. These reactions are not extendable to higher carboxylic acids or aminoacids and their drastic conditions do not allow the use of fragile optically active carboxylic acids such as aminoacids.

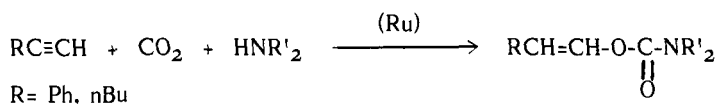
We have devoted ourselves to the search of catalytic conditions for the addition of carbamates and carboxylic acids to inexpensive alkynes. This programme led us to discover new catalytic syntheses of vinylcarbamates, enol esters and β -oxopropyl esters and carbamates. The study of the interaction between terminal alkynes and arene ruthenium(II) complexes - the best catalyst precursors - led us to discover new metal carbene complexes and new route to unsaturated metal carbene complexes. These two aspects of the **activation of alkynes** : the **catalytic syntheses** and the formation of **new metal carbene complexes** with ruthenium derivatives will be reported here.

I. CATALYTIC SYNTHESIS FROM ALKYNES

1. Syntheses of vinylcarbamates

Vinylcarbamates have been shown to be useful intermediates for the access to agricultural chemicals or to transparent polymers. Vinylcarbamates are usually made by multi-step syntheses involving phosgene at one step. We have considered the possibility to replace phosgene by carbon dioxide.

We have first found that $\text{Ru}_3(\text{CO})_{12}$ catalysed the addition of ammonium carbamates - the stabilized form of carbamic acids - to phenylacetylene and hexyne. The reaction is carried out in an autoclave under a 50 bar initial pressure of CO_2 , in the presence of 2 equivalents of diethylamine at 125-140°C (ref. 6).



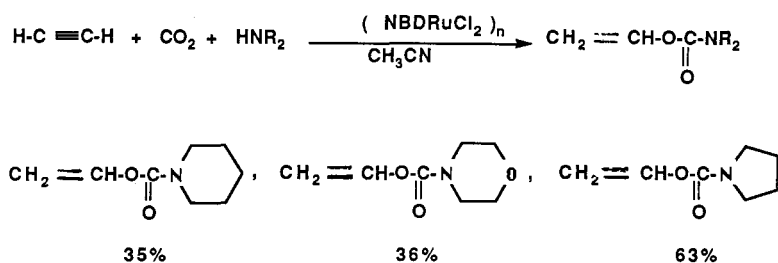
The reaction was markedly improved using mononuclear ruthenium catalysts such as $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, $(p\text{-cymene})\text{RuCl}_2$, $(p\text{-cymene})\text{RuCl}_2\text{PMe}_3$, $\text{C}_6\text{Me}_6\text{RuCl}_2(\text{PMe}_3)$ or $(\text{norbornadiene})\text{RuCl}_2(\text{py})_2$. In that case the reaction is **regiospecific**: the carbamate adds only to the terminal carbon of the alkyne. A stereoselectivity was observed, the Z isomer being always the major product. This reaction can not be performed with disubstituted alkynes. The observed by-product correspond to the dimerisation of the alkyne. The reaction was extendable to secondary amines such as morpholine, piperidine, pyrrolidine (ref. 7,8).

Simple vinylcarbamates are the most useful monomer precursors to transparent polymers. They can be prepared using the same reaction by addition of CO_2 and secondary amine to acetylene itself. The catalysts used are either $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (ref. 9,10) or $(\text{Ru}(\text{Norbornadiene})\text{Cl}_2)_n$ (ref. 11) (Scheme 1).

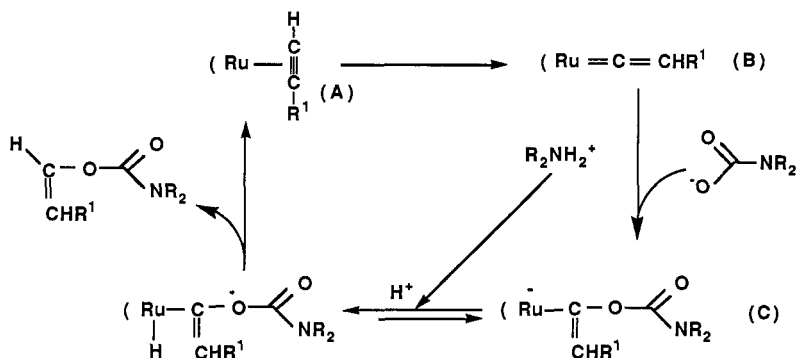
The formation of vinylcarbamates from CO_2 and amine is **specific** of terminal alkynes and **regiospecific**. These observations led us to postulate a mechanism with a ruthenium-vinylidene active species and a mechanism according to Scheme 2. It is well-established that η^2 -coordinated terminal alkyne-metal complex (A) readily rearranged into an η^1 -vinylidene-metal intermediate (B) and that the coordinated carbon of (B) is the electrophilic site (ref. 12). Therefore addition of the carbamate to the coordinated carbon of (B) should give the intermediate (C) and then on protonation at the metal center, followed by reductive elimination, the vinylcarbamate is expected to be formed.

This new catalytic synthesis of vinyl carbamates illustrates a novel use of CO_2 as a reagent instead of a multi-step reaction involving phosgene derivatives. It suggests that the metal-vinylidene can be considered as catalytic active species.

Scheme 1



Scheme 2

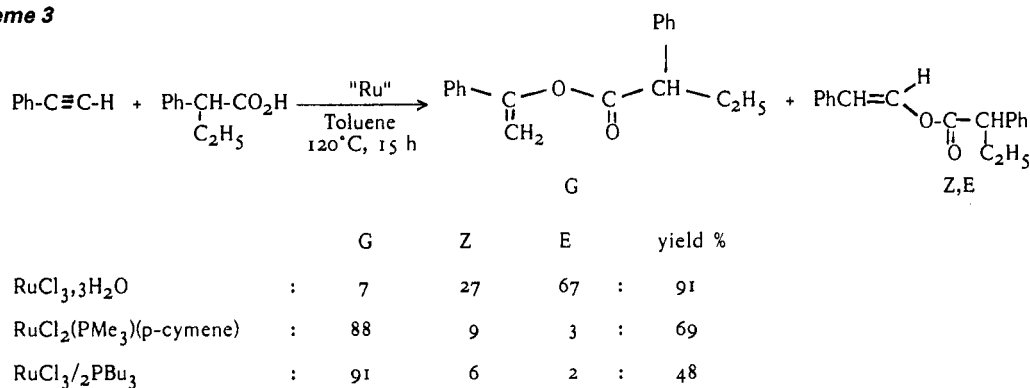


2. Syntheses of enol esters

Enol esters present an interest as polymer precursors or as mild acylating reagents. Acylations were used for the access to acylfluoride with release of acetone (ref. 13), acylarenes in the presence of Lewis acids, or β -diketones (ref. 14). They appear to be especially efficient reagents when the oxygen atom is bonded to the substituted vinylcarbon atom. Enol esters were usually prepared either by catalysed transesterification of vinylacetates (ref. 15) or by coupling of enolates with vinylmercury derivatives (ref. 16).

We have found that mononuclear ruthenium complexes could catalyse the addition of carboxylic acids to phenylacetylene in toluene at 100°C. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ does not lead to the regioselective addition to alkynes. When a basic phosphine was added, a regioselectivity was observed: the major formed isomer corresponded to the addition of the carboxylate to the substituted carbon of the alkyne. Of special interest was the $\text{RuCl}_2(\text{PMe}_3)(p\text{-cymene})$ catalyst precursor which led to high yield and stereoselectivity and allowed the temperature to be decreased to 80°C. It thus appears that the reaction conditions are much milder for the addition of carboxylic acids than for that of carbamates to alkyne (ref. 17) (Scheme 3).

Scheme 3

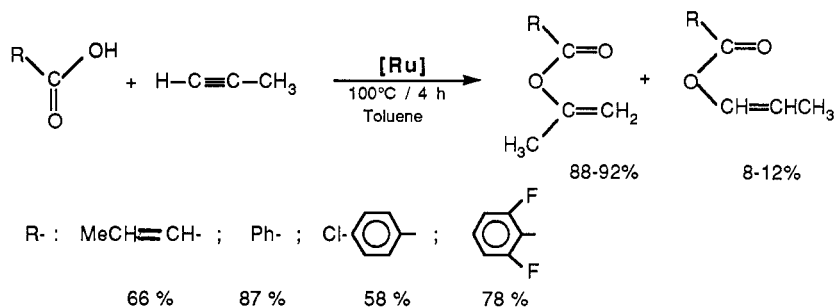


The addition of para-fluorobenzoic acid and pivalic acid to hexyne has been studied in the presence of $\text{RuCl}_2(\text{PPh}_3)(p\text{-cymene})$. High yields and regioselectivity were obtained. The reaction with para-fluorobenzoic acid was only slower than that with benzoic acid. The ester derivative of pivalic acid, difficult to make by classical methods due to the bulkiness of the t-butyl group, was obtained in good yield (78%) by addition of the acid to hexyne (ref. 18).

A variety of unsaturated carboxylic acids add to propyne using $\text{RuCl}_2(\text{PPh}_3)(p\text{-cymene})$ as catalyst precursor. The obtained corresponding esters are the most useful reagents, as on protonation they release acetone and allow mild acylations. Even the 2,6-difluorobenzoate derivative was obtained in 78% only after 4 h at 100°C (ref. 18) (Scheme 4).

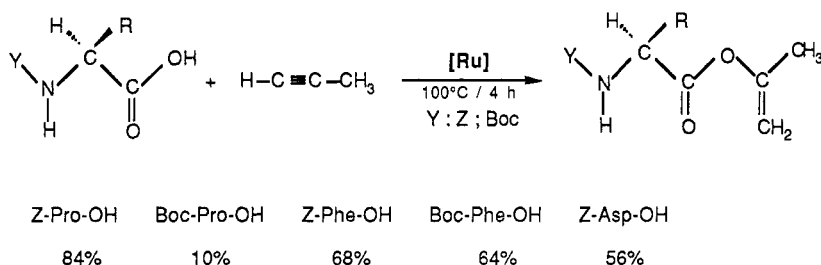
Aminoacids do not add to alkynes but N-protected aminoacids do. For instance, Z- and Boc-Proline add to acetylene itself to produce simple optically active vinyl esters of interest as new polymer precursors. With acetylene the best catalyst was found to be $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (ref. 18).

Scheme 4



A wide variety of optically active Z- and Boc-N-protected amino esters were obtained by addition of the corresponding N-protected amino acids to propyne in the presence of $\text{RuCl}_2(\text{PPh}_3)(p\text{-cymene})$. The advantage of this reaction is that only one isomer was observed, the isomer corresponding to the addition of the carboxylate to the substituted alkyne carbon. The low yield (10%) obtained with Boc-proline was raised to 68% simply by replacing the PPh_3 by PMe_3 ligand in the ruthenium complex and for a duration of 10 h instead of 4 h (ref. 19) (Scheme 5).

Scheme 5



The hydrolysis of the optically active ester obtained from Z-proline and propyne, led to a Z-proline sample which had the same optical rotation as the starting Z-proline ($[\alpha]_D = -53^\circ$). Thus, it can be assumed that both processes, addition to alkynes and hydrolysis of esters, take place without racemisation. Primary amines were easily acylated by enol-esters at room temperature to afford optically active amides.

Addition of carboxylic acids to alkyne has initially been reported by Shvo et al. using $\text{Ru}_3(\text{CO})_{12}$ as catalyst precursor (ref. 20). Recently, Y. Watanabe and T. Mitsudo have obtained significant results in addition of a variety of carboxylic acids to alkynes (ref. 21). They use $\text{Ru}(\eta^5\text{-C}_8\text{H}_{11})_2$ as catalyst with two equivalents of PBU_3 and need, for the addition of saturated acids, fumaric anhydride as co-catalyst. Their system presents the advantage with respect to the $\text{RuCl}_2(\text{PR}_3)(\text{arene})$ complexes of allowing the addition of carboxylic acids containing a hydroxy group. T.B. Marder et al. (ref. 22) have studied the rhodium(I) catalysed cyclisation of alkynoic acids into alkyldiene lactones. Their studies suggest that one initial intermediate might be a carboxylate, hydrido Rhodium(III) intermediate arising from O-H oxidative addition of the CO_2H group to the electron-rich rhodium(I) complex.

The study of the addition reaction of carboxylic acids to alkynes catalysed by $\text{RuCl}_2(\text{PR}_3)(\text{arene})$ complexes has revealed the following points:

- . the presence of a basic PR_3 ligand allows milder conditions and higher regioselectivity,
- . the arene ligand is lost under the reaction conditions,
- . the addition to disubstituted alkynes is also possible but requires more drastic conditions, and
- . the carboxylate group which adds to the alkyne does not coordinate to the ruthenium center, and consequently the alkyne triple bond does not insert into the carboxylate O-Ru bond.

Based on these observations, a mechanism can be proposed with (i) displacement of the arene, (ii) η^2 -coordination of the alkyne to the ruthenium(II) center, (iii) external addition of the carboxylate to the substituted carbon and (iv) on ruthenium protonation followed by reductive elimination, formation of the enol ester. An alternative route may consist in the protonation at the ruthenium center giving an electrophilic activation, before the carboxylate addition.

The rearrangement of the η^2 -alkyne into a η^1 -vinylidene ruthenium moiety is expected to take place under more drastic conditions, those required for the addition of carbamates.

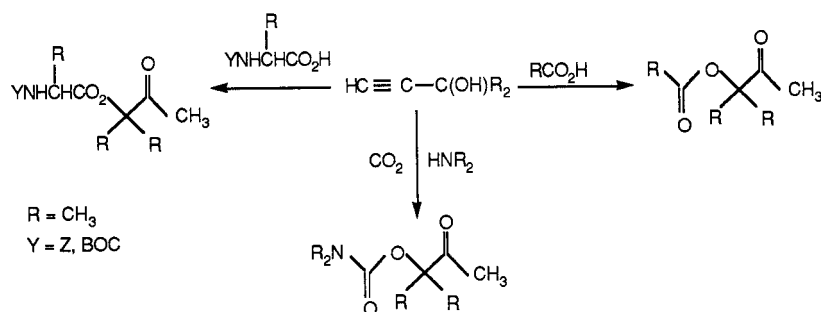
3. Syntheses of β -oxopropyl esters and carbamates

Carboxylic acids such as PhCO_2H , $\text{PhCH}(\text{Et})\text{CO}_2\text{H}$, $\text{CH}_3\text{CH}=\text{CHCO}_2\text{H}$, or $\text{HO}_2\text{CCH}=\text{CHCO}_2\text{H}$ add to propargyl alcohols, another type of inexpensive terminal alkynes, in the presence of ruthenium catalyst. O- β -oxopropyl esters are obtained under very mild conditions (60°C , 6 h). Starting from dimethyl propargyl alcohol, the obtained ester has its oxygen atom bonded to the substituted carbon atom. The ester formation can thus be explained by addition of the carboxylate to the coordinated triple bond, intramolecular transesterification, protonation of the functional alkyl-ruthenium intermediate and reductive elimination of the oxopropyl esters. The reaction can be extended to N-protected amino acids and optically active β -oxopropyl esters and diesters can be prepared very easily (ref. 23) (Scheme 6).

Ammonium carbamates, generated directly from CO_2 and secondary amines, also react with propargyl alcohols to give, under mild conditions, β -oxopropyl carbamates (ref. 24) (Scheme 6).

These catalytic methods of synthesis of activated O- β -propyl esters and carbamates presents advantages by its simple one step reaction, directly from carboxylic acids or CO_2 and amines, over the known methods involving β -oxoalkylhalides or hydroxypropanones (ref. 23, 25).

Scheme 6



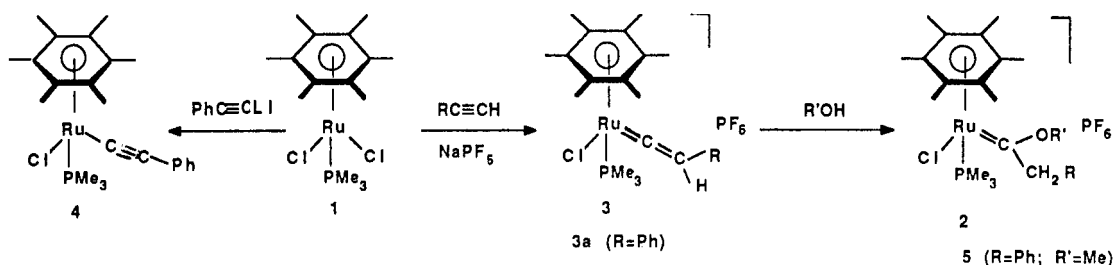
II. NEW RUTHENIUM-CARBENE COMPLEXES FROM ALKYNES

1. Arene-ruthenium carbene and vinylidene complexes

Ruthenium-vinylidene intermediates were postulated as active catalytic species in the synthesis of vinylcarbamates from terminal alkynes. As an attempt to support such a possibility we have investigated the stoichiometric interaction between terminal alkynes and $\text{RuCl}_2(\text{PMe}_3)(\text{C}_6\text{Me}_6)$ **1**, one of the best catalyst precursors.

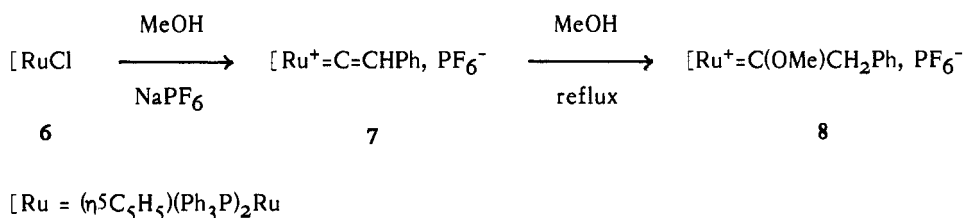
In non polar solvents no reaction was observed. In methanol and in the presence of one equivalent of NaPF_6 , at room temperature within a few minutes the red arene-ruthenium-carbene **2** were formed. The formation of ruthenium-carbene complexes appears to be general with phenylacetylene, *t*-butylacetylene or propyne. It takes place with alcohols such as methanol, ethanol or isopropanol but the rate decreases when the substitution increases: $\text{MeOH} > \text{EtOH} > \text{iPrOH}$ (ref. 26,27) (Scheme 7).

Scheme 7



The complexes **2** appear to be the first isolated arene-ruthenium-carbene derivatives and are chiral derivatives with four different ligands bonded to the ruthenium centre. The formation of complexes **2** can be explained via that of arene-ruthenium-vinylidene intermediates **3** by addition of the alcohol to the electrophilic coordinated carbon. However, complexes **3** can not be observed under the reaction conditions even at room temperature. We have isolated and characterized one of these by using an indirect route. Protonation with HBF_4 of phenylacetylid-ruthenium derivative **4** in ether led to the isolation of the first arene-ruthenium-vinylidene complex **3a**, which was characterized by ^{13}C nmr (δ ppm: 360 ($\text{Ru}=\text{C}$, $^2\text{J}_{\text{PC}} = 20.6$ Hz); 112.6 ($=\text{CH}$, $^1\text{J}_{\text{CH}} = 198$ Hz). Complex **3a** in the presence of methanol gave the carbene complex **5** within a few seconds at room temperature (ref. 27). This observation supports that complexes of type **3** are intermediates in the formation of carbene complexes **2**, and that they are extremely reactive.

Isoelectronic vinylidene and carbene ruthenium derivatives of the cyclopentadienyl-ruthenium series have been obtained by M.I. Bruce et al. (ref. 28). They display strong differences in behaviour as compared to the arene-ruthenium analogues: (i) $\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{PPh}_3)_2$ **6** does not catalyse the addition of carbamates to alkynes, (ii) the vinylidene complex **7** can be isolated from methanol solution, after a reflux of half-an-hour, and is stable toward the addition of methanol: the formation of the carbene complex **8** was completed only after 24 h in refluxing methanol.



We have compared the electrochemical properties of the two sets of complexes **1,5** and **6,8** by cyclic voltammetry. Both precursors show reversible oxidation but at lower potential + 0.53 V (vs SCE) for **8** than + 0.73 V for **1**. Thus, the $[(C_6Me_6)Ru(Cl)PMe_3]$ moiety is less electron rich than the $[CpRu(PPh_3)_2]$ moiety and does not stabilize as much the ruthenium-vinylidene moiety.

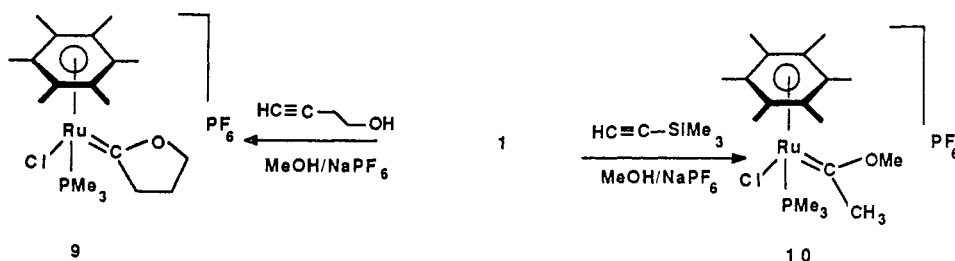
The carbene complexes **5** and **8** also behave differently. The arene complex **5** is oxidized reversibly at $E_{1/2}^+ = + 1.15$ V whereas the cyclopentadienyl complex **8** is oxidized irreversibly at $E_{D^+} = + 1.27$ V. This is consistent with the occurrence of a stable $Ru(III)/Ru(II)$ carbene couple in the arene series only.

The straightforward formation of arene-ruthenium-carbene from terminal alkyne and via reactive vinylidene intermediates can be extended to functional alkynes for the access to new carbene derivatives (Scheme 8).

4-hydroxy but-1-yne in methanol leads to the formation of the cyclic carbene **9**. This reaction shows that the intramolecular addition of the hydroxy group is favoured with respect to that of the intermolecular addition of methanol to the intermediate vinylidene carbon.

Trimethylsilylacetylene allows the access to the simple carbene complex **10** which can not be produced directly from acetylene itself. Its formation is consistent with the alcoholysis of the C-Si bond of the intermediate (ref. 26).

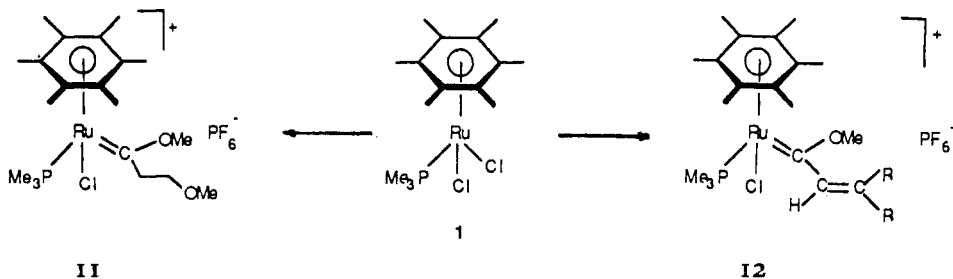
Scheme 8



Arene ruthenium(II) complexes readily react with propargyl alcohol itself in methanol in the presence of $NaPF_6$. Complex **11** was isolated. Its formation is consistent with the loss of H_2O and the addition of two moles of methanol. The same complex **11** was obtained from methyl propargyl ether (ref. 29) (Scheme 9).

Disubstituted propargyl alcohols $HC\equiv C(OH)R_2$ ($R_2 = Me_2, Ph_2, (CH_2)_5$) react with the hexamethylbenzene ruthenium derivative **1** in methanol differently. The reaction gives access to vinylcarbene complexes **12** in one step and in good yields. Vinylcarbene derivatives have already been prepared, but using multi-step reactions carried out only from metal carbonyl complexes (ref. 30). Starting with the diphenyl propargyl alcohol, the formation of the red vinylcarbene at room temperature is much slower (24 h) than with the dialkylpropargyl alcohol (20 min.), and a violet intermediate was initially produced. By quenching the reaction after 20 min the violet intermediate was isolated and identified to an allenylidene ruthenium complex $(\eta^6-C_6Me_6)Ru(C=C=CPh_2)(Cl)(PMe_3)PF_6$ **13**. Consequently, we can suggest that from propargyl alcohol itself an allenylidene intermediate is also produced which adds methanol at carbon 3 and then at carbon 1, whereas disubstitution prevents addition of methanol at carbon 3 to give complexes **12** (Scheme 9).

Scheme 9



Diphenyallenylidene ruthenium complex $[\text{Ru}(\text{C}=\text{C}=\text{CPh}_2)(\text{C}_5\text{H}_5)(\text{PMe}_3)_2]\text{PF}_6$ **14** has already been obtained from diphenylpropargyl alcohol and $\text{Ru}(\text{C}_5\text{H}_5)\text{Cl}(\text{PMe}_3)_2$ **6** in ethanol by J.P. Selegue (ref.31). The stability of complex **14**, which does not afford the vinylcarbene analogous to **12**, again points out the striking difference in behaviour of the arene and cyclopentadienyl ruthenium derivatives. This difference is thought to be due, on the basis of electrochemical studies to the less electron releasing capability of the $\text{Ru}(\eta^6\text{-arene})\text{Cl}(\text{PR}_3)^+$ unit which provides a better electrophilic activation with respect to a $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)_2^+$ moiety.

The electrochemistry studies of the arene vinylcarbene ruthenium complexes **12** is of special interest. The cyclic voltammetry shows that the first one-electron oxidation at $E_{1/2} = + 1.13$ V (R=Ph) is reversible. A second oxidation wave is observed at $E_p^a = + 1.57$ V and is irreversible. The corresponding oxidized product is chemically transformed into a species which is irreversibly reduced at + 0.1 V (ref. 29). This observation strongly supports that the second oxidation involves the carbon-carbon double bond and that new chemistry involving unsaturated carbene complexes can be expected.

CONCLUSION

This contribution points out that (arene) $\text{RuX}_2(\text{PR}_3)$ complexes display many talents for both catalysis and access to new carbene complexes from alkynes.

They are among the best catalyst precursors for the regioselective syntheses of vinylcarbamates, enol esters or O- β -oxopropyl carbamates and esters in only one-step intermediates from terminal alkynes or propargyl alcohols with ammonium carbamates or carboxylic acids. They especially allow mild conditions for the access to optically active N-protected α -amino vinyl esters.

They allow activation of terminal alkynes in polar solvents to produce, on displacement of chloride, new carbene ruthenium(II) complexes which retain the η^6 -arene ligand. The activation is provided by the reactive arene-ruthenium-vinylidene and -allenylidene from terminal alkynes and disubstituted propargyl alcohols, respectively.

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