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Ru-mediated selective addition reactions of carboxylic acids to internal and terminal alkynes

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ABSTRACT

This study examined the nucleophilic addition of trichloroacetic acid to internal alkynes using Ru=CHPhCl$_2$(PCy$_3$)(IPr) (IPr: [1,3-Bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazo-2-ylidene]). This reaction was performed in good yield with high Z-selectivity under mild experimental conditions. The same ruthenium complex was also shown to catalyse carboxylic acid (acetic acid, trichloroacetic acid, trans-2-octenoic acid, 4-cyclooctenoic acid) addition to terminal alkynes. These reactions proceeded in 80–100% yield, showing a high stereoselectivity favouring the gem isomer. The productivity and selectivity of the addition reaction was found to depend on the nature of the carboxylic acid that was used. With higher acidities, the yield of the reaction increased but the stereoselectivity decreased. The reactions of enoic acids, showed a high selectivity towards carboxylic acid addition to the triple bond of terminal alkynes, rather than triple bond addition to the double bond of the enoic acids. To evaluate the results obtained from the carboxylic acid addition reaction of terminal alkynes, the homodimerisation of terminal alkynes (phenylacetylene, 1-octyne, 1-heptyne) was also studied. The homodimerisation of terminal alkynes is found to proceed with high gem selectivity when employing aliphatic alkynes, whereas the reaction resulted in high Z-selectivity with aromatic alkynes, showing that the selectivity is dependent on the nature of the alkyne used.

1. Introduction

The reaction behavior of alkynes is one of the most interesting and important subjects in organic chemistry, and this topic has wide applications in all areas of chemistry and materials science [1–4]. For example, the dimerisation of alkynes is a very useful method to synthesise enynes and di- and oli-goacetylene moieties, which are widely used in the synthesis of natural products, pharmaceuticals and supramolecules [5–8]. Another type of alkyne reaction is the nucleophilic addition of carboxylic acids to triple bonds, resulting in the formation of enol-esters [9–12]. Enol-esters are significant intermediates for the selective generation of enolates, the acylation of carbonyl compounds and *O*- and *N*-acylation under mild conditions [13,14]. Both of these alkyne reactions can be catalysed by transition metal complexes [15–18]. Low valent ruthenium complexes play a prominent role in the formation of carbon–carbon and carbon-heteroatom bonds, as they can show high regio and stereoselectivity and many mechanisms using these metals have been studied in detail [19,20]. Another advantage of using Ru-based catalysts in alkyne reactions is their ability to generate stable and active metal–vinylidene complexes [21,22]. These vinylidene species are organometallic intermediates that are spontaneously produced from alkynes with the initial metal complexes. Furthermore, some ruthenium complexes catalyse these reactions more easily due to bulky and strong electron donating groups, including many *N*-heterocyclic ligands [23]. In most cases, from these alkyne reactions, a mixture of regio (tail-to-tail vs. head-to-tail) and stereo (*E*/*Z*/gem) isomers is obtained [24] (Scheme 1). The homodimerisation and carboxylic acid addition reactions of terminal alkynes have been reported by several research groups, using various transition metal catalysts [24–28]. Recently, Demonceau and co-workers have reported the activity of ruthenium–arene complexes bearing imidazol(in)um-2-dithiocarboxylate ligands in the synthesis of enol-esters. However, under standard conditions, this catalyst is poorly active and shows poor selectivity, though the catalytic activity can be improved by using microwave or conventional heating [29]. More recently, the same group reported novel tethered (η1:η6-phosphanoarene)ruthenium complexes as catalyst precursors for enol-ester synthesis. When compared to other catalyst systems reported to date, the reactions in this study are slower, but high selectivities can be obtained [30].

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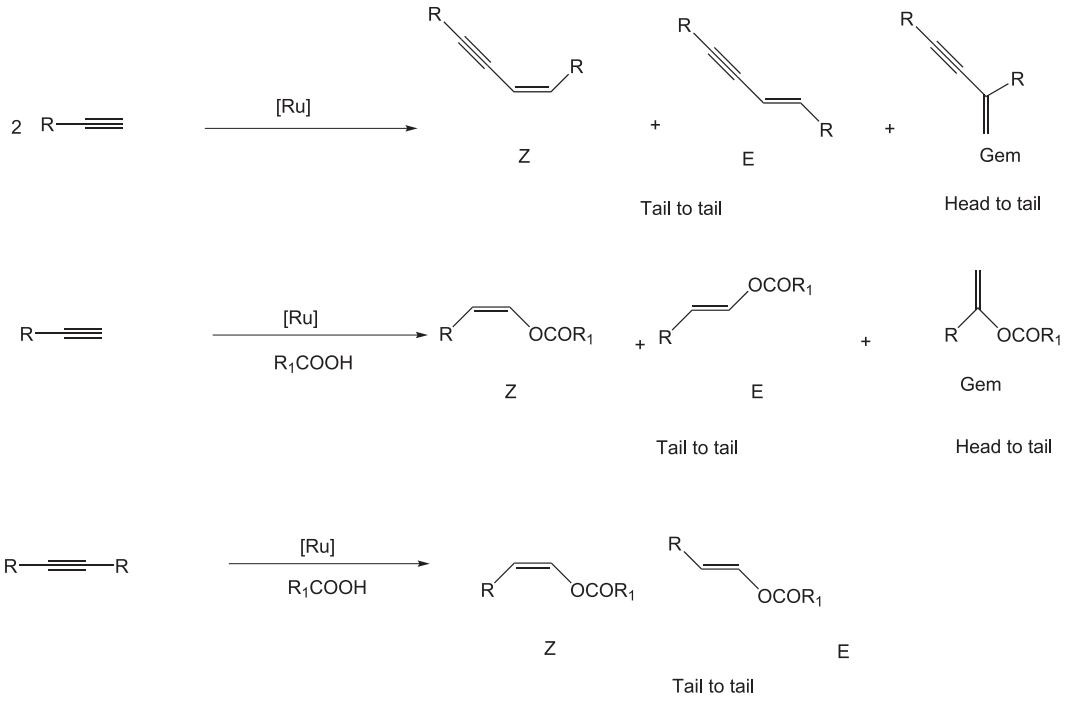


Scheme 1. Representation of homodimerisation of terminal alkynes and addition reactions of carboxylic acids to terminal and internal alkynes.

The catalyst, $[Ru(PPh_3)_2(CH_3CN)_3Cl][BPh_4]$, reported by Bhattacharjee and Tripathy [31] was found to be an effective catalyst for the regiospecific addition of carboxylic acids to alkynes, but this catalyst required the addition of a Lewis acid or a Lewis base to enhance the reaction yields. Verpoort and co-workers reported the activity of several ruthenium complexes [32] in enol-ester synthesis reactions and showed that the selectivity of addition to alkynes is dependent on the acidity of the carboxylic acid that is added [33].

Selective carboxylic acid addition to internal alkynes for the preparation of enol-esters has not been studied before. To the best of our knowledge there have been only two reports dealing with the reaction of benzoic acids with internal alkynes to produce cyclic compounds [34,35].

In this study, we report the synthesis of novel enol-esters that were obtained from the reaction of trichloroacetic acid with internal alkynes using $Ru{=}CHPhCl_2(PCy_3)(IPr)$ as a catalyst. The homodimerisation and nucleophilic addition reactions of terminal alkynes using carboxylic acids containing linear, cyclic and olefinic moieties are also presented and discussed.

2. Results and discussion

2.1. Nucleophilic addition of carboxylic acids to internal alkynes

Table 1 shows the results of nucleophilic addition of several carboxylic acids, including acetic acid, trichloroacetic acid, trans-2-octenoic acid and 4-cyclooctenoic acid, to different internal alkynes using $Ru{=}CHPhCl_2(PCy_3)(IPr)$ as the catalyst. Three internal alkynes, 4-octyne, 3-hexyne and 2-hexyne (two symmetric, one asymmetric), are chosen for enol-ester synthesis in these experiments. Acetic acid, trans-2-octenoic acid and 4-cyclooctenoic acid gave no nucleophilic addition product after 24 h. Only trichloroacetic acid addition could be accomplished in relatively high yields (~70%). 4-octyne and 3-hexyne yielded 73% (*Z*:*E*, 72:28) and 75% (*Z*:*E*, 74:26) yields, respectively, with the stereoselectivities given. Using an asymmetrical alkyne, 2-hexyne, the addition of the acetyl group to the triple bond may well proceed from both sides of the triple bond, yielding four isomers (Scheme 2).

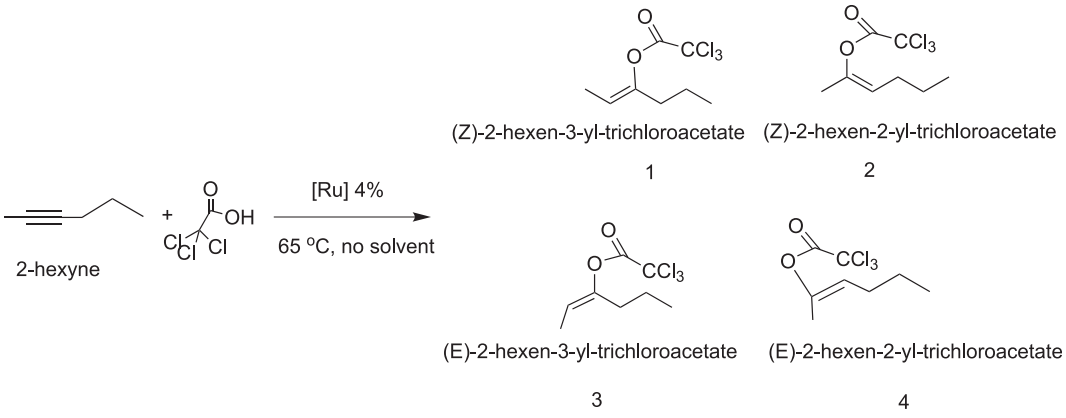
2.2. Nucleophilic addition of carboxylic acids to terminal alkynes

The nucleophilic addition of carboxylic acids (acetic acid, trichloroacetic acid, trans-2-octenoic acid and cyclooctenoic acid) to terminal alkynes (1-pentyne, 1-heptyne and 1-octyne) was also

Table 1
Addition reactions of carboxylic acids to internal alkynes.

Alkyne	Acid	Time[a] (h)	Yield[b] (%) Gem:*Z*:*E* (%)
C_3H_7—≡—C_3H_7	Trichloroacetic acid	9	73 0:72:28
	Acetic Acid	24	0
	Trans 2-octenoic acid	24	0
	4-Cyclooctenoic acid	24	0
C_2H_5—≡—C_2H_5	Trichloroacetic acid	7	75 0:74:26
	Acetic Acid	24	0
	Trans 2-octenoic acid	24	0
	4-Cyclooctenoic acid	24	0
H_3C—≡—C_3H_7	Trichloroacetic acid	5	74[c] 0:31:10 (2nd C-link) 0:39:21 (3rd C-link)
	Acetic acid	24	0
	Trans 2-octenoic acid	24	0
	4-Cyclooctenoic acid	24	0

[a] Time represents the time period at which the conversion reaches a plateau or is complete.
[b] Reaction conditions are as follows: 65 °C, 4% catalyst loading, no solvent.
[c] Four isomers are obtained.



Scheme 2. Isomeric products of asymmetric internal alkynes reacted with trichloroacetic acid.

tested in the presence of the Ru complex at 65 °C without solvent. The effect of the amount of carboxylic acid added in these reactions was investigated by changing the acid:alkyne ratio from 1:1 to 2:1 and 4:1. According to our results, the reaction of 4 equivalents of acid with 1 equivalent of the alkyne achieved the maximum yield in the shortest period of time.

Trichloroacetic acid reacted with both terminal and internal alkynes, whereas the other three acids reacted only with the terminal alkynes. Table 2 shows the reaction of 1-octyne and 1-heptyne with several carboxylic acids. The reaction of trichloroacetic acid with 1-octyne yielded addition products showing an isomer of ratio (gem:*Z*:*E*) of 24:56:20 isomer ratio in 90% yield. This isomer ratio changes towards the gem isomer when acetic acid is used. The reaction of acetic acid with 1-octyne yielded isomers in a ratio of 84:9:7 (gem:*Z*:*E*) and in 82% yield. The results shown in Table 3 summarise our optimum conditions for high conversion of the product in comparison with those reported using other catalytic systems. As shown in Table 3, $[Ir(cod)Cl]_2$ catalysed [36] the desired reaction at elevated temperatures (100 °C), but required 15 h and the addition of a base. This reaction produced the head-to-tail isomer with 81% selectivity. With the $RuCl_x$(*p*-cymene)(triazol-5-ylidene) [24] catalyst, the reaction occurred at 100 °C and required 22 h, producing the tail-to-tail isomer with 67% selectivity. Our catalytic system catalysed the same reaction at 65 °C, requiring 8 h and producing the tail-to-tail isomeric product with a selectivity of 84%. The addition of acetic acid to 1-octyne using the Grubbs first generation catalyst resulted in a yield of only 33%, with a selectivity of 85% for tail-to-tail [33]. We can conclude that the substitution of the PCy_3 ligand with the N-heterocyclic triazol-5-ylidene ligand [37] dramatically changes the isomer ratio towards the head-to-tail isomer while maintaining a high yield. This catalyst comparison shows that changing the ligand environment of the metal and the using different acids and alkynes can reverse the observed product distribution.

For the trans 2-octenoic and 4-cyclooctenoic acids, the double bonds of both acids were surprisingly unreactive (Table 1, Scheme 3). The reaction prefers, instead, the addition of the carboxyl group of the acid to the triple bond of the terminal alkyne, rather than the addition of the triple bond of the terminal alkyne to the double bond of the carboxylic acid. Addition of trans 2-octenoic acid to 1-heptyne resulted in an 89% yield, with high Z-selectivity, whereas the reaction with 4-cyclooctenoic acid resulted in an 82%, with high gem selectivity (Table 2). These selectivity differences can be explained by examining the differences in the enoic acid structures; the trans nature of the 2-octenoic acid shifts the isomeric products from the gem selectivity to the high Z-selectivity.

2.3. Homodimerisation of terminal alkynes

The activity of the Ru complex towards enyne formation was investigated using several terminal alkynes (Table 4). All dimerisation reactions were performed using a catalyst ratio of (catalyst:alkyne) 1:25 and without solvent. To test the effect of reaction temperature on the reaction activity, different temperatures ranging from 20 to 100 °C were examined. The homodimerisation

Table 2
Addition reactions of carboxylic acids to terminal alkynes.

Alkyne	Acid	Time[a] (h)	Yield[b,c] (%)	Homodimerisation (%)	Vinylation (%) Gem:*Z*:*E* (%)
C_6H_{13}—	Trichloroacetic acid	2	100	10	90 24:56:20
	Acetic Acid	8	82	0	82 84:9:7
	Trans 2-octenoic acid	6	80	0	80 16:82:2
	4-Cyclooctenoic acid	6	89	3	97 96:4:0
C_5H_{11}—	Trichloroacetic acid	3	100	14	86 18:58:24
	Acetic acid	6	86	0	86 85:10:5
	Trans 2-octenoic acid	6	89	0	89 10:87:3
	4-Cyclooctenoic acid	6	98	18	82 94:6:0

[a] Time represents the time period at which the conversion reaches a plateau or is complete.
[b] Yield and selectivity is determined by GC-MS.
[c] Reaction conditions are as follows: 65 °C, 4% catalyst loading, no solvent.

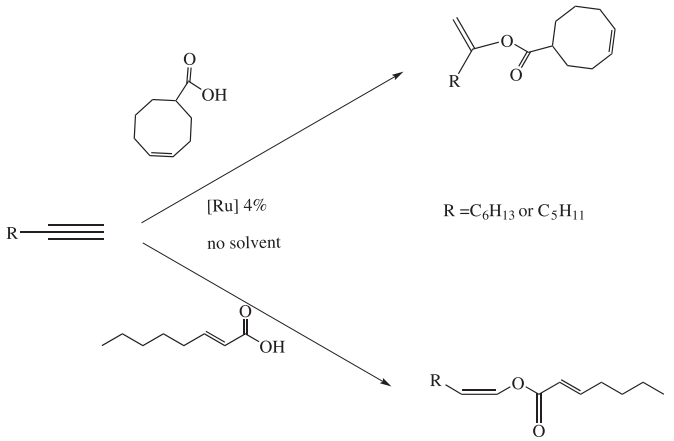
Table 3
A comparison for addition reaction of acetic acid to 1-octyne using various catalyst systems.

Catalyst	Time (h)	Temperature (°C)	Yield (%)	HT (%)	TT (%)	Refs.
$RuCl_x$(*p*-cymene)(triazol-5-ylidene)	22	110	95	33	67	[24]
$RuCl_x$(*p*-cymene)(triazol-5-ylidene)	64	110	45	48	52	[24]
$Ru{=}CHPhCl_2(PCy_3)_2$	5	110	33	15	85	[33]
$Ru{=}CHPhCl_2(PCy_3)$(triazol-5-ylidene)	4	110	78	90	10	[37]
$RuCl_2(PPH_3)_2$(triazol-5-ylidene)	0.5	110	100	80	20	[32]
$[Ir(cod)Cl]_2$	15	100	95	81	19	[36]
$Ru{=}CHPhCl_2(PCy_3)$(IPr)	8	65	82	84	16	This study

of 1-octyne in the presence of the Ru complex proceeded, surprisingly, at 20 °C. The reaction yield stayed constant after 72 h, with a yield of 82%. At the same temperature, 1-heptyne produced a 55% yield of the products after 72 h. The reaction using 1-pentyne, however, which has a shorter backbone as compared to 1-heptyne and 1-octyne, resulted in only a 20% yield after the same period of time, and some oligomeric product formation was also observed.

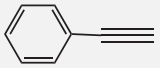
The same alkyne set was tested using a molar ratio of the catalyst and alkyne of 1:25 (catalyst:alkyne) at 65 °C, again without solvent. The reaction yield for the reaction of 1-octyne reached 94% after 6 h, giving the homodimerisation products with a high gem selectivity (94:5:2, gem:*Z*:*E*). The homodimerisation reaction was also attempted using 1-heptyne and 1-pentyne. The reaction of the Ru complex with 1-heptyne resulted in a 77% with a high selectivity for the gem product (84:4:12, gem:*Z*:*E*), whereas the reaction involving 1-pentyne resulted in only a 20% yield of the homodimerisation product, with some oligomerisation products also visible after 24 h. The Ru complex was also tested in the homodimerisation reaction of phenylacetylene, the yield of this reaction was 82% at 20 °C and required 72 h, whereas at 65 °C the reaction was completed within 1.5 h with an isomer content of 9:90:1 (gem:*Z*:*E*). A comparison of the homodimerisation reaction of phenylacetylene with various catalyst systems, in different reaction conditions and the enyne yield and selectivity is shown in Table 5.

$RuCl_2(=C=CHPh)(PPr_3)_2$ catalysed the homodimerisation of phenylacetylene at room temperature after 3 h with a total yield of 99% and producing 97% of the tail-to-tail isomer [38]. However, this catalyst system required the addition of a base. The $Ru{=}CHPhCl_2(PCy_3)_2$ catalyst resulted in a yield of 21% after 5 h at 110 °C, producing 92% of the tail-to-tail isomer [33]. The Ru=



Scheme 3. Addition reactions of trans 2-octenoic acid and 4-cyclooctenoic acid to terminal alkynes.

Table 4
Homodimerisation reaction conditions and product distributions of terminal alkynes.

Alkyne	T (°C)	Time[a] (h)	Yield[b,c] (%)	Gem (%)	*Z* (%)	*E* (%)
C_6H_{13}—	65	6	94	94	5	2
	20	72	82	92	6	2
C_5H_{11}—	65	5	77	84	4	12
	20	72	55	82	5	13
	65	1.5	100	9	90	1
	20	72	82	9	86	5

[a] Time represents the time period at which the conversion reaches a plateau or is complete.
[b] Yield and selectivity is determined by GC-MS.
[c] Reactions are carried out in free solvent media, 4% catalyst loading.

$CHPhCl_2(PCy_3)$(triazol-5-ylidene) catalyst, which contains NHC ligands, resulted in a 33% yield with a head-to-tail isomer selectivity of 98% after 4 h at 110 °C [37]. When compared to this catalyst, our catalytic system results in a 100% yield in the homodimerisation reaction of phenylacetylene, occurring within 8 h at 65 °C and producing 90% of the tail-to-tail (*Z*) isomer without any base addition.

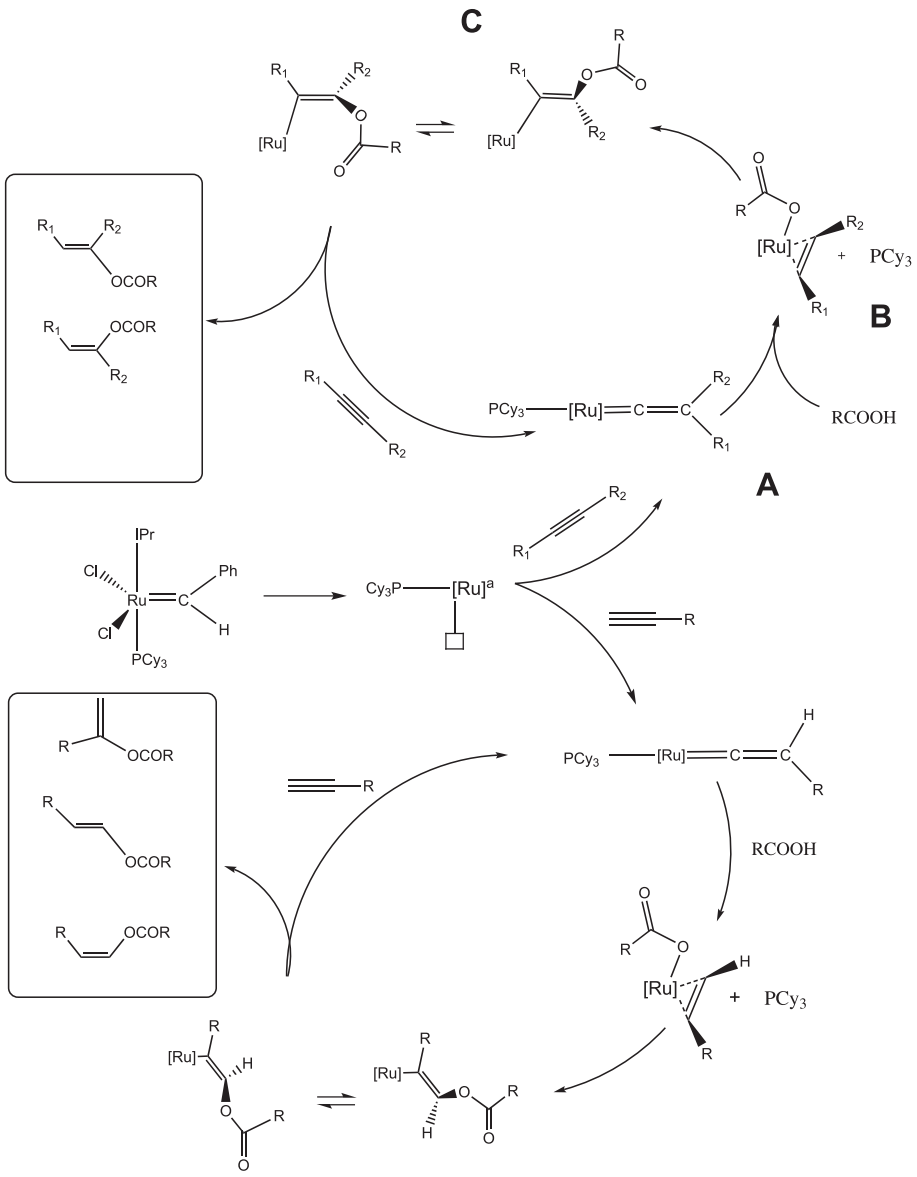
From comparing the aliphatic terminal alkynes used in this study, including 1-octyne (C_8H_{14}), 1-heptyne (C_7H_{12}) and 1-pentyne (C_5H_8), we can easily conclude that increasing the backbone length of the alkyne favours the homodimerisation reaction of these alkynes in the presence of our Ru complex under the given reaction conditions. These results also show that the rate of enyne formation at 20 °C is fairly slower than that at 65 °C. In addition, we observed that when increasing reaction temperatures, the regio and stereoselectivity of the reaction remain the same. However, the selectivity of the reaction does change with the nature of the alkyne. While the major homodimerisation products of alkyl acetylenes are gem-selective (~90%), the reactions of arylalkyne, phenylacetylene, give highly Z-selective products (~90%).

2.4. Spectroscopic investigation of reaction pathways

^1H NMR and ^{31}P NMR studies were carried out to further understand the catalytic activity of Ru complexes in the carboxylic acid addition reaction with internal alkynes. For this aim, an NMR tube was charged with 0.02 g of the Ru complex, which was dissolved in $CDCl_3$ at 65 °C. The disappearance of peak at 19.6 ppm, belonging to the benzylidene ligand, was confirmed by ^1H NMR. After this, a mixture of ten equivalents of the 4-octyne and one equivalent of the acid was added and the solution was stirred at 65 °C for 3 h, after which a new coordinated PCy_3 signal and a free

Table 5
A comparison for homodimerisation of phenlacetylene using various catalyst systems.

Catalyst	Time (h)	Temperature (°C)	Yield (%)	HT (%)	TT (%)	Refs.
$RuCl_x$(*p*-cymene)(triazol-5-ylidene)	8	110	53	42	58	[24]
$RuCl_x$(*p*-cymene)(triazol-5-ylidene)	64	110	60	10	90	[24]
$[RuH(CH_3CN)(NP_3)]OTf$	11	110	92	0	100	[26]
$Ru{=}CHPhCl_2(PCy_3)_2$	5	110	21	8	92	[33]
$Ru_2(\mu\text{-}CH_2)(CO)_4(\mu\text{-}dppm)_2$	24	75	69	100	0	[40]
$RhCl(PPh)_4$	30	20	34	59	41	[39]
$Ru{=}CHPhCl_2(PCy_3)$(triazol-5-ylidene)	4	110	33	98	2	[37]
$RuCl_2(=C=CHPh)(PPr_3)_2$	3	20	99	3	97	[38]
$Ru{=}CHPhCl_2(PCy_3)$(IPr)	8	65	100	10	90	This study



Scheme 4. Assumed reaction mechanism for addition reactions of carboxylic acids with internal and terminal alkynes ([a]: [Ru] represents RuL_n the unidentified intermediate).

phosphine signal were observed in the ^{31}P NMR spectrum. The formation of a new peak at 66.1 ppm in the ^{31}P NMR spectrum confirmed the presence of the newly coordinated PCy_3 ligand. Although we were able to confirm benzylidene ligand cleavage, we failed to isolate the catalyst, and thus the exact nature of the active species remains unclear. Our proposed mechanism is shown in Scheme 4. We believe that the reaction proceeds by a mechanism similar to that of Ru-catalysed carboxylic acid addition to terminal alkynes [35]. Coordination of the internal alkyne to the ruthenium centre affords intermediate **A**. Addition of carboxylic acid results in PCy_3 cleavage, forming a new intermediate **B**. Finally, C–O coupling results in the formation of isomeric products.

3. Conclusion

A systematic investigation of the addition reaction of carboxylic acids with internal and terminal alkynes, catalysed by Ru=$CHPhCl_2(PCy_3)(IPr)$, was studied. Results indicated a decreasing reaction rate for trichloroacetic acid addition to terminal and internal alkyne. The pattern in the reaction rate is as follows: 1-octyne > 1-heptyne > 1-pentyne > 2-hexyne > 3-hexyne > 4-octyne. The rates of the homodimerisation reactions of terminal alkynes followed a pattern as follows: phenylacetylene > 1-octyne > 1-heptyne > 1-pentyne. The nature of the alkyne has a strong influence on the reaction regioselectivity: phenylacetylene shows very high Z-selectivity, whereas alkyl acetylenes have gem selectivity. In addition, the reactions of trans-2-octenoic acid and the other acids showed that not only is the nature of the alkyne important, but the nature of the carboxylic acid also has a significant role in determining the isomer selectivity of carboxylic acid addition to terminal alkynes.

4. Experimental

4.1. Materials

1-octyne, 1-heptyne, 1-phenylacetylene, 4-octyne, 2-hexyne, 3-hexyne, trichloroacetic acid and acetic acid were purchased from

Merck and used as received. The ligand (IPr: 1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene) and the Ru complex $Ru{=}CHPhCl_2(PCy_3)(IPr)$ were synthesised according to previous literature methods [41–43].

4.2. Instrumentation

^1H NMR and ^{31}P NMR spectra were recorded at 25 °C with a Bruker GmbH 400 MHz high performance digital FT NMR spectrometer using $CDCl_3$ as solvent. Tetramethylsilane was used for the ^1H NMR reference and H_3PO_4 for the ^{31}P NMR reference. GC-MS analyses were performed with a Shimadzu GCMSQP5050A using an Optima column-5, 1.0 μm (50 m × 0.32 mm), and a temperature range of 50–300 °C (15 °C/min). The carrier gas was helium with an elution rate of 1 mL/min.

4.3. General procedure for carboxylic acid addition reactions

The alkyne (0.58 mmol) and 4 mol equivalents of the acid (2.29 mmol) were added to a pre-heated reactor. After addition of Ru-catalyst (0.02 g, 0.023 mmol), the reaction mixture was stirred at 65 °C under an atmosphere of nitrogen. In order to determine the yield and product distributions, small samples were periodically drawn out from the solution and analysed by the GC-MS. The structural identifications were carried out by ^1H NMR analysis on samples withdrawn from the reaction mixtures at maximum yield.

4.4. General procedure for homodimerisation reactions

The Ru-catalyst (0.02 g, 0.023 mmol) and the terminal alkyne (0.58 mmol) were added to a pre-heated reactor. The reaction mixture was stirred at 65 °C under an atmosphere of nitrogen. In order to determine the yield and product distributions, small samples were periodically drawn out from the solution and analysed by the GC-MS. The structural identifications were carried out by ^1H NMR analysis on samples withdrawn from the reaction mixtures at maximum yield.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.05.018.

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