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Selective transformations of alkynes with ruthenium catalysts

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The electrophilic activation of terminal alkynes by suitable ruthenium(II) catalyst precursors has provided selective access to enol esters, functional dienes, ketoesters and furans. The step-by-step modification of the ligands of simple complexes such as (arene)$RuCl_2(PR_3)$, $[Ru(\mu\text{-}O_2CH)(CO)_2(PR_3)]_2$ or (diphosphine)$Ru(allyl)_2$, has allowed the determination of efficient catalytic conditions for regio- and stereo-selective additions to alkynes. The utilization of electron-rich ruthenium(II) complexes containing the bulky pentamethylcyclopentadienyl ligand, has made possible the catalytic carbon–carbon bond forming reaction from alkynes and allyl alcohol to give unsaturated aldehydes.

Introduction

Transition-metal complexes are powerful catalysts for organic synthesis and polymerization, for when the suitable ligands are associated with the metal centre, they can offer chemio-, regio- or stereo-selectivity under mild conditions. During the last decade, ruthenium catalysts have brought a tremendous contribution to organic synthesis not only for enantioselective hydrogenation with chiral ruthenium complexes[1] or for mild oxidation reactions,[2] but also for the activation of simple unsaturated hydrocarbon molecules to produce functional derivatives[3–5] or polymers,[6] thus avoiding the use of toxic reagents. As ruthenium catalysts tolerate most functional groups they have been used to promote new methods for carbon–heteroatom and carbon–carbon bond formation by combination of two substrates with atom economy.[7]

Our experience in the stoichiometric activation of alkynes by organoruthenium derivatives[8] has offered an evaluation of the electrophilicity of ruthenium(ii) precursors in activation processes. These studies have aided progress towards the field of catalysis for the selective transformation of alkynes for which several aspects have been considered: (i) the study of simple catalytic additions to alkynes provided by electrophilic activation with ruthenium(ii) complexes in order to achieve excellent regioselectivity and avoid the formation of by-products; (ii) the possibility of step-by-step modification of the catalyst, by using tunable ligands, in order to create activity at the metal centre and favour regioselectivity; and (iii) the formation from alkynes of simple reagents that are useful synthetic intermediates or polymer precursors.

Here, we describe some aspects of ruthenium-catalysed syntheses: the Markovnikov and *anti*-Markovnikov additions to alkynes, the synthesis and uses of the resulting enol esters, the recovery of the ruthenium catalysts, the stereoselective transformation of prop-2-yn-1-ols and the synthesis of functional furans, dienes or unsaturated aldehydes. All these reactions are performed using air-stable ruthenium catalysts which can be easily prepared and used in organic synthesis.

Ruthenium-catalysed synthesis of enol esters *via* selective addition of carboxylic acids to alkynes

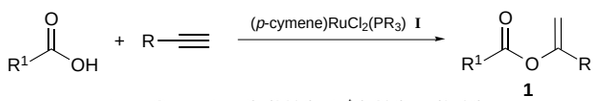
Enol esters have specific industrial applications as monomers for the production of various polymers and copolymers.[9] They are also useful reagents for carbon–carbon and carbon–heteroatom bond formation *via* the generation of enolates or acylation reactions. Although mercury(ii)-assisted carboxylation of alkynes[10] constitutes an efficient route to enol esters, an environment-friendly process would be preferred. We have considered the possibility of electrophilic activation of alkynes by ruthenium(ii) complexes towards the addition of carboxylates. While $RuCl_3 \cdot xH_2O$ can be used to catalyse the addition of carboxylic acids to phenylacetylene at 120 °C with no regioselectivity,[11] by contrast, (arene)$RuCl_2(PR_3)$ **I** complexes emerged as very efficient catalysts for the regioselective Markovnikov addition of carboxylates to the internal carbon of the triple bond of terminal alkynes, and the production of alk-1-en-2-yl esters **1** (Scheme 1).[11,12] A variety of carboxylic acids can thus be added directly to aliphalic alkynes such as hex-1-yne and propyne at 80–100 °C in toluene.

The ruthenium-catalysed addition of carboxylic acids has been used for the production of functional dienes, the 2-acyloxy-1,3-dienes **2** from conjugated enynes (Scheme 2).[13]

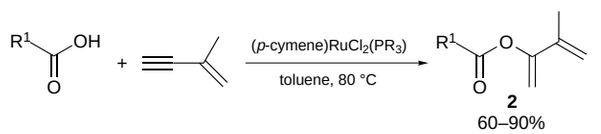
In the presence of (arene)$RuCl_2(PR_3)$ catalysts, these reactions took place under mild conditions and without racemization of the substrates. Thus, the addition of optically pure *N*-protected aminoacids led to optically pure *N*-protected amino acid enol **3**[14] and dienol **4**[13] esters in good yields and high regioselectivity (Scheme 3).

Uses of enol esters as acylation reagents

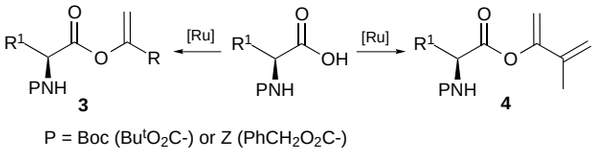
Enol esters have been used in a variety of reactions involving carbon–carbon bond formation, such as acylation of carbonyl compounds,[15] palladium-catalysed allylation,[16] arylation[17] and aldol-type condensation,[18] cyclopropanation,[19] Diels–Alder cycloaddition[20] and hydroformylation.[21] However, the most widespread use of enol esters in organic synthesis is in the acylation of alcohols and amines,[22] including enzymatic chemistry.[23] Alk-2-enyl esters are much more reactive than alkyl esters and can be used as efficient acylating reagents. In addition, they release a neutral ketone as the only by-product and therefore are appropriate for the acylation of substrates



Scheme 1



Scheme 2



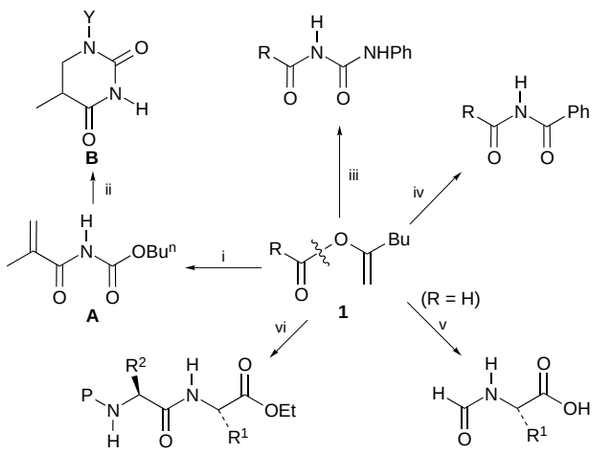
Scheme 3

sensitive to acids (from acyl chloride or anhydrides) or bases (such as dimethylaminopyridine).

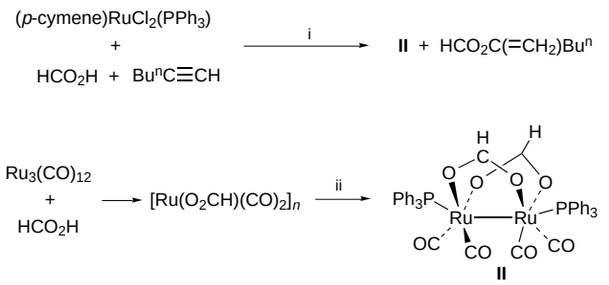
Thus, hex-1-en-2-yl formate is an efficient and easy-to-handle formylating reagent for the preparation of formamides at room temperature from primary and secondary amines, and esters from alcohols at 50 °C in the presence of catalytic amounts of imidazole (Scheme 4).[24] The *N*-formylation of unprotected amino acids was also possible in THF at 70 °C, and formyl-leucine, -alanine, -phenylalanine and -glycine were prepared in 84, 91, 87 and 91% isolated yields, respectively. Esters of amino acids were also efficiently acylated by enol esters derived from *N*-protected amino acids to produce dipeptides.[25] Compounds of the type $H_2NC(O)Y$ (Y = alkyl, aryl, OR, NR_2), which could not be acylated by enol esters, react upon the addition of a stoichiometric amount of NaH, allowing the one-pot acylation of amides, carbamates and ureas in high yields.[26] Of special interest is the butyl methacryloylcarbamate **A**, which reacts readily with primary amines to afford dihydropyrimidinediones **B** (Scheme 4).[27]

However, (arene)$RuCl_2(PR_3)$ **I** complexes were not efficient catalysts for the addition of oxalic acid and α-hydroxy acids to terminal alkynes. The use of the binuclear derivative $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ **II**, an easy-to-handle, air-stable ruthenium complex produced by treatment of (*p*-cymene)-$RuCl_2(PPh_3)$ with formic acid in the presence of hex-1-yne or by reaction of $[Ru(O_2CH)(CO)_2]_n$ with PPh_3[26] according to Scheme 5, made possible the addition of oxalic acid to hex-1-yne and propyne at 100 °C to afford dihex-1-en-2-yl **5** and diisopropenyl **6** oxalates, respectively (Scheme 6).[28] Compounds **5** and **6** actually led to a variety of α-dicarbonyl compounds by stepwise reactions with alcohols (**C**), amines (**D**) or aminoalcohols (**E**) (Scheme 7).

Mandelic acid could also be added to alkynes in the presence of **II** to afford alk-1-en-2-yl mandelates **7** in THF, whereas



Scheme 4 Acylation of nucleophiles with enol esters. *Reagents and conditions*: i, NaH, $H_2NCO_2Bu^n$, room temp.; ii, Y-NH_2, room temp.; iii, NaH, $H_2NCONHPh$, room temp.; iv, NaH, H_2NCOPh, room temp.; v, $H_2NCHR^1CO_2H$, THF, 70 °C; vi, $H_2NCHR^1CO_2Et$, KCN (cat.), room temp.



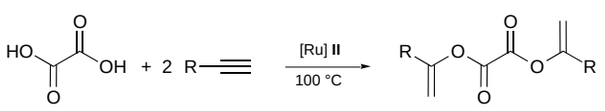
Scheme 5 Preparation of complex **II**. *Reagents and conditions*: i, 60 °C; ii, PPh_3, Et_2O, reflux, 4 h.

dioxolanones **8** were formed stereoselectively in toluene *via* a subsequent ruthenium(ii) electrophilic activation of the double bond of the enol ester **7** towards the addition of the hydroxy group (Scheme 8).[29]

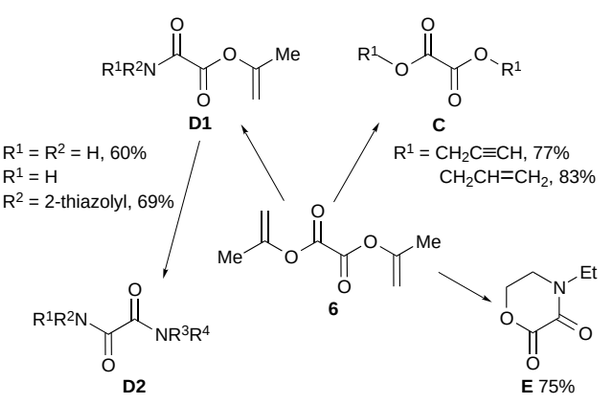
$[Ru(O_2CH)(CO)_2(PR_3)]_2$ complexes appeared to be the best catalysts for the Markovnikov addition of carboxylic acids to unfunctionalized alkynes, especially the terminal unconjugated octa-1,7-diyne which was transformed into the dienyl esters **9** in >80% isolated yields after reaction at 80 °C for 8 h (Scheme 9).

Alkenylruthenium complexes, such as (hexamethylbenzene)RuCl(PMe_3)[C(OMe)=CHR] **III** (R = Me, Ph), prepared from the reaction of (η^6-C_6Me_6)$RuCl_2(PMe_3)$ with terminal alkynes in the presence of $NaPF_6$ in methanol followed by deprotonation with Bu^tOK, also appeared to be very good catalyst precursors. These alkenylruthenium complexes were very efficient for the preparation of dioxolanones **8** with good diastereoselectivity.[30] They were particularly active for the preparation of enol **10** and dienol **11** methacrylates (Scheme 10), both of which are excellent precursors for the preparation of polymers by copolymerization and polycondensation, respectively.[30]

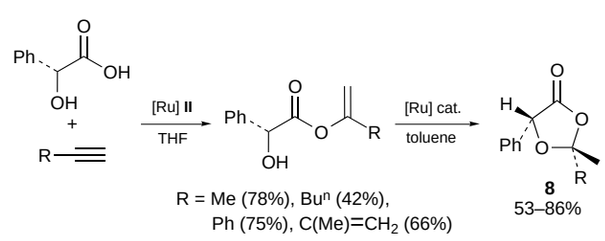
For the above reactions to be economically useful, easy recovery of the ruthenium catalyst is required. A simple solution



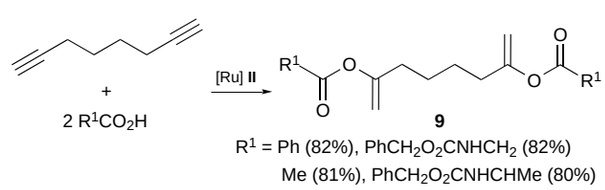
Scheme 6



Scheme 7



Scheme 8



Scheme 9

was found to be modification of the solubility of the ruthenium catalyst. The easy coordination of the polymeric diphenylphosphinoalkane $Ph_2P(CH_2CH_2)_nCH_2CH_3$, prepared by BuLi-initiated polymerization of ethene followed by reaction with Ph_2PCl, led to the preparation of the binuclear ruthenium complex $[Ru(O_2CH)(CO)_2\{Ph_2P(CH_2CH_2)_nCH_2CH_3\}]_2$.[31] This complex (**IV**; n = 50) was soluble in toluene at 100 °C and catalysed the addition of carboxylic diacids to terminal alkynes (Scheme 11). When the reaction mixture was cooled to room temperature the complex became insoluble, the diester **12** was isolated and the catalyst could be recovered unchanged by simple filtration and used again at least six times without loss of activity and regioselectivity.

Mechanism

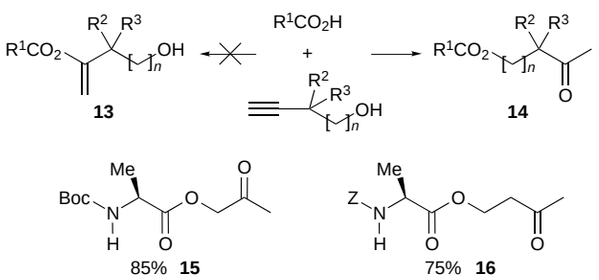
Although the catalytic mechanism has not yet been determined fully, an important feature for the addition of the carboxylate to C(2) of terminal alkynes is the presence of a monophosphine coordinated to the ruthenium centre. The nature of the phosphine does not seem to be crucial, as PMe_3, PBu_3 and PPh_3 led to similar results. We have shown by performing cross-reactions that the carboxylate ligand attached to the ruthenium centre in either $[Ru(O_2CR)(CO)_2(PPh_3)]_2$ or (arene)Ru-$Cl(O_2CR)$ complexes did not add to the alkyne, but only to the carboxylate generated from the free carboxylic acid used as reagent. The fact that the reaction proceeds *via* external attack of the nucleophilic carboxylate to the electrophilically activated alkyne rules out the possibility of insertion of the triple bond into an Ru–O(carboxylate) bond.

Catalytic synthesis of ketoesters

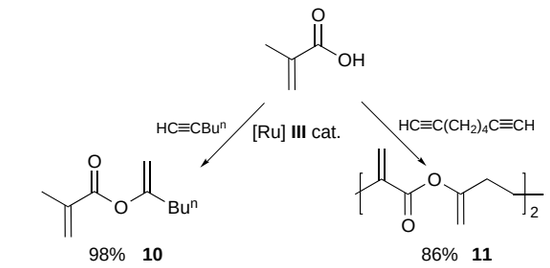
The ruthenium(ii)-catalysed addition of carboxylic acids to prop-2-ynylic and but-3-ynylic alcohols did not lead to the expected hydroxy enol esters **13**, but to ketoesters **14** (Scheme 12).[32] At 60 °C, (arene)$RuCl_2(PPh_3)$ complexes catalysed the addition of N-protected amino acids to prop-2-ynylic[33] and but-3-ynylic[32] alcohols to give β-oxopropyl **15** and γ-oxobutyl **16** esters without racemization. For the addition of carboxylic acids to sterically hindered alkynols, the use of $[Ru(O_2CH)(CO)_2(PPh_3)]_2$ **II** was required, as exemplified by the selective transformation of steroids **17** containing both an alkynyl and a hydroxy group attached to C(17). In that case, the addition took place without racemization and with retention of the configuration of C(17) and led to steroids **18** (Scheme 13).[34] The mechanism of this reaction involves the addition of the carboxylate to C(2) of the alkyne followed by internal transesterification. When the geometry of the starting hydroxy alkyne did not allow the intramolecular transesterification, hydroxylated enol esters were formed. This was confirmed by the addition of carboxylic acids to (*E*)-3-methylpent-2-en-4-yn-1-ol, which selectively afforded the hydroxylated 2-carboxy-1,3-dienes **19** in good yields (Scheme 14).[32]

Catalytic synthesis of furans

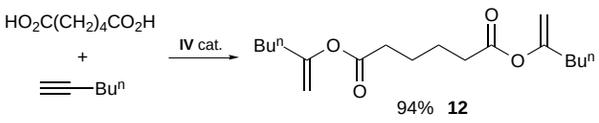
(*Z*)-3-Methylpent-2-en-4-yn-1-ol has suitable geometry for the intramolecular addition of the hydroxy group to the triple bond, under electrophilic ruthenium-catalysis conditions. Indeed, at 60 °C in the presence of a catalytic amount of (*p*-cymene)Ru-$uCl_2(PPh_3)$ **I**, furan **20** was formed selectively (Scheme 15),resulting from cyclization of the starting enynol.[35] This reaction, which took place under neutral conditions, corresponded to the first ruthenium-catalysed Markovnikov intramolecular addition of a hydroxy group to a non-activated terminal triple bond. We have shown that the absence of a base and the relatively low reaction temperature (< 110 °C) made



Scheme 12

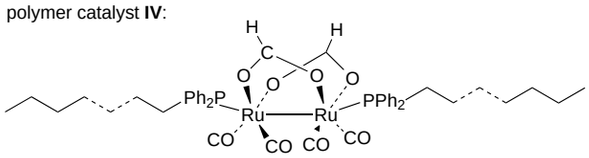


Scheme 10

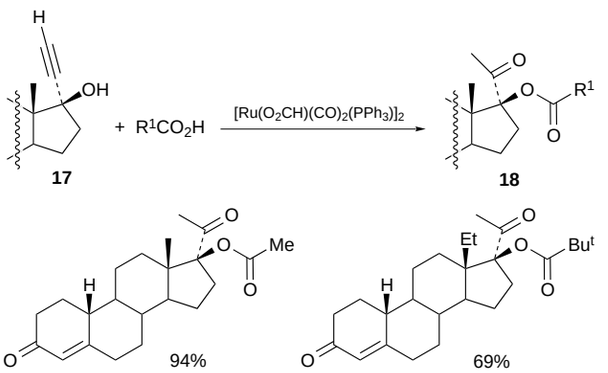


constant yield for seven successive reactions

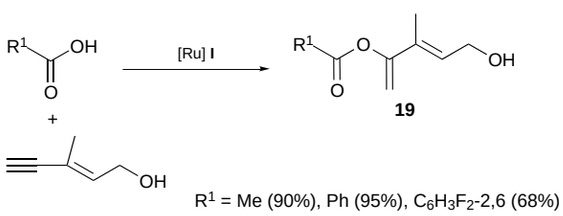
polymer catalyst **IV**:



Scheme 11



Scheme 13



Scheme 14

possible the cyclization of enynols containing trimethylsilylethynyl or cyanide groups,[36] the starting (*Z*)-enynols being easily prepared by reaction of organometallic derivatives with the corresponding (*Z*)-aldehyde resulting from the oxidation of the unsubstituted (*Z*)-enynol.

Synthesis of (*Z*)-enol esters: *anti*-Markovnikov addition of carboxylic acids to alkynes

After developing the catalytic Markovnikov addition of carboxylic acids to terminal alkynes, it became a challenge to perform the *anti*-Markovnikov addition corresponding to the reverse regioselectivity. The idea was to generate vinylidene–ruthenium species able to make the terminal carbon of the alkyne electrophilic. Such an example of activation of terminal alkynes was shown in the regioselective synthesis of vinylic carbamates **21** by the reaction of secondary amines, CO_2 and terminal alkynes in the presence of (arene)$RuCl_2(PR_3)$ catalyst precursor (Scheme 16), which can be explained *via* the formation of a ruthenium–vinylidene [Ru=C=CHR^1] active species.[37]

Our approach to the reversal of the regioselectivity of the addition to alkynes was to modify the ruthenium catalysts, first by introducing hydrocarbon ligands, labile under acidic conditions, to provide vacant coordination sites, and secondly by replacing the monophosphine ligands by bidentate diphosphines which are known to stabilize intermediate organometallic catalytic species. New ruthenium complexes containing two allylic ligands and a tunable diphenylphosphinoalkane were prepared according to a known method (Scheme 17).[38]

The step-by-step lengthening of the hydrocarbon chain from one to four carbons between the two diphenylphosphino groups made it possible to observe important differences in the catalytic behaviour of these catalyst precursors. The complex (dppb)Ru(2-methylallyl)$_2$ was shown to be the best catalyst precursor, in terms of reactivity and regioselectivity, for the addition of benzoic acid to the C(1) of terminal alkynes in good yields in toluene at 65 °C (Table 1).[39]

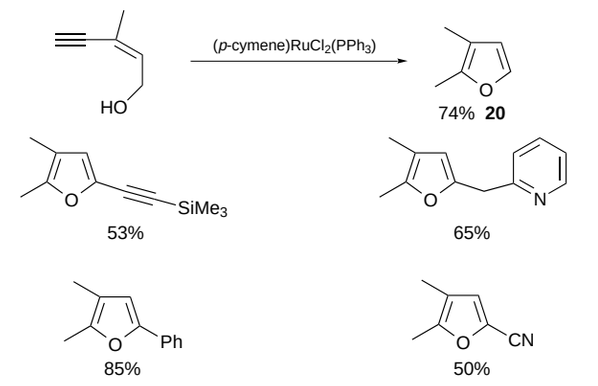
Moreover, the stereoselectivity was excellent and (*Z*)-enol esters of type **22** could be obtained in > 95% stereoselectivity (Scheme 18). The regio- and stereo-selectivities of this addition were very dependent on (i) the bulkiness of both the carboxylic acid and the alkyne, (ii) the reaction temperature, and (iii) the acidity of the carboxylic acid. In general terms, we have shown that the lower the reaction temperature, the higher the regio- and stereo-selectivities, but a minimum temperature had to be found to obtain a reasonable reaction rate.[40]

Saturated and unsaturated aliphatic acids, and substituted aromatic acids have allowed the preparation of a variety of new (*Z*)-enol esters upon addition to hex-1-yne and phenylacetylene. The absence of racemization under mild temperature conditions made it possible to synthesise optically pure (*Z*)-enol amino acid esters **23** from N-protected amino acids. In the presence of catalytic amounts of (dppb)Ru(2-methylpropenyl)$_2$, this reaction could be extended to octa-1,7-diyne to stereoselectively produce (*Z*,*Z*)-1,8-dienyl esters **24**, by contrast to the isomers **9**. This *anti*-Markovnikov addition could be extended to conjugated enynes when bulky carboxylic acids were used. The most efficient catalyst precursor was (dppb)Ru(2-methylallyl)$_2$ which led to 1-carboxy-1,3-dienes **25** at 40–65 °C in good yields and very high stereoselectivity with benzoic and *N*-protected amino acids (Scheme 19).

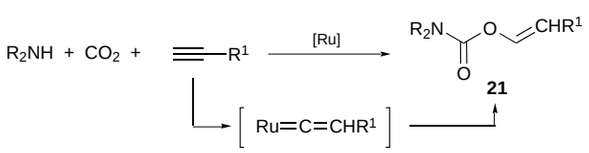
The addition of carboxylic acids to trimethylsilylacetylene was also possible in the presence of (dppb)Ru(2-methylpropenyl)$_2$ as catalyst precursor, but in this special case, the bulkiness of the alkyne allowed a more rapid reaction at 50–60 °C in the presence of (dppe)Ru(2-methylallyl)$_2$ as catalyst, affording functional trimethylsilylated alkenes in > 98% regio- and stereo-selectivity. The same reactivity was observed in the addition to bulky methyl prop-2-yn-1-yl ethers. By using (dppe)Ru(2-methylpropenyl)$_2$ as catalyst precursor, the rate of the reaction could be improved drastically and 81% yield of the (*Z*)-benzoate **26** was obtained with 100% stereoselectivity for the (*Z*)-isomer (Scheme 20).

The presence of an additional functionality close to the triple bond did not affect the reaction; (*Z*,*Z*)-4-methoxybuta-1,3-dienyl esters **27** were prepared at 65 °C in toluene in the presence of (dppb)Ru(2-methallyl)$_2$ as catalyst precursor with stereoselectivities > 97% from (*Z*)-1-methoxybut-1-en-3-yne (Scheme 21).

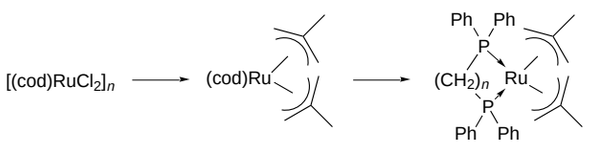
It is noteworthy that (diphosphine)Ru(2-methylpropenyl)$_2$ complexes were not able to promote the regioselective addition of carboxylic acids to the terminal carbon of the triple bond of prop-2-ynylic alcohols. Only ketoesters were formed, indicating that the regioselectivity of the addition of carboxylic acids was influenced by the presence of the hydroxy group as with (*p*-cymene)$RuCl_2(PPh_3)$ or $[Ru(O_2CH)(CO)_2(PPh_3)]_2$. This



Scheme 15



Scheme 16



Scheme 17 *Reagents and conditions*: $Ph_2P(CH_2)_nPPh_2$, hexane, reflux, 5 h

Table 1 Synthesis of hexenyl benzoates: influence of the nature of the diphosphine ligand in (diphosphine)Ru(methallyl)$_2$ catalyst precursors

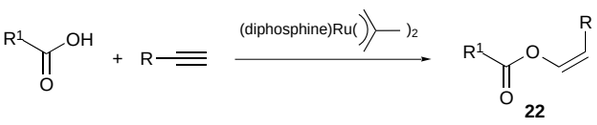
		Product selectivity (%)		
Diphosphine	Reaction time/h	Hex-1-en-1-yl benzoate (*Z*)	Hex-1-en-1-yl benzoate (*E*)	Hex-1-en-2-yl benzoate
$Ph_2PCH_2PPh_2$ (dppm)	3	16	4	80
$Ph_2PCH_2CH_2PPh_2$ (dppe)	24	72	21	7
$Ph_2PCH_2CH_2CH_2PPh_2$ (dppp)	24	69	6	25
$Ph_2PCH_2CH_2CH_2CH_2PPh_2$ (dppb)	2.5	98	2	0

behaviour clearly exhibited the determinant role of the hydroxy group of alkynols.

This method offers the first stereoselective synthesis of (*Z*)-enol esters in one step from terminal alkynes and carboxylic acids. These (*Z*)-esters are formally masked aldehydes allowing the functionalization at C(1) of terminal alkynes: two equivalents of secondary amines reacted with (*Z*)-enol esters at room temperature to afford (*E*)-enamines **28** in very high yields (Scheme 22). This two-step synthesis of enamines from terminal alkynes and amines represents a complementary method to the mercury-catalysed addition of amines to alkynes which leads to enamines resulting from the addition of the amine to the internal carbon of the triple bond.

Catalytic synthesis of unsaturated aldehydes and acetals: oxidative coupling of allyl alcohol with alkynes

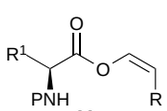
The coupling of terminal alkynes with allyl alcohol promoted by $RuCl(PPh_3)_2(C_5H_5)$–NH_4PF_6 to afford unsaturated ketones has been demonstrated to result from the formation of the ruthenium–vinylidene intermediate $[Ru{=}C{=}CHR(PPh_3)(C_5H_5)]^+$, followed by the addition of the alcohol to the electrophilic carbene carbon atom.[41] We have shown that the use of an analogous ruthenium(ii) catalyst, $RuCl(cod)(C_5Me_5)$ **V**, which contains a labile ligand (cod = cycloocta-1,5-diene) and an electron-donating, bulky C_5Me_5 group led to a quite different reaction. The carbon–carbon coupling of the C≡C and the C=C bonds led to the formation of γ,δ-unsaturated aldehydes **29a** and **29b** (Scheme 23).[42] It is noteworthy that the reaction can be carried out in water (allyl alcohol–water, 1 : 8) to achieve the best yields, and that the formation of the branched isomer was always favoured, it was the only product from the bulky *tert*-butylacetylene (Table 2).



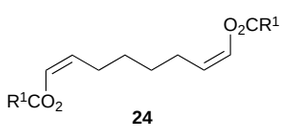
22

R = Bu^n; R^1 = Ph (95%), Ph_2CH (97%), $Bu^tO_2CNHCH(CH_2Ph)$ (97%)
R = Ph; R^1 = Bu^n (92%), CF_3 (90%), $MeOCH_2$ (96%), 2-HO-C_6H_4 (94%)

Scheme 18

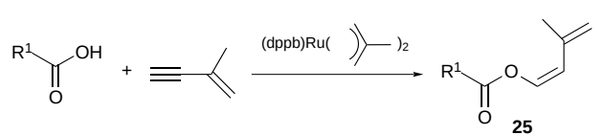


23



24

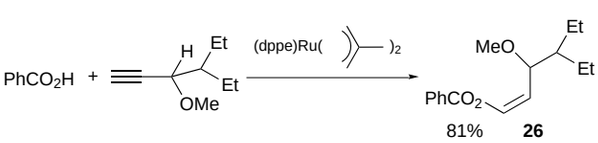
R^1 = H (88%), Me (85%), Ph (92%),
$PhCH_2O_2CNHCH_2$ (89%)



25

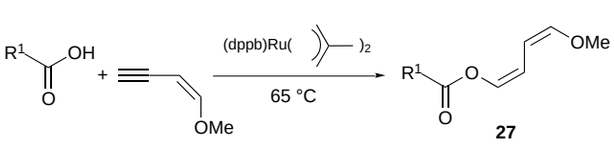
R^1 = Ph (92%), *n*-C_4H_9 (77%)

Scheme 19



81% **26**

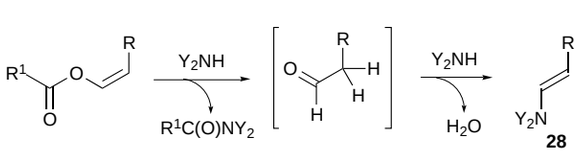
Scheme 20



27

R^1 = Ph (81%), $PhCH_2$ (76%),
$MeOCH_2$ (69%)

Scheme 21



28

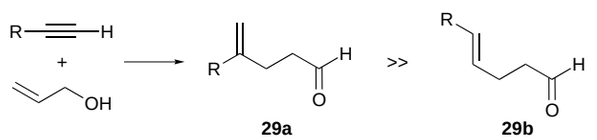
Scheme 22

The reaction when applied to symmetrically substituted alkynes, constituted an excellent method for the production of the corresponding γ,δ-unsaturated aldehydes **30** (Scheme 24).[43] Moreover, it showed that the reaction was not restricted to terminal alkynes and did not involve a vinylidene intermediate. The experiments suggested that the mechanism involved the displacement of cod and the oxidative coupling of C≡C and C=C bonds to generate intermediate **F** or **G**. The bulkiness of the R group favoured the formation of **F** and thus that of isomer **29a**.

It is noteworthy that the ruthenium(iv) precursor, $RuCl_2(\eta^3\text{-}CH_2CH{=}CH_2)(C_5Me_5)$, also catalysed the above reaction. However, the precursor was expected to partially form ruthenium(ii) species *via* the loss of allyl chloride, but in the presence of ruthenium(iv) species, the aldehydes were transformed into the corresponding acetals with allyl alcohol.

Conclusion

The selective catalytic reactions described show that slight modifications of ruthenium(ii) catalyst precursors allow the activation of alkynes, to achieve high regioselectivity in the

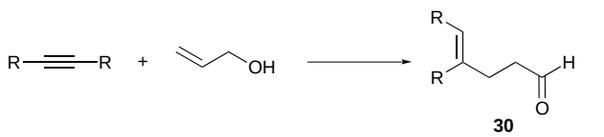


29a **29b**

Scheme 23 *Reagents and conditions*: [Ru^{II}] **V** (cat.), room temp., 10–15 min

Table 2 Formation of γ,δ-unsaturated aldehydes **29**

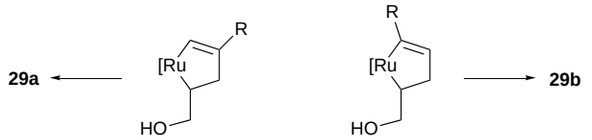
R	Yield (%)	Branched : linear **29a** : **29b**
Ph	85	75 : 25
C_6H_{13}	83	80 : 20
$(CH_2)_2OH$	75	58 : 42
p-$MeOC_6H_4$	82	68 : 32
Bu^t	60	100 : 0



30

R = Et (89%), Ph (95%)

Scheme 24



F **G**

Scheme 25

formation of carbon–heteroatom bonds. By contrast, the use of electron-rich ruthenium(ii) complexes favours the formation of carbon–carbon bonds by oxidative coupling of C≡C and C=C bonds. The tolerance of ruthenium(ii) complexes for functional groups, which we observed in the synthesis of enol esters, carboxydienes, ketoesters, steroids, furans and unsaturated aldehydes, may presage an important development of the use of ruthenium complexes in catalysis and polymerization in the near future.

Christian Bruneau graduated as Engineer in chemistry in Rouen (1974) and obtained his Doctorate degree at the National School of Chemistry in Rennes (ENSCR). He was appointed research engineer at CNRS in 1980, and since 1986 he has been developing his research at the University of Rennes (URA CNRS 415) in the field of homogeneous catalysis by transition-metal complexes. His main research interests are in activation of alkynes, catalytic transformations of CO_2 and carbonates and enantioselective hydrogenation.

The recent research interests of Pierre Dixneuf are in the fields of activation of molecules by metal complexes, especially ruthenium derivatives, for selective organic catalysis and the design of unsaturated, carbon-rich organometallics. He was born in Anjou and studied in Rennes (Bretagne). He prepared his doctorate with Professor R. Dabard and did postdoctoral research in Brighton with Professor M. F. Lappert. Professor in Rennes since 1978, he is now the head of a Research Unit, associated with the CNRS, on molecular chemistry and electrochemistry: 'Organometallics and catalysis'. He has been honoured by the awards of the A. von Humboldt Foundation and the French Académie des Sciences. He is a 1996 Laureate of the JSPS (Japan) invited fellowship.

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