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Addition of carboxylic acids to alkynes catalysed by ruthenium complexes

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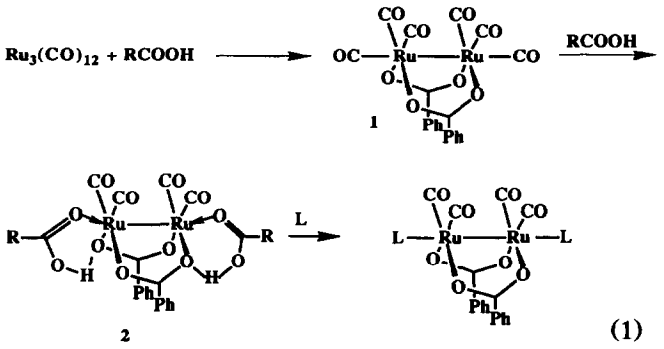
Abstract

The addition of carboxylic acids to alkynes has been found to be catalyzed by $Ru_3(CO)_{12}$ as well as by dimeric ruthenium carboxylate complexes of general structure $[Ru(RCOO)(CO)_2(L)]_2$. The reaction yields vinyl esters. It was found to be general with respect to both the acid and the alkyne. A rearranged regioisomer vinyl ester is also formed in the reactions with phenylacetylenes. A stereospecific kinetically controlled *syn*-addition of the carboxylic acid to the triple bond has been observed. Regioselectivity with asymmetrical alkynes is poor. Observation of an order of reaction of 1/2 with respect to $[Ru(PhCOO)(CO)_2(PhCOOH)]_2$, the catalyst, indicates that the active catalytic species are mononuclear ruthenium complexes. A stoichiometric reaction modelled on the catalytic reaction was monitored by infrared spectroscopy and finally quenched with PPh_3. The quenching products were identified as new mononuclear ruthenium complexes, and these identifications greatly facilitated understanding of the mechanism leading to a suggested catalytic cycle.

1. Introduction

The chemistry of dodecacarbonyltriruthenium(0) and carboxylic acids has been studied by us [1] and others [2]. In a recent report [1b] a reactivity pattern depending on the type of the carboxylic acids was revealed. The initial central reaction (eqn. (1)) gives complexes of type **1**, which are the primary products.



1 **2** (1)

In the presence of CO and acid, **1** and **2** are in equilibrium. The molecular structure of **2** (R = Ph) was determined by X-ray crystallography [1b,c]. It has a unique structure having both η^2-carboxylato and η^1-carboxylic acid ligands bound to the same Ru atom. A family of such complexes was prepared and characterized [1b]. With straight chain aliphatic acids, **1** does not give **2** but readily polymerizes to give complexes of the type $[Ru(RCOO)_2(CO)_2]_n$. With aromatic and branched aliphatic acids such polymerization is inhibited, and complexes of type **2** were isolated. Water and amines, and phosphine ligands (L) can replace the side-bound carboxylic acid in **2** as well as the CO groups in **1**, giving rise to complexes of the type $[Ru(RCOO)(CO)_2(L)]_2$ (eqn. (1)).

We undertook the above investigation [1b] in order to aid the study of a previously described reaction [3], namely the addition of carboxylic acids to alkynes catalyzed by $Ru_3(CO)_{12}$ (eqn. (2)).

$$RCOOH + R'C{\equiv}CR' \rightarrow \underset{(3)}{RCOO(R')C{=}CHR'} + \underset{(4)}{RCOOCH{=}CR'_2} \quad (2)$$

The products of the above reaction are *E* and *Z* isomers of the vinyl ester, **3**, and a rearranged vinyl ester isomer, **4**. In the present work we have found that the chemo, regio-, and stereo-selectivities range from formation of a single product to that of a mixture of

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TABLE 1. Addition of carboxylic acids to alkynes [a]

Run	Alkyne	Acid	Catalyst	Time (h)	Conv. [b] (%)	Distribution (%) [c]		
						E	*Z*	Rearr [e]
1	$(^nPr)_2C_2$	MeCOOH	$Ru_3(CO)_{12}$	17	92	100		
2	$(^nPr)_2C_2$	PhCOOH	$Ru_3(CO)_{12}$	17	92	100		
3	$(^nPr)_2C_2$	*p*-FC_6H_4COOH	$Ru_3(CO)_{12}$	4	90	100		
4	$(MeO_2C)_2C_2$	MeCOOH	$Ru_3(CO)_{12}$	17	95	100		
5	$(MeO_2C)_2C_2$	PhCOOH	$Ru_3(CO)_{12}$	17	95	100		
6	Ph_2C_2	MeCOOH	$Ru_3(CO)_{12}$	22	55	82	9	9
7	Ph_2C_2	MeCOOH	$[Ru(MeCOO)(CO)_2]_n$	19	50	85	7	8
8	Ph_2C_2	Me_3CCOOH	$Ru_3(CO)_{12}$	20	77	87	13 [d]	
9	Ph_2C_2	PhCOOH	$Ru_3(CO)_{12}$	17	81	14	65	21
10	Ph_2C_2	PhCOOH	$[Ru(MeCOO)(CO)_2]_n$	20	66	20	60	
11	Ph_2C_2	*p*-FC_6H_4COOH	$Ru_3(CO)_{12}$	11	85	22	26	52
12	Ph_2C_2	*p*-MeC_6H_4COOH	$Ru_3(CO)_{12}$	19	80	88	8	4

[a] [Alkyne] = [Acid] = 0.2 M; $[Ru_3CO_{12}]$ = 0.004 M; $[Ru(MeCOO)(CO)_2]_n$ = 0.012 M in toluene. The reaction was carried out at 145°C within a glass sleeve under nitrogen in a closed stainless steel reactor.
[b] The extents of conversion of the alkynes were determined by GLC analysis using an internal standard.
[c] The isomer distribution was determined from the areas of their respective GLC peaks.
[d] The rearranged and the Z isomers have identical GLC retention times, and together they formed 13% of the product mixture.
[e] Rearranged vinyl ester isomers of type **4** (see text).

the three vinyl ester isomers, depending on the alkyne and carboxylic acid used. Carboxylic acids are known to add to alkynes in the presence of Hg salts and strong acids [4], Lewis acids [5], Ag salts [6], strong acids [7], or Pd^{II} in the presence of triethylamine [8].

Following our report of the $Ru_3(CO)_{12}$-catalyzed addition of carboxylic acids to alkynes [3], Watanabe *et al.* [9] described the same reaction with bis-(cyclopentadienyl)Ru^{II} as catalyst in the presence of tributylphosphine and maleic anhydride; good yields and selectivity were obtained in most cases. They proposed a mechanism whereby a carboxylate anion attacks a coordinated alkyne [9].

In the present study we have investigated qualitative and quantitative aspects of the reaction [3] shown in eqn. (2), as well as its mechanism and the catalytic cycle. No reaction was detected in the absence of the ruthenium catalyst.

2. Results and discussion

The results obtained for reaction (2) with various acids, alkynes, ruthenium catalysts, and experimental conditions are listed in Tables 1 and 2. The features of the results are discussed below.

2.1. The alkyne

From Table 1 (and also Table 2) it is clear that the addition reaction is general with respect to the nature of the alkyne. Both electron poor and rich alkynes such as dimethyl acetylenedicarboxylate (DMAD) and 4-octyne react. Figure 1 indicates the following order of reactivity: 4-octyne > DMAD > Ph_2C_2, with a maximum rate factor of *ca.* 3. Monosubstituted alkynes (Table 2) are substantially more reactive than disubstituted ones.

TABLE 2. Addition of benzoic acid to asymmetrical alkynes catalyzed by $Ru_3(CO)_{12}$ [a]

Run	Alkyne	Time (h)	Conv. [b] (%)	Distribution of isomers (%) [c]					
				Markovnikov		anti-Markovnikov		Rearr [d]	
				E	*Z*	*E*	*Z*	*E*	*Z*
13	PhC≡CH	17	96	23		15	62		
14	$^nBuC{\equiv}CH$	20	96	59		20	20		
15	$^nC_5H_{11}C{\equiv}CPh$	20	86	33	trace	43	5	15	trace

[a] [Alkyne] = [Acid] = 0.2 M; $[Ru_3(CO)_{12}]$ = 0.002 M (for Run 13), 0.004 M (for Runs 14 and 15). Reaction conditions as described in footnote a, Table 1.
[b] Extents of conversions were determined by GLC analyses with an internal standard.
[c] Isomer distribution was determined from the ratios of the areas of their GLC signals.
[d] Rearranged vinyl ester isomers of type **4** (see text).

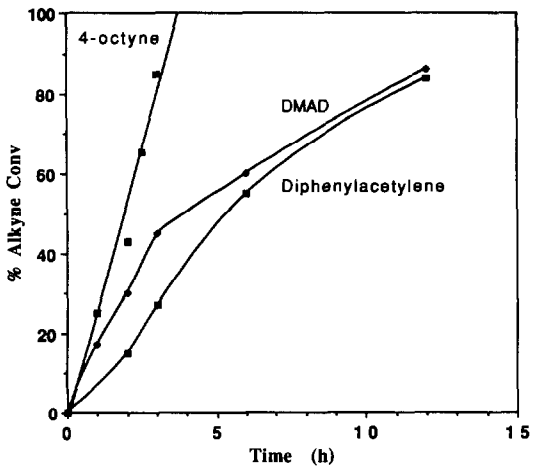


Fig. 1. Rates of reaction of benzoic acid with various alkynes. Conditions: [alkyne] = [PhCOOH] = 0.2 M; [{Ru(PhCOO)(CO)$_2$-PhCOOH}$_2$] (**5a**) = 0.006 M; internal standard [*cis*-Decalin] = 0.08 M in toluene at 110°C.

2.2. The acid

The rate of conversion of diphenylacetylene to vinyl esters was found to depend to some extent on the nature of the carboxylic acid used. The following order was established from the data in Table 1: *p*-FC_6H_4COOH > PhCOOH > *p*-MeC_6H_4COOH > Me_3CCOOH > MeCOOH (Runs: 6, 8, 9, 11 and 12). This order roughly follows the order of acidity of the acids used. In Run 6 (Table I) when acetic acid was used, the acetato polymer complex [Ru(MeCOO)$(CO)_2]_n$ separated from the reaction mixture. It was collected at the end of the reaction and successfully recycled not only with acetic acid (Run 7, Table 1) but also with benzoic acid (Run 10, Table 1). Among the acids used, only with acetic acid was the reaction heterogeneous in the catalyst. Nevertheless, the catalyzed addition reaction could be carried out with a wide variety of carboxylic acids.

2.3. The rearranged isomer

It is evident from tables 1 and 2 that the rearranged isomer of the general structure **4** is formed only with aromatic alkynes (Runs 6–12, Table 1, and Run 15, Table 2). With phenylacetylene (Run 13, Table 2), it is impossible to distinguish between normal and rearranged isomers. In separate experiments, (*E*)- and (*Z*)-1-benzoyloxy-1,2-diphenylethylene were each subjected to the original reaction conditions; no 1-benzoyloxy-2,2-diphenylethylene, the rearranged isomer, could be detected. Also, when Run 9 (Table 1) was carried out at two different temperatures there was no change in the ratio of normal to rearranged isomer. These results indicate that the rearranged vinyl ester isomer is a primary reaction product. For the acids used, the rate of formation of the rearranged isomer follows the order: *p*-FC_6H_4COOH > PhCOOH > aliphatic acids. This observation is of importance in analyzing the mechanism of formation of the rearranged vinyl esters (*vide infra*).

2.4. Stereochemistry

The stereochemical mode of addition of the carboxylic acids to a triple bond is a very important guide to the reaction mechanism. With the symmetrical alkynes of Table 1, the formation of an *E*-vinyl ester product implies *syn* addition to the triple bond and, indeed, stereospecific *syn* addition of a variety of acids to 4-octyne and DMAD was observed (Table 1). The single isomer, (*E*)-4-acetoxy-4-octene (Run 1, Table 1) was identified by comparing the chemical shift (^{1}H NMR) of its vinylic H ($\delta = 5.13$) with that for the *Z*-isomer ($\delta = 4.95$), obtained by acetoxymercuration of 4-octyne [10], followed by reduction with zinc. The *E*-stereochemistry of 4-benzoyloxy-4-octene was established by NOE, which was detected between the vinyl H and C-6 (and not C-3) methylene protons (4.4%) as well as between the C-3 and C-5 methylene protons (1%).

With the vinyl esters of 4-octene it was not clear *a priori* which isomer is thermodynamically the more stable. It was found that the *E*-stereoisomers that were stereospecifically generated with the various acids must be the kinetically stable isomers as well as the kinetically controlled products. Thus, heating (*E*)-4-benzoyloxy-4-octene in toluene for 17 h at 145°C in the presence of $Ru_3(CO)_{12}$ (closed reactor) resulted in an *E*/*Z* ratio of 86/14. The chemical shift of the vinylic H of the new isomer ($\delta = 5.12$ ppm), compared with that of the *E*-isomer ($\delta = 5.25$ ppm), confirms the assigned stereochemistry. (*E*)-4-acetoxy-4-octene decomposed under the above conditions (no acid was present in the above two experiments).

DMAD and benzoic acid (Run 5, Table 1) give a single isomer of dimethyl α-benzoyloxymaleate. The *E* configuration was assigned to it on the basis of the chemical shift of its vinylic H ($\delta = 6.24$ ppm), compared to 6.79 ppm for the *Z* isomer isolated from a different reaction (*vide infra*).

DMAD adds acetic acid stereospecifically to give (*E*)-dimethyl-α-acetoxymaleate (Run 4, Table 1), compared with the 90% selectivity (*E*-isomer) and 60% yield observed with silver salts as catalysts [6].

All the experiments with diphenylacetylene resulted in the formation of a mixture of *E*, *Z* and the rearranged stereoisomers (Table 1). Thus, all isomers of α-acetoxystilbene were identified by comparison with literature data [11]. Their relative distributions were determined by GLC and NMR analyses. That the

Z-isomer, obtained by the addition of carboxylic acids to diphenylacetylene is a thermodynamically controlled product while the E-isomer (*syn* addition) is a kinetically controlled product, was demonstrated by the following experiment. Refluxing of a mixture of diphenylacetylene, benzoic acid and $Ru_3(CO)_{12}$ in toluene for 12 h resulted in a mixture of α-benzoyloxystilbenes having a Z/E ratio of 0.037. Further heating of the above reaction mixture (17 h), but at 145°C (closed reactor), resulted in a Z/E ratio of 2.36. It is noteworthy that the concentration of the rearranged isomer remained constant throughout this experiment. The above results were confirmed by subjecting pure (E)-α-benzoyloxystilbene (after chromatographic purification) to the original catalytic reaction conditions. After 17 h at 145°C, a Z/E ratio of 2.33 was recorded. The variation in stereoselectivity (Table 1) may be attributed to the different thermodynamic properties of the various vinyl esters of stilbene. From the mechanistic point of view it is important to appreciate that ruthenium-based active catalytic species induce a stereospecific *syn* addition of carboxylic acids to the triple bond of alkynes. This stereoselectivity rules out simple Lewis acid type catalysis. Indeed, under the above experimental conditions, $RuCl_3$, *does not* induce addition of carboxylic acids to alkynes.

2.5. *Regioselectivity*

The regioselectivity of the catalytic addition of benzoic acid to a triple bond was examined with the following asymmetrical alkynes: 1-hexyne, phenylacetylene, and 1-phenyl-1-heptyne. It was analyzed in terms of Markovnikov (M) and anti-Markovnikov (AM) modes of addition, exemplified by eqn. (3) for a terminal alkyne (R′ = H). The results are presented in Table 2.

$$\mathrm{RC{\equiv}CR' + PhCOOH \rightarrow \underset{\text{Markovnikov (M)}}{PhCOO(R)C{=}CH_2} + \underset{\text{Anti-Markovnikov (AM)}}{RCH{=}C(R')OOCPh}\ \underset{(E)+(Z)}{} \qquad (3)}$$

(R = aryl, alkyl; R′ = H, alkyl)

With the terminal alkynes (Runs 13 and 14, Table 2) only the AM addition products can form E and Z isomers. Furthermore, it is impossible to distinguish between an AM and a rearranged isomer. The regioisomers and their stereochemistry were identified by the coupling constants of the vinylic protons in the ^1H NMR spectra.

It was important to determine whether the distribution of the regioisomers is kinetically controlled. To this end the percent distribution was examined as a function of the reaction time of the M and AM isomers of benzoyloxy styrene. The results are presented in Table 3.

TABLE 3. Addition of benzoic acid to phenylacetylene at 100°C [a]

Time (h)	Conv. [b] (%)	Isomer distribution (%) [c]	
		Anti-Markovnikov (E + Z)	Markovnikov
0.5	34	84	16
1.0	77	82	18
2.0	98	81	19
3.0	100	81	19

[a] [Phenylacetylene] = [Benzoic acid] = 0.2 M; $[Ru_3CO_{12}]$ = 0.002 M; other reaction conditions as described in footnote a, Table 1.
[b] Conversions were determined by GLC analyses with an internal standard.
[c] Isomer distribution was determined from the ratios of their GLC signals.

Clearly, the isomer ratio stays constant throughout the reaction, therefore the M and AM (or rearranged) isomers must be primary and not interconvertible reaction products. Also, comparing the results in Table 3 at 100°C and Table 2 (Run 13) at 145°C again reveals a constancy (within limits of experimental error) in the ratio of the two regioisomers. These results indicate that the two regioisomers are formed from a single intermediate.

The higher amount of the M isomer obtained with 1-hexyne (59%), compared to phenylacetylene (23%), was rather surprising (Table 2) since classical organic chemistry considerations would predict the opposite relationship. However, it is conceivable that the AM regioisomers (E and Z) of 2-benzoyloxystyrene (run 13, Table 2) are actually rearranged products. It is unlikely that the AM products from 1-hexyne (run 14, Table 3) have also been formed *via* rearrangement, as no such products were encountered with alkyl acetylenes such as 4-octyne.

Six isomers of benzoyloxy 1-phenyl-1-heptene were isolated and identified from the reaction of 1-phenyl-1-heptyne and benzoic acid (Run 15, Table 2). Two stereoisomers (E-isomer predominating) were obtained for each regioisomer, accompanied by two stereoisomers of the rearranged product (for structural assignment see Experimental section).

In conclusion, Runs 13 and 14 (Table 2) truly reflect the extent of the regioselectivity of the addition reaction which seems to be quite poor. The origin of this behaviour will be discussed later in terms of the proposed catalytic cycle.

3. Mechanism studies

From the preparative point of view, the most practical catalyst for reaction 2 is the commercially available

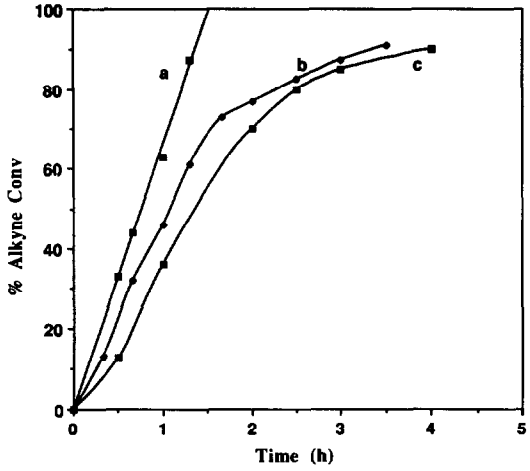


Fig. 2. Rates of reaction of 4-fluorobenzoic acid and 4-octyne with the following catalysts: a. $[Ru(4\text{-}FC_6H_4COO)(CO)_2(4\text{-}FC_6H_4\text{-}COOH)]_2$; b. $[Ru(4\text{-}FC_6H_4\ COO)(CO)_3]_2$; c. $Ru_3(CO)_{12}$. Conditions: [4-octyne] = [p-FC_6H_4COOH] = 0.2 M; [Ru] = 0.012 M; internal standard [naphthalene] = 0.08 M in toluene in a closed reactor at 145°C.

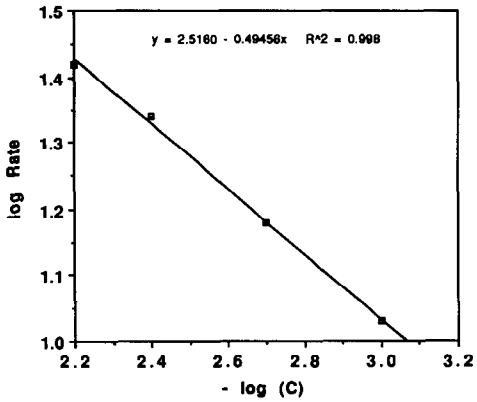


Fig. 3. Log plot of the rate of reaction of benzoic acid and 4-octyne as a function of the concentration of $[\{Ru(PhCOO)(CO)_2PhCOOH\}_2]$ (**5a**). Conditions: [PhCOOH] = [4-octyne] = 0.2 M; internal standard [*cis*-decalin] = 0.08 M in toluene at 110°C.

dodecacarbonyltriruthenium(0) complex. However, since the conditions of reaction (1) prevail during the catalysis, Ru_3CO_{12} was found to disappear in accordance with eqn. (1) at an early stage of the catalytic reaction (IR & TLC). Since complexes of type **2** (eqn. (1)) could be independently prepared and characterized [1b], it was of interest to examine their catalytic activity in the addition reaction of carboxylic acids to alkynes. Figure 2 presents comparative data for rates.

Identical Ru atom concentrations were used in the three experiments (Fig. 2). Significantly, Ru_3CO_{12} gives the lowest rate, especially at the beginning of the catalysis, with a tendency towards equality at longer reaction times. Similar studies using benzoic acid and DMAD with $[Ru(PhCOO)(CO)_2PhCOOH]_2$ (**5a**) and $[Ru(PhCOO)(CO)_2PPh_3]_2$ (**6**) revealed practically identical rates up to 75% conversion. Clearly, dinuclear complexes of type **5**, which are formed *in situ* from Ru_3CO_{12} in the presence of carboxylic acids [1b], are efficient catalysts for the addition of carboxylic acids to alkynes.

The dependence of the rate of addition (initial) of benzoic acid to 4-octyne on the concentration of the catalyst (**5a**) was studied. The results, displayed as a log plot (Fig. 3), indicate an order of 0.5 with respect to the catalyst. Such an order implies the dissociation, in the reaction mixture, of the dinuclear Ru complex into two catalytically active mononuclear species. Thus, under the reaction conditions, the starting trinuclear complex undergoes a transformation to di- and eventually mono-nuclear species, the latter being catalytically active.

This important mechanistic conclusion led us to look more closely at the mononuclear species, whose behaviour might shed light on the nature of the catalytic process. The dinuclear complexes $[Ru(PhCOO)(CO)_2PhCOOH]_2$ (**5a**) and $[Ru(PhCOO)(CO)_2PPh_3]_2$ (**6**) were selected for this study. Valuable information regarding catalytic reactions and catalytic species may be gained by examining stoichiometric reactions, thereby simplifying the investigation.

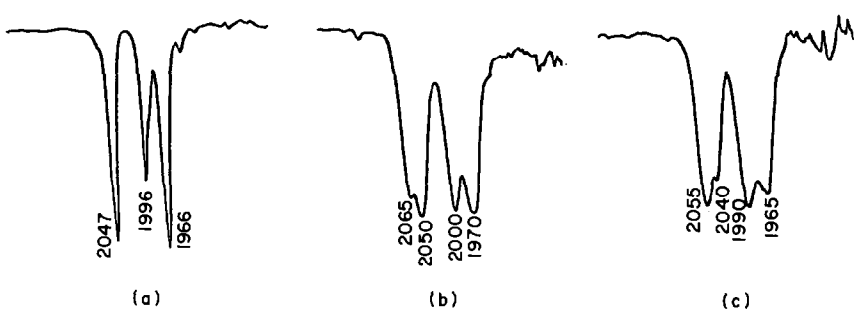


Fig. 4. Infrared spectral changes for a solution of $[Ru(PhCOO)(CO)_2PhCOOH]_2$ (**5a**) and DMAD in toluene: (a) at ambient temperature; (b) after 1 h reflux; (c) after addition of PPh_3.

Such an approach was undertaken in the present study using infrared spectroscopic monitoring. It was confirmed that the basic infrared spectral features of the catalytic and the stoichiometric reaction mixtures were similar. Several experiments under various conditions are described below.

3.1. Experiment 1

A solution of complex **5a** and DMAD (4 equiv.) in toluene was refluxed under nitrogen (no acid added). Several attempts to isolate stable complexes from this reaction mixture failed. Therefore, after cooling of the reaction solution to room temperature, triphenylphosphine was added in order to stabilize the system. The progress of the reaction was monitored by FTIR spectroscopy and the results are presented in Fig. 4. After 1 h (Fig. 4b) the spectrum (CO stretching bands) became constant, with four bands of equal intensity. Addition of PPh_3 shifted all four bands to lower wave numbers (Fig. 4c). At this point, chromatography of the reaction mixture on silica gave complexes **7a** [12] and **8a** in 30 and 4% yields, respectively, as well as five organic compounds (Scheme 1). The molecular structures of **7–9**, which are new compounds, will be discussed later. The above products (Scheme 1) are indicative of the nature of the reactions taking place during catalysis.

It is important to note that no trace of the starting complex (**5a**), nor of its phosphine derivative (**6**), could be detected in the final reaction mixture (after the addition of PPh_3). Significantly, although neither **7** nor **8** carries an alkyne (or a modified alkyne), it is an *alkyne* that induces a quantitative and fast fragmentation of the dinuclear complex $[Ru(PhCOO)(CO)_2PhCOOH]_2$ (**5a**). That such a fragmentation was not induced by the added triphenylphosphine was verified in a separate experiment, in which **5a** and PPh_3, under the above reaction conditions, were found to give only $[Ru(PhCOO)(CO)_2PPh_3]_2$ (**6**).

The infrared bands (CO stretching) of the isolated **7a** (2050, 1990 cm^{-1}) and **8a** (2040, 1970 cm^{-1}) are also present in the composite spectrum (Fig. 4c). However the near equal intensity of the above two sets of bands is at variance with the ratio of the isolated **7a** (30%) and **8a** (4%). This may indicate the presence, in the reaction mixture, of still another complex which has IR CO bands close to those of **8a** but which does not survive the isolation conditions (*vide infra*).

3.2. Experiment 2

Experiment 1 was repeated, but after the reaction mixture attained a stable infrared spectrum (Fig. 4b), two equivalents of benzoic acid were added, and heating was resumed for an additional 30 min. Now the infrared spectrum indicated the presence of the starting complex **5a**. Addition of triphenylphosphine followed by chromatography did indeed give $[Ru(PhCOO)(CO)_2PPh_3]_2$ (**6**), in addition to **7a** and **8a** (no attempt was made to isolate organic products).

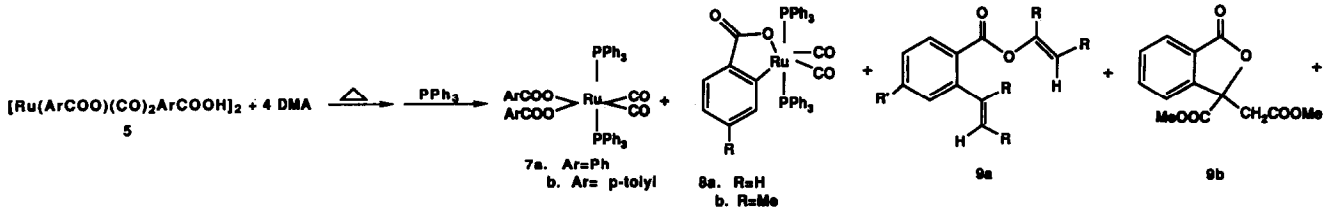
3.3. Experiment 3

Experiment 2 was repeated but, after addition of the acid and heating for 30 min as described above, 2 equiv. of DMAD were added, followed by additional heating. The infra red spectrum of the resulting solution reverted to that observed in Experiment 1 (Fig. 4b).

Although qualitative, the results from the above three experiments clearly indicate the existence of an equilibrium (eqn. (5)):

$$\mathbf{5a} + \mathrm{DMAD} \rightleftharpoons \mathbf{7'} + \mathbf{8'} + \mathrm{PhCOOH} \qquad (5)$$

We do not know the identity of **7'** and **8'** (derivatives of **7** and **8**), but when treated with PPh_3 they must have given rise to **7** and **8**, respectively. The original species **7'** and **8'** must be regarded as unstable participants in the catalytic cycle and their identification is an important objective of this study. They probably contain loosely bound alkyne ligands, which would account for the observed changes in the equilibrium of reaction 5 as described above. The same general behaviour was also observed on replacing DMAD by 4-octyne. However, with this alkyne the equilibrium described above was shifted somewhat to the left, as complex **5a** did not disappear completely (IR), consequently giving rise to



Scheme 1.

a small amount of **6** which was isolated after quenching with PPh_3. Thus, DMAD, an electron deficient alkyne, breaks down dimer **5a** more efficiently, or alternatively forms more stable fragmentation products, than 4-octyne (it is known that electron deficient π systems form stronger coordination bonds to transition metals [13]).

The extent to which the end-bound PhCOOH ligands play a role in the fragmentation of **5a** could be estimated from the experiments described below. $[Ru(PhCOO)(CO)_2PPh_3]_2$ (**6**), which lacks the end-bound acid ligand, exhibits the following behaviour in refluxing toluene: a. thermal stability; b. lack of reaction with added benzoic acid; c. lack of reaction with added excess of PPh_3 and d. stability in the presence of DMAD (in clear contrast to **5a**).

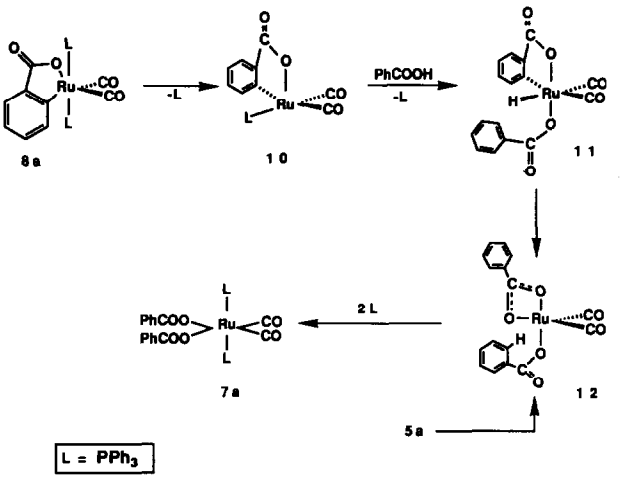
Only upon heating a toluene solution of **6** with *both* DMAD and PhCOOH did infrared spectral changes take place; addition of an excess of PPh_3 followed by chromatography gave the starting material **6** and **7**.

Similar behaviour was encountered using the acetato complex [2f] $[Ru(MeCOO)(CO)_2PPh_3]_2$ which gave the known complex [2a] $Ru(MeCOO)_2(CO)_2(PPh_3)_2$, iso-structural with **7**, in good yield.

The above results indicate that both an *alkyne* and *acid* are required for the fragmentation of the starting dinuclear complex. In the case of Experiment 1, the required acid is present as a side-coordinated acid ligand in **5a**.

The experiment described in Scheme 1 was also carried out with *p*-toluic acid thereby generating complexes **7b** and **8b**, which were important in structural elucidation (*vide infra*). The interconversion of **7b** and **8b** was examined, and when a solution of **8b** in toluene was refluxed with *p*-toluic acid for 1 h, **7b** was obtained quantitatively. The reverse reaction could not be effected simply by the heating of **7**, but, when heated in the presence of 2 equiv. of DMAD, the reaction solution gave infrared bands at 2075, 2040, 2010 and 1970 cm^{-1}.

The understanding of the above transformation (**8** to **7**) is of mechanistic importance. A possible reaction route based on established organometallic chemistry is depicted in Scheme 2 (L = PPh_3). Both **8a** and **7a** are coordinatively saturated Ru^{II} complexes. The transformation **8a** → **7a** involves the breaking of the Ru–C, which requires a proton. This can be provided by oxidative addition of benzoic acid to **10**, giving the hydrido complex **11**. Reductive elimination of benzene from **11** leads to **12**, which by switching of the hapticity of the carboxylato ligand from $\eta^2 \dashrightarrow \eta^1$ followed by ligation of L (PPh_3) generates the stable complex **7a**. Although **8a** is of structural interest, it is most probably of no relevance to the present catalytic system in as much as it has no counterpart with aliphatic carboxylic acids, and in the presence of an acid was found to be quantitatively and rapidly transformed into **7**. Complex **12**, probably with an additional ligand, must be generated from **5a** during the catalysis (*vide infra*). Although less active than **5a**, both **7a** and **8a** were found to be catalytically active for the addition of carboxylic acids to alkynes.

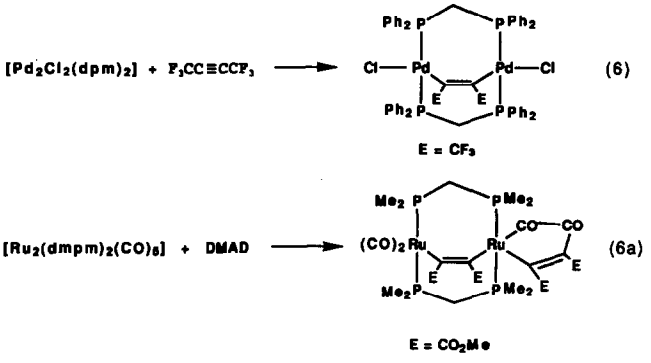


Scheme 2.

4. Mechanistic propositions

Granted that the active catalytic species are mononuclear, there are two related mechanistic problems to be *addressed*: a. specification of the fragmentation pathway for **5a**; and b. identification of the molecular species of the catalytic cycle and their mode of operation.

Regarding the first problem, an alkyne is required for the fragmentation of **5a** into mononuclear species (*vide supra*). Precedents were found for double oxidative addition of an alkyne to a M–M bond as depicted in eqn. (6) [13] and (6a) [14].



(6)

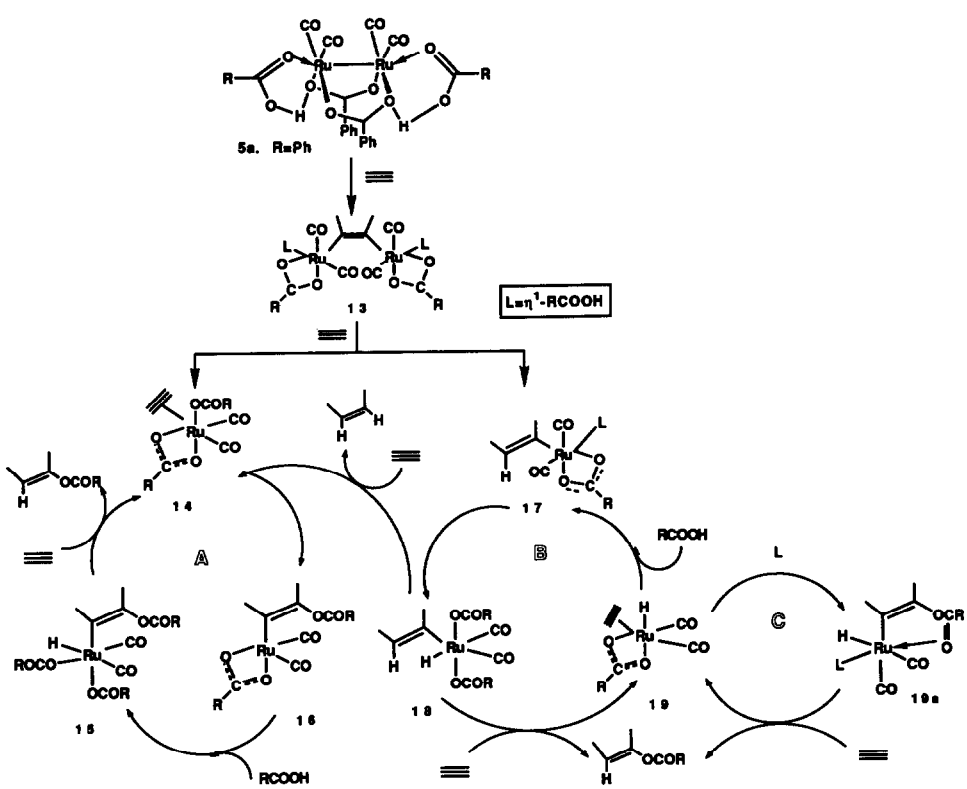
(6a)

As a working hypothesis we assume that the above reaction is the first step in the fragmentation of **5a**, as depicted in the first step of the catalytic cycle in Scheme 3. The scheme was constructed on the basis of the following facts and suggestions. a. the active catalytic species are mononuclear; b. the fragmentation of **5a** to mononuclear species requires both an alkyne and a carboxylic acid; c. the catalytic cycle must contain species that can be captured by triphenylphosphine, thus generating **8** with aromatic acids, and **7** with all types of acids; d. all transformations can be interpreted in terms of well known reactions in organometallic chemistry, specifically oxidative addition, reductive elimination and insertion reactions are of importance; e. alkynes and carboxylic acids are the reactants. In all cases their coordination to the metal centre is a prerequisite for their chemical interaction; f. metal bound (σ) carboxylic acids can undergo a facile rearrangement ($\eta^1 \rightleftharpoons \eta^2$) and may consequently function as one or three electron ligands; g. the Ru atom possesses an 18-electron configuration in most of the intermediates, and may be in either the 0, II or IV oxidation states.

The discussion is based on Scheme 3.

Addition of an alkyne to **5a** splits the Ru–Ru bond to generate a new dimer, **13**. The carboxylic acid ligands (L) are still side-bound to Ru in the η^1 coordination mode, as in the original complex **5a**. Now, in the presence of an alkyne, **13** fragments into the two mononuclear species **14** and **17**. This fragmentation may be viewed in terms of a three-stage process: a. vacation of a coordination site on one Ru atom (left side) by $\eta^2 \rightarrow \eta^1$ rearrangement of the carboxylato ligand; b. oxidative addition of the side bound η^1-RCOO-H (L) to the above Ru atom; c. reductive elimination of H-alkenyl generating simultaneously species **14** and **17**, with the latter stabilized by coordination of an alkyne molecule.

It is noteworthy that the overall fragmentation of **5a** requires both an alkyne and acid, in accord with our experimental findings. Complexes **14** and **17** are now the starting points for the three adjoining catalytic cycles A, B and C. These cycles may operate independently or concurrently at different rates. A cycle consumes an alkyne and a carboxylic acid and generates a vinyl ester as a product. Each cycle is driven by three chemical reactions at the Ru atom: insertion, oxidative addition, and reductive elimination. On demand, aided by the $\eta^2 \dashrightarrow \eta^1$ rearrangement of the σ-bound carboxylate ligand, a ruthenium coordination site may be either vacated (η^1 state) or occupied (η^2 state). Many experimental observations can be accounted for in terms of this minimum number of mechanistic features. It must



Scheme 3.

be stated at the outset that the mechanism whereby a metal-coordinated alkyne is attacked by a non-coordinated carboxylate anion, as proposed by Watanabe [9] for his system, must be ruled out in the present case. This must be so in view of the experimentally established *syn* addition (*vide supra*) of the elements of RCOO–H to the triple bond in our case, contrasting with the *anti* addition observed in Watanabe's system [9].

The principal difference between the three cycles in Scheme 3 is the order of the formal addition of the elements of carboxylic acid to the coordinated alkyne. Whereas in cycles A and C the addition of RCOO (**14** → **16**; **19** → **19a**) precedes that of H, in cycle B the order is reversed, *i.e.* the addition of H (**19** → **17**) precedes that of RCOO (**18** → **19**). Mechanistically, in cycles A and C the alkyne is inserted into the Ru–O bond, while in B it is inserted into the Ru–H bond. It is not a simple matter to estimate the relative rate of these two types of processes. Intermediate **19** is unique in having both insertion options to select from. Therefore **19** can serve as a common intermediate for cycles B and C. Complex **18** is also unique in having available two reductive elimination routes. One route (**18** → **19**) propagates cycle B, whereby oxygen and carbon are reductively eliminated. In the second route (**18** → **14**), hydrogen and carbon are reductively eliminated and alkene is formed. Indeed, when DMAD was used, dimethyl fumarate was isolated as a by-product in both the stoichiometric and the catalytic reactions (Scheme 1). The isomerization of dimethyl maleate to dimethyl fumarate under the experimental conditions is highly probable. It should be noted that while **19** can support both cycles B and C, the transformation **18** → **14** is unidirectional and may in principle terminate cycle B.

A related system was found to behave similarly [15]. Thus, diphenylacetylene inserts into the M–H bond of $HRu(CF_3COO)(CO)(PPh_3)_2$ to give the vinyl complex $Ru[C(Ph)=CHPh](CF_3COO)(CO)(PPh_3)_2$ (analogous to **17**), which in the presence of CF_3COOH yielded *cis*-stilbene and $Ru(CF_3COO)_2(CO)(PPh_3)_2$ (analogous to **14**).

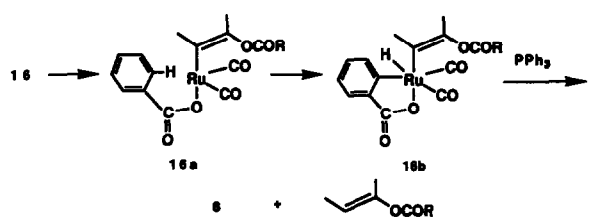
The Ru atom oscillates between the (II) and (IV) oxidation states in cycles A and B. Although as written, the oxidation state of the Ru atom in cycle C seems to be constant (II), when all intermediates are considered, it can be shown actually to oscillate between the values of (0) and (II).

The quenching of the chemical activity of Scheme 3 with PPh_3 should reveal some of its participants. Complexes of type **7**, isolated by quenching the catalytic as well as the stoichiometric reactions, constitute chemical evidence for the viability of complexes **15** in cycle A and **18** in cycle B. They are considered to be intercepted by PPh_3 along the reductive elimination routes: **15** → **14** and (or) **18** → **19**. These findings lend strong support to Scheme 3.

The reaction of complex **19** with added PPh_3 should have given rise to $HRu(RCOO)(CO)_2(PPh_3)_2$ (**19b**). Complexes of this type are known [16] but were found to be unstable in solution when exposed to air. The CO infrared stretching bands of **19b** ($R = CF_3$) [16b] are: 2048 and 1982 cm^{-1}. It should be recalled that in Fig. 4c the intensities of the infrared bands at 2040 and 1965 cm^{-1} were puzzling. Conceivably, most of the intensity of these bands could have arisen from complex **19b** (R = Ph), which was formed upon the quenching of the reaction mixture with PPh_3 (Scheme 1) and could be detected by IR but did not survive the isolation procedure.

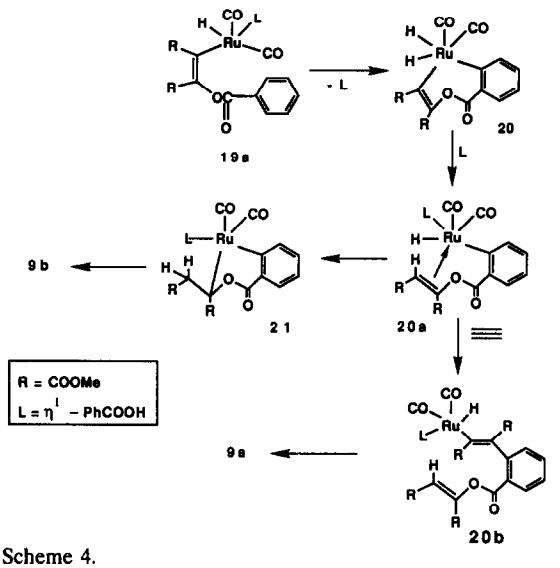
It should be noted that Scheme 3 includes three hydrido complexes, **15**, **18**, and **19**. The presence of Ru-hydrido complexes in the catalytic reaction mixture was confirmed by an NMR experiment. A solution of DMAD and **5a** in toluene-d_8 in an evacuated sealed NMR tube was kept at 100°C for 2 h. The ^1H NMR spectrum, recorded after cooling to ambient temperature showed three strong signals at $\delta = -18.1$, -18.3 and -18.4. Although we have no way of correlating these NMR data with any of the hydrido complexes of Scheme 3, these results support our proposed Scheme 3. It is noteworthy that both the quenching with PPh_3 and the NMR experiments revealed a group of *hydrido* complexes. Consequently, they must be fairly stable under the experimental conditions and their accumulation, which enables their detection, implies that the rate limiting steps are associated with their decomposition, rather than formation, in the catalytic reaction routes.

Complex **8**, also obtained in the quenching experiment (Scheme I), is believed to be generated from **16** (Scheme 3) by the following transformation:



Of course this transformation applies only to aromatic carboxylic acids, but is indicative of the presence of **16** in Scheme 3.

It is now necessary to consider the formation of **9a** and **9b**, which were presented in Scheme 1. These two organic products were isolated from the stoichiometric



Scheme 4.

reactions and detected in the catalytic reaction mixtures (NMR). A plausible route for their formation is presented in Scheme 4.

Scheme 4 starts with **19a** (from Scheme 3), which undergoes cyclometallation (oxidative addition) to give **20**, a dihydride species, which upon intramolecular reductive elimination of the alkene gives **20a**. Complex **21** is formed by an intramolecular insertion of the coordinated double bond into the Ru–H bond. Finally ring closure *via* a reductive elimination can generate the isolated **9b**.

Alternatively, insertion of an alkyne (subsequent to its coordination) into the Ru–C(Ar) bond of **20a** leads to **20b**, which upon reductive elimination of the alkenyl moiety generates the isolated **9a**. Thus **20a** serves as a common intermediate for formation of both **9a** and **9b**. It should be pointed out that traces of these products were detected (NMR) also in the *catalytic* reaction mixture involving DMAD and benzoic acid.

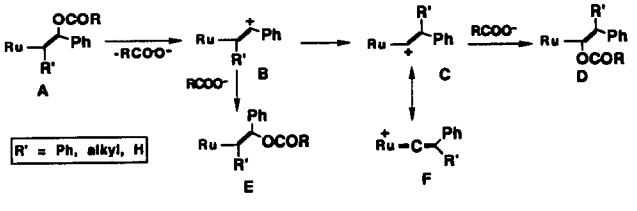
The successful logical accommodation of all five compounds outlined in Scheme 1 within the catalytic cycles of Scheme 3 is gratifying. We now consider the selectivity problems.

We should recall the lack of regioselectivity in the addition of carboxylic acids to the non-asymmetrical alkynes (Table 2), and the experimentally based claim for a single intermediate in the formation of the Markovnikov and anti-Markovnikov vinyl ester regioisomers. Given that in the insertion step the Ru atom always seeks the electron-rich end of the triple bond, then the regioselectivity will be determined by the order of the addition of the elements of RCOO and H to that bond. Therefore, a carboxylate followed by a hydride addition (cycle A and C) will necessarily generate a Markovnikov type addition product, while cycle B, characterized by the opposite addition order, will form the anti-Markovnikov products. Complex **19** (Scheme 3) satisfies the demand for a single intermediate in the reaction pathway leading to the two regioisomeric vinyl esters (*vide supra*). The extent of the regioselectivity will depend on the relative activities of the different cycles, and these are difficult to assess.

In terms of Scheme 3, the stereochemical outcome of the addition of carboxylic acid to the triple bond in the various alkynes is seen to depend on the stereospecificity of the insertion and reductive elimination steps. Insertions of π systems into M–H bonds are considered to proceed *via* a 4-membered transition state, thus yielding *syn* addition products with alkynes [17] (cycle B). We assume that this also applies in the case of the insertion of an alkyne into a Ru–O bond (cycles A and C). The final product in both cycles is obtained by reductive elimination involving the sp^2 carbon atom of the σ-bound alkene. Thus, a combination of *syn* insertion of the alkyne and retention of configuration on the eliminating sp^2 carbon atom means an overall kinetically controlled *syn* addition of RCOO–H to a triple bond, as indeed observed (*vide supra*).

Regarding the process whereby a rearranged vinyl ester isomer is formed, the following experimental facts should be recalled: a. at least one phenyl group should be bound to the sp carbon atom of the alkyne; b. the stronger the carboxylic acid used the faster is the rearrangement reaction; c. the rearranged vinyl ester isomer is a primary reaction product, probably formed from one of the intermediates of Scheme 3.

It is significant that the rearranged isomer is always accompanied by isomerization of the kinetically-controlled *E* vinyl ester to its *Z* isomer (entries 6–12, Table 1) although neither one of these vinyl esters is involved in its formation (*vide supra*). Formation of a vinyl cation followed by a 1,2 shift of a phenyl group are suggested in order to account for the formation of the rearranged isomer. Since the normal vinyl esters are stable under the experimental conditions, we conclude that the said rearrangement involves an alkyne-bound ruthenium intermediate. A mechanistic inter-



Scheme 5.

pretation is proposed in Scheme 5. In the Scheme, **A** represents a complex such as **15** or **19a** in Scheme 3. Dissociation of a carboxylate anion is a reasonable feature in carbocation chemistry, particularly when the dissociating group is α to a phenyl group, and the reaction medium is polar (acid). The experimental observation that stronger carboxylic acids lead to higher yields of the rearranged isomer (compare entries 6–12, Table 1) may be due to the fact that the conjugate base of a strong acid is a better ionizing group than that of a weak acid. A 1,2 shift of the migrating group R in **B** leads to a new carbocation **C**, which upon capturing a carboxylate anion will generate **D**, isomeric with **A**. Since this rearrangement has been observed with diphenylacetylene (R = Ph), 1-phenyl-1-heptyne (R = alkyl), and probably phenylacetylene (R = H), this must mean in terms of Scheme 5, that at least one Ph group is located α to the ionizing site, thereby providing the driving force for the transformation **A** → **B**. The driving force for the transformation **B** → **C** may have its origin in the stabilization of the latter by back-donation from an occupied Ru orbital to the adjacent empty carbon orbital described in terms of resonance structure **F**. In similar previously recorded transformations, phenylacetylene has been found to form a rearranged vinylidene complex *via* H migration (eqn. (7)) [18].

$$RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5) + PhCCH \xrightarrow{NH_4PF_6} [Ru(C{=}CHPh)(PPh_3)_2(\eta^5\text{-}C_5H_5)]PF_6 \quad (7)$$

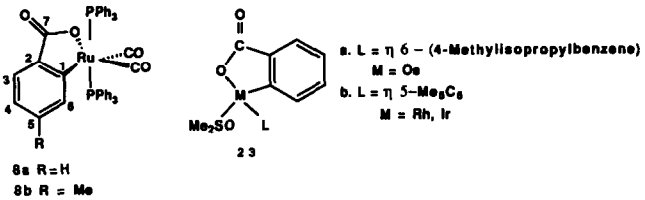
The transformation **B** → **E** accounts for the observed kinetic isomerization of the double bond. It should be noted that intermediate **A** can originate from cycles A and C only.

In conclusion, the catalytic addition of carboxylic acids to alkynes involves a complex series of chemical events. From the above discussion it is not possible to identify precisely the active catalytic cycle in Scheme 3, but adoption of Scheme 3 does allow us to place a large body of new experimental results in a framework of chemical logic, all soundly based on known organometallic chemistry.

5. Molecular structures

We finally consider the molecular structures of **7**, **8**, **9a** and **9b**, which were isolated from the stoichiometric reaction mixture (Experiment 1), as described by Scheme 1.

The molecular structure of **7a** (a new complex) was recently determined by X-ray crystallography [12]. This is the only X-ray structural study of this type of complex, and provides unequivocal proof of their stereochemistry. Thus, **7b** must be considered to be isostructural with **7a**. In the case of complexes **8a** and **8b**, all attempts to obtain crystals of X-ray quality failed. To the best of our knowledge, only three cyclometallated benzoic acid complexes of type **8** are known (**23a** and **23b**) [19]. The iridium complex **23b** was characterized by X-ray analysis [19a].



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The elemental analyses for **8a** and **8b** are made to agree with calculated values only by adding to the molecular formula one molecule of water. Negative DCI mass spectral analysis of **8b** gave a strong peak at m/z 788 (M^+–CO). The infra red data in dichloromethane are as follows; **8a**: 2040, 1970, 1640, 1620, 1580, 1490, 1440, 1310 cm^{-1}; **8b**: 2040, 1970, 1620, 1590, 1490, 1440, 1315 cm^{-1}. The two bands in the 2000 cm^{-1} region are indicative of two CO ligands, while the pair of bands in the 1600 and 1300 cm^{-1} region is assigned to the symmetric and antisymmetric stretching modes of the CO_2 moiety of the five-membered ring in **8a** and **8b**. The magnitude of the difference between the two frequencies in indicative of a *mono-hapto* Ru bound carboxylate.

NMR data were most informative. **8a**: ^1H NMR ($CDCl_3$): δ 6.71 (t, J = 7.3 Hz, H5); 6.79 (t, J = 7.3 Hz, H4); 7.19 (d, J = 7.3 Hz, H6); 7.46 (d, J = 7.3, H3); 6.96 and 7.53 (m, 30H, PPh_3). **8b**: ^1H NMR ($CDCl_3$): δ 2.06 (s, Me); 6.47 (d, J = 7.8 Hz, H4); 6.66 (d, J = 7.8 Hz, H3); 6.82 (s, H6); 7.27 and 7.35 (m, 30H, PPh_3).

The multiplet pattern for the signals from H atoms of the metallo-aromatic ring as well as the integration ratios between the latter and the PPh_3 H atoms, 4:30 in **8a** and 3:30 in **8b**, strongly support the structures proposed for these two compounds. Particularly convincing is the singlet for H6 at δ 6.82 in the spectrum of **8b**, which is due to the presence of a Me group at C5. ^{31}P-NMR ($CDCl_3$): δ 29.35 (**8a**); δ 30.47 (**8b**).

The ^{13}C-NMR spectral data for **8a** and **8b** are presented in Table 4. A low field signal at 171 ppm in the CMR spectrum was assigned to the Ru bound aromatic carbon atom of **8a** and **8b**. Its multiplicity (triplet) and the splitting magnitude, $^2J(P\text{–}C)$, confirm the presence of two equivalent PPh_3 groups. The two low field triplets at 194 and 204 ppm (CO) with identical splitting constant $^2J(P\text{–}C)$ indicate non-equivalence of the two CO ligands and a *cis* disposition of the latter relative to the two equivalent phosphine ligands, thus establishing the stereochemical relationship of all

TABLE 4. CMR data for **8a** and **8b** [a]

C atom	δ **8a**	δ **8b**
1	171.1(t,J(P-C) 10.9 Hz)	171.5 (t,J(P-C) 11.8 Hz)
2	142.3(s)	139.8(s)
3	129.9(d)	129.7(s)
4	122.4(d)	123.3(d)
5	130.5(d)	137.4(s)
6	137.2(d)	138.0(d)
Me	–	21.6(q)
COO	179.2(s)	179.6(s)
CO	194.4(t,J(P-C) 11.5 Hz)	194.6(t,J(P-C) 10.4 Hz)
CO	204.5(t,J(P-C) 11.5 Hz)	202.3(t,J(P-C) 11.8 Hz)
PPh_3		
1	130.6(d,J(P-C) 23.5 Hz)	130.6(d,J(P-C) 23.5 Hz)
2,6	133.9(t,J(P-C) 4.5 Hz)	133.9(t,br)
3,5	128.2(d)	128.2(d)
4	130.2(d)	130.3(d)

[a] Spectra were recorded in $CDCl_3$ solutions at 360 MHz.

the ligands around the Ru atom as depicted in structure **8**. Furthermore, there is an excellent agreement between CMR chemical shifts for the ring carbon of **8a** and **8b** and the reported ones for **23a** and **23b** [19]. It should be pointed out that **8a** and **8b** are the first reported examples of ruthenium *ortho*-metallated benzoate complexes.

The molecular structures of **9a** and **9b** were assigned from spectral data. Mass spectral data were satisfactory (see Experimental section). The ^{13}C NMR spectrum of **9a** exhibits four OMe signals, the ^1H-NMR two vinyl H signals and a pattern of four adjacent aromatic H atoms. All carbon atoms could be accounted for in the CMR spectrum of **9a** (see Experimental section). The *E* configuration was assigned to the two double bonds of **9a** since the chemical shifts of the two vinylic H atoms are practically identical (6.25 and 6.24 ppm) and equal to that of dimethyl α-benzoyloxymaleate (6.24 ppm). The ^1H NMR spectrum of **9b** exhibits two OMe signals, a pattern of four adjacent aromatic H signals, and an AB quartet for the methylene protons. All the carbon atoms could be accounted for in the CMR spectrum of **9b** (see Experimental section).

Finally, the addition of carboxylic acids to alkynes was briefly examined on a preparative scale (see Experimental section). The reactions were carried out with acetic acid as a solvent (and reactant), and α-acetoxy stilbene and α-acetoxy maleate were isolated in 64% and 37% yield, respectively.

6. Experimental section

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on a 360 MHz spectrometer with TMS as internal standard unless indicated otherwise; 85% H_3PO_4 solution was used as external standard for ^{31}P NMR measurements. Spin coupling values (*J*) are reported in Hz. IR spectra were recorded in methylene chloride solutions unless indicated otherwise.

6.1. Catalytic addition reactions of carboxylic acids to alkynes

The ruthenium dinuclear complexes were made as described elsewhere [1b]. The % conversions of the alkynes and distributions of the vinyl esters are listed in Tables 1 and 2 and were determined as described in the footnotes of these Tables. The conditions employed in the catalytic reactions experiments are also described in the footnotes of Tables 1 and 2. All catalytic runs were carried out by the typical procedure given below for run 1. GLC analyses for the reactions of 4-octyne, 1-hexyne and 1-phenyl-1-heptyne were carried out on 150 × 0.5 cm glass columns packed with 20% SE 30 on Gaschrom Q, while for the experiments with diphenylacetylene, phenylacetylene and dimethyl acetylenedicarboxylate the packing was 20% SE 30 on Chrom W, AW, DMCS.

The solvent from the final catalytic reaction mixtures was removed in vacuum and the residue was subjected to column chromatography on silica with mixtures of methylene chloride–petroleum ether (b.p. 60–80°C) as eluents. The results are described below.

6.1.1. Reaction of 4-octyne with acetic acid (Run 1, Table 1)

A solution in toluene of acetic acid (0.120 g, 2.0 mmol) and 1-methylnaphthalene (internal standard) was prepared in a 10 ml volumetric flask. The catalyst, $Ru_3(CO)_{12}$ (26 mg, 0.04 mmol) was weighed into a glass sleeve, in which a small magnetic bar was placed. The contents of the volumetric flask were transferred into a glass sleeve, which was inserted into a 35 ml stainless steel reactor equipped with a dip pipe for sampling. The reactor was purged with nitrogen, tightly closed, and then placed in a thermoregulated oil bath at 145°C equipped with a magnetic drive. Samples were withdrawn periodically in order to monitor the progress of the reaction (GLC). After 17 h the reaction was terminated by cooling the reactor to ambient temperature, and the extent of conversion was determined by GLC (Table 1). The final reaction mixture was heterogeneous. The solid precipitate was filtered off and identified as the polymeric $[Ru(OCOMe)(CO)_2]_n$. The filtrate was evaporated *in vacuo*, and the residue chromatographed on a silica column with mixtures of methylene chloride and petroleum ether as eluent to give a

* Reference number with an asterisk indicates a note in the list of references.

clear liquid, (*E*)-4-(acetoxy)-4-octene [20*], ^{1}H NMR (300 MHz): 0.94 (t, J = 7.4, Me), 0.95 (t, J = 7.4, Me), 1.44 (dq, J = 7.4, 4H), 2.04 (q, J = 7.4, 2H), 2.13 (s, Me), 2.25 (t, J = 7.4, 2H), 5.13 (t, J = 7.4, 1H). IR: 1750, 1680 cm^{-1}. MS: m/z 170 (M^+, 3%), 43 ($MeCO^+$, 100%).

6.1.2. Reaction of 4-octyne with benzoic acid (Run 2, Table 1)

After chromatography there was obtained (*E*)-4-(benzoyloxy)-4-octene, ^{1}H NMR: δ 0.94 (t, J = 7.5, Me), 0.96 (t, J = 7.3, Me), 1.45 (sext, J = 7.5, 2H), 1.51 (sext, J = 7.5, 2H), 2.1 (q, J = 7.3, 2H), 2.36 (t, J = 7.5, 2H), 5.26 (t, J = 7.3, 1H), 7.45 (t, J = 7.4, 2H), 7.58 (tt, J = 7.4 and 1.3, 1H), 8.09 (dd, J = 7.4 and 1.3, 2H). IR: 1720, 1685 cm^{-1}. MS: m/z 232 (M^+, 13%), 127 (M^+–105), 105 ($PhCO^+$, 100%).

(*Z*)-4-(benzoyloxy)-4-octene. A solution of (*E*)-4-(benzoyloxy)-4-octene (23 mg, 0.1 mmol), and $Ru_3(CO)_{12}$ (6 mg, 0.01 mmol) in toluene (1 ml) was heated in a sealed reactor at 145°C for 24 h. GC analysis indicated 13% of (*Z*)-(4-benzoyloxy)-4-octene. ^{1}H NMR of the mixture showed the following new signals: 0.88 (t, J = 7.4, Me), 1.40 (sext, J = 7.4, 2H), 1.95 (q, J = 7.4, 2H), 2.28 (t, J = 7.4, 2H), 5.12 (t, J = 7.4, 1H).

6.1.3. Reaction of 4-octyne with p-fluorobenzoic acid (Run 3, Table 1)

After chromatography there was obtained (*E*)-4-(4-fluorobenzoyloxy)-4-octene, ^{1}H NMR: 0.95 (t, J = 7.3, Me), 0.96 (t, J = 7.3, Me), 1.45 (sext, J = 7.3, 2H), 1.51 (sext, J = 7.3, 2H), 2.1 (q, J = 7.3, 2H), 2.36 (t, J = 7.3, 2H), 5.26 (t, J = 7.3, 1H), 7.11 (t, J = 8.5, 2H), 8.1 (q, J = 8.7 and 5.4, 2H). IR: 1730, 1690 cm^{-1}. MS: m/z 250 (M^+, 3%), 123 ($FC_6H_4CO^+$, 100%). A control experiment omitting the catalyst did not produce any noticeable chemical change.

6.1.4. Reaction of dimethyl acetylenedicarboxylate (DMAD) with acetic acid (Run 4, Table 1)

After chromatography there was obtained dimethyl-α-acetoxymaleate [21*], ^{1}H NMR: δ 2.18 (s, Me), 3.68 (s, Me), 3.73 (s, Me), 5.97 (s, 1H). ^{13}C-NMR δ 19.74q, 51.67q, 52.28q, 114.6 (d, =CH), 146.64 (s, =CO), 161.3s, 163.66s, 167.17s. IR (CCl_4): 1784, 1740, 1670 cm^{-1}. MS: m/z 171 (M^+–OMe, 2%), 143 (M^+–MeCOO, 73%), 113 (61%), 101 (76%), 43 ($MeCO^+$, 100%).

6.1.5. Reaction of dimethyl acetylenedicarboxylate (DMAD) with benzoic acid (Run 5, Table 1)

After chromatography there was obtained dimethyl-α-benzoyloxymaleate, ^{1}H NMR: δ 3.82 (s, Me), 3.87 (s, Me), 6.24 (s, 1H), 7.50 (t, J = 7.3, 2H), 7.66 (t, J = 7.3, 1H), 8.10 (d, J = 7.3, 2H). ^{13}C-NMR δ 52.0 (q, OMe), 52.7 (q, OMe), 115.3 (d, =CH), 128.6 (d, C3, C5), 130.2 (d, C2, C6), 133.9 (d, C4), 134.2 (s, C1), 147.3 (s, =CO), 161.5 (s, –COO), 163.5 (s, COOMe), 164.0 (s, COOMe). IR: 1740, 1670 cm^{-1}. MS: m/z 264 (M^+, 7%), 232 (M^+–MeOH, 4%), 205 (M^+–MeCOO, 100%).

6.1.6. Reaction of diphenylacetylene with acetic acid (Run 6, Table 1)

Chromatography of the reaction mixture gave three isomeric vinyl esters: a. (*E*)-1-(acetoxy)-1,2-diphenylethylene [10], ^{1}H NMR: 2.18 (s, Me), 6.45 (s, 1H), 7.14 (s, br, 6H), 7.33 (m, 4H). IR: 1760, 1680 cm^{-1}. MS: m/z 238 (M^+, 2%); b. (*Z*)-1-(acetoxy)-1,2-diphenylethylene [11a], ^{1}H NMR: d 2.30 (s, Me), 6.70 (s, 1H), 7.14 (s, br, 6H), 7.33 (m, 4H). IR: 1760, 1680 cm^{-1}. MS: m/z 238 (M^+, 2%); c. 1-(acetoxy)-2,2-diphenylethylene [11b], ^{1}H NMR. δ 2.13 (s, Me), 7.14 (br, 6H), 7.33 (m, 4H), 7.63 (s, 1H). IR: 1760, 1680 cm^{-1}. MS: m/z 238 (M^+, 2%).

6.1.7. Reaction of diphenylacetylene with pivalic acid (Run 8, Table 1)

Chromatography of the reaction mixture gave three isomeric vinyl esters, each contaminated by the other two: a. (*E*)-1-(trimethylacetoxy)-1,2-diphenylethylene, ^{1}H NMR (60 MHz): δ 1.27 (s, 9H), 6.43 (s, 1H), 7.17 (s, 6H), 7.35 (m, 4H). IR: 1760, 1680 cm^{-1}. MS: m/z 280 (M^+, 5%); b. (Z)-1-(trimethylacetoxy)-1,2-diphenylethylene, ^{1}H NMR (60 MHz): δ 1.35 (s, 9H), 6.72 (s, 1H), 7.17 (s, 6H), 7.35 (m, 4H). IR: 1760, 1680 cm^{-1}. MS: m/z 280 (M^+, 5%); c. 2,2-diphenyl-1-(trimethylacetoxy) ethylene, ^{1}H NMR (60 MHz): δ 1.18 (s, 9H), 7.17 (s, 6H), 7.35 (m, 4H), 7.70 (s, 1H, =CH). IR: 1760, 1680 cm^{-1}. MS: m/z 280 (M^+, 5%).

6.1.8. Reaction of diphenylacetylene with benzoic acid (Run 9, Table 1)

Chromatography of the reaction mixture gave three isomeric vinyl esters: a. (*E*)-1-(benzoyloxy)-1,2-diphenylethylene [22a], ^{1}H NMR: δ 6.60 (s, =CH), 7.18 (s, 6H), 7.29 (m, 2H), 7.50 (m, 5H), 8.15 (dd, J = 8.2 and 2.5, 2H). ^{13}C-NMR: 120.3 (d, HC=), 127.3d, 128.3d, 128.6d, 128.9d, 130.2d, 133.5d, 147.6 (s, =CO), 164.8 (s, COO); b. (*Z*)-1-(benzoyloxy)-1,2-diphenylethylene [22a], ^{1}H NMR: δ 6.80 (s, =CH), 7.30 (m, 6H), 7.58 (m, 7H), 8.23 (dd, J = 8.2 and 2.5, 2H). ^{13}C-NMR: 120.2 (d, =CH), 127.3d, 128.2d, 128.5d, 128.8d, 128.9d, 130.0d, 133.4d, 147.8 (s, =C–O), 165.1 (s, COO). MS: m/z 300 (M^+, 11%), 182 (Ph_2CO^+, 57%), 105 ($PhCO^+$, 100%); c. 1-(benzoyloxy)-2,2-diphenylethylene [22], ^{1}H NMR: δ 7.33 (s, 7H), 7.41 (s, 5H), 7.50 (m, 1H), 7.92 (s, =CH), 7.99 (dd, J = 7.6 and 2.0, 2H). ^{13}C-NMR: δ 127.8, 128.2, 128.5, 130.2, 132.5 (=CH), 133.6. MS: m/z 300

(M^+, 65%), 167 ($Ph_2C{=}CH^+$, 83%), 105 ($PhCO^+$, 100%); d. a mixture of (*E*) and (*Z*)-1-(benzoyloxy)-1,2-diphenylethylene in a ratio of 3:7 (GC analysis) resulted upon heating (*E*)-1-(benzoyloxy)-1,2-diphenylethylene (30 mg, 0.1 mmol) and $Ru_3(CO)_{12}$ (8 mg, 0.01 mmol) in toluene (2 mL) in a closed reactor at 145°C for 17 h (no rearranged isomer, 1-(benzoyloxy)-2,2-diphenylethylene, could be detected).

6.1.9. Reaction of diphenylacetylene with p-fluorobenzoic acid (Run 11, Table 1)

Chromatography of the reaction mixture gave three isomeric vinyl esters: a. (*E*)-1-(4-fluorobenzoyloxy)-1,2-diphenylethylene, ^1H NMR (90 MHz): δ 6.59 (s, =CH), 7.15 (m, 6H), 7.20 (t, $J = 8.5$, 2H), 7.44 (m, 4H), 8.20 (dd, $J = 8.9$ and 5.3, 2H). IR: 1725, 1670 cm^{-1}; b. (*Z*)-1-(4-fluorobenzoyloxy)-1,2-diphenylethylene, ^1H NMR (90 MHz): δ 6.80 (s, =CH), 7.15 (m, 6H), 7.20 (t, $J = 8.5$, 2H), 7.44 (m, 4H), 8.16 (dd, $J = 8.9$ and 5.4, 2H). IR: 1725, 1670; c. 1-(4-fluorobenzoyloxy)-2,2-diphenylethylene, ^1H NMR: δ 7.08 (t, $J = 8.1$, 2H), 7.33 (br, 6H), 7.40 (m, 4H), 7.89 (s, =CH), 7.98 (dd, J = 8.8 and 5.4, 2H). IR: 1725, 1670 cm^{-1}. MS: *m/z* 318 (M^+, 1.5%), 1.67 ($Ph_2C{=}CH^+$, 2%), 123 ($4\text{-}FC_6H_4CO^+$, 100%).

6.1.10. Reaction of diphenylacetylene with p-toluic acid (Run 12, Table 1)

Chromatography of the reaction mixture gave three isomeric vinyl esters: a. (*E*)-1-(4-methylbenzoyloxy)-1,2-diphenylethylene, ^1H NMR: δ 2.43 (s, Me), 6.59 (s, =CH), 7.27 (d, $J = 8.2$, 2H), 7.30 (m, 10H), 8.04 (d, $J = 8.2$, 2H); b. (*Z*)-1-(4-methylbenzoyloxy)-1,2-diphenylethylene was obtained in the trace amount in a mixture with a *E* isomer. Extra signals observed in ^1H NMR: δ 2.47 (s, Me), 6.79 (s, =CH); c. 1-(4-methylbenzoyloxy)-2,2-diphenylethylene, ^1H NMR: δ 2.40 (s, Me), 7.29 (d, $J = 8.5$, 2H), 7.38 (t, $J = 6.8$, 10H), 7.88 (d, $J = 8.5$, 2H), 7.90 (s, CH).

6.1.11. Reaction of phenylacetylene with benzoic acid (Run 13, Table 2)

Chromatography of the reaction mixture gave three isomeric vinyl esters: a. (*E*)-β-benzoyloxystyrene, ^1H NMR: 6.58 (δ, $J = 12.7$, 1H), 7.36 (t, $J = 7.3$, 2H), 7.48 (t, $J = 7.3$, 1H), 8.10 (d, $J = 12.7$, 1H), 8.14 (dd, $J = 7.3$ and 1.5, 2H). IR: 1740, 1660 cm^{-1}. MS: *m/z* 212; b. (*Z*)-β-benzoyloxystyrene, ^1H NMR (60 MHz): δ 5.83 (d, $J = 7.5$, 1H), 7.40 (m, 8H), 8.18 (d, $J = 7.5$, 1H), 8.15 (d, $J = 7.3$, 1H). IR: 1740, 1660 cm^{-1}. MS: *m/z* 212 (M^+); c. α-benzoyloxystyrene, ^1H NMR (60 MHz): δ 5.15(d, $J = 3$, 1H), 5.60 (d, $J = 3.1$, 1H), 7.45 (m, 8H), 8.28 (dd, $J = 7.5$ and 2.0, 2H). IR: 1740, 1660 cm^{-1}, MS: *m/z* 212 (M^+).

6.1.12. Reaction of 1-hexyne with benzoic acid (Run 14, Table 2)

The *E* and *Z* isomers emerged from the chromatographic column as a 1:1 mixture. a. (*E*)-1-(benzoyloxy)-1-hexene, ^1H NMR: δ 2.29 (dq, $J = 7.1$ and 1.2, 2H), 5.60 (dt, $J = 12.3$ and 7.5, 1H), 7.32 (d, $J = 12.5$, 1H); b. (*Z*)-1-(benzoyloxy)-1-hexene, ^1H NMR: 2.1 (dq, $J = 7.1$ and 1.2, 2H), 5.0 (q, $J = 7.1$, 1H), 7.27 (d, $J = 7.0$, 1H). IR (mixture): 1730, 1740, 1670 cm^{-1}. MS: *m/z* (mixture) 204 (M^+, 2%), 105 ($PhCO^+$, 100%); c. 2-(benzoyloxy)-1-hexene [9], ^1H NMR: δ 0.92 (t, $J = 7.2$, Me), 1.38 (sext, $J = 7.2$, 2H), 1.52 (quint, $J = 7.4$, 2H), 2.34 (t, $J = 7.4$, 2H), 4.83 (d, $J = 1.1$, 1H), 4.86 (d, $J = 1.1$, 1H), 7.46 (t, $J = 7.4$, 2H), 7.58 (t, $J = 7.4$, 1H), 8.09 (dd, $J = 7.4$ and 1.3, 2H). IR: 1740, 1670 cm^{-1}. MS: *m/z* 204 (M^+, 1%), 147 (5%), 134 (8%), 105 ($PhCO^+$, 100%).

6.1.13. Reaction of 1-phenyl-1-heptyne with benzoic acid (Run 15, Table 2)

Four major isomers of benzoyloxy 1-phenyl-1-heptene were separated and are listed in the order of emergence from the chromatography column: a. (*Z*)-1-(benzoyloxy)-2-phenyl-1-heptene, ^1H NMR: δ 0.86 (t, 7.3, Me), 1.30 (m, 4H), 1.49 (quint, $J = 7.3$, 2H), 2.46 (t, $J = 7.3$, 2H), 7.30 (t, $J = 7.1$, 1H), 7.36 (d, $J = 7.1$, 2H), 7.39 (s, 1H), 7.40 (m, 5H), 7.95 (dd, $J = 7.1$ and 1.3, 2H); b. (*E*)-1-(benzoyloxy)-2-phenyl-1-heptene, ^1H NMR: δ 0.86 (t, 7.3, Me), 1.34 (m, 4H), 1.49 (quint, $J = 7.3$, 2H), 2.74 (t, $J = 7.3$, 2H), 7.40 (s, br, 5H), 7.51 (t, $J = 7.4$, 2H), 7.63 (t, $J = 7.4$, 1H), 7.66 (s, 1H), 8.15 (dd, $J = 7.4$ and 1.3, 2H). IR: 1730, 1673 cm^{-1}. MS: *m/z* 294 (M^+, 3%), 196 (4%), 130 (12%), 122 (56%), 120 (57%), 105 ($PhCO^+$, 100%); c. (*E*)-2-(benzoyloxy)-1-phenyl-1-heptene, ^1H NMR: δ 0.84 (t, $J = 7.4$, Me), 1.29 (m, 4H), 1.57 (quint, $J = 7.4$, 2H), 2.62 (t, $J = 7.4$, 2H), 6.39 (s, 1H), 7.31, (m, 5H), 7.47 (t, $J = 7.4$, 2H), 7.60 (t, $J = 7.4$, 1H), 8.14 (dd, $J = 7.4$ and 1.4, 2H). IR: 1735, 1673 cm^{-1}; d. (*E*)-1-(benzoyloxy)-1-phenyl-1-heptene, ^1H NMR: δ 0.87 (t, $J = 7.4$, 3H), 1.29 (m, 4H), 1.47 (quint, $J = 7.4$, 2H), 2.28 (q, $J = 7.4$, 2H), 5.59 (t, $J = 7.4$, 1H), 7.32 (m, 5H), 7.46 (t, $J = 7.5$, 2H), 7.55 (t, $J = 7.5$, 1H), 8.11 (d, $J = 7.5$, 2H). MS: *m/z* 294 (M^+, 5%), 196 (14%), 189 (M^+ –PhCO, 14%).

6.2. Stoichiometric reactions

6.2.1. Reaction of DMAD and [Ru(PhCOO)(CO)$_2$-PhCOOH]$_2$ (5a)

A solution in dry toluene (10 ml) of DMAD (284 mg; 2 mmol) and complex **5a** (400 mg; 0.5 mmol) (Fig. 4a) was refluxed under nitrogen for 1 h, then cooled to ambient temperature (Fig. 4b). Triphenylphosphine (524 mg; 2 mmol) was added (Fig. 4c), the toluene

evaporated off *in vacuo*, and the residue chromatographed on a silica column. Elution with methylene chloride-petroleum ether (1:1) gave dimethyl-α-(benzoyloxy) maleate (see catalysis part, Experimental section) (120 mg; 45%) followed by dimethyl α-(benzoyloxy)fumarate (50 mg; 19%), ^{1}H NMR: δ 3.72 (s, Me), 3.87 (s, Me), 6.79 (s, 1H), 7.51 (t, J = 7.5a, 2H), 7.65 (t, J = 7.5, 1H), 8.15 (dd, J = 7.5 and 1.3, 2H). Further elution of the column with methylene chloride gave dicarbonyldibenzoate bis(triphenylphosphine) ruthenium(II) (**7a**), (250 mg, 27%).

Subsequent elution with a solution of 1% methanol in methylene chloride gave **9a** (17 mg, 4%). IR: 1735 cm^{-1}, MS (EI): m/z 406 (M^+, 4%), 247 (M^+–HO(CO_2Me)=CCOOMe, 100%). ^{1}H NMR: δ 3.74 (s, 3H), 3.81 (s, 3H), 3.85 (s, 6H), 6.24 (s, =CH), 6.25 (s, =CH), 7.43 (dd, J = 7.7 and 1.3, 1H), 7.54 (dt, J = 7.7 and 1.3, 1H), 7.65 (dt, J = 7.7 and 1.3, 1H), 8.09 (dd, J = 7.7 and 1.3, 1H). ^{13}C-NMR: 52.28q, 52.33q, 52.63q, 52.98q, 115.8(d, =CH), 128.2d, 129.3d, 130.9d, 131.4d, 133.7d, 137,7s, 141.8s, 146.8s, 161.4s, 163.4s, 164.2s, 165.3s, 166.0s. Further elution of the column gave triphenylphosphine oxide (64 mg, 12%), m.p. 145°C. With 2% methanol in methylene chloride there was obtained **8a** (32 mg, 4%). Anal. Found: C, 65.78; H, 4.70. $C_{45}H_{34}O_4P_2Ru \cdot H_2O$ calcd.: C, 65.93; H, 4.15% (for spectral data see text).

With 3% methanol in methylene chloride there was obtained **9b**. IR: 1775, 1730–1740 cm^{-1}. MS (DCl methane): m/z 265 (MH^+, 100%). ^{1}H NMR: δ 2.95 (d, J = 16.9, 1H), 3.61 (d, J = 16.9, 1H), 3.70 (s, 3H), 3.81 (s, 3H), 7.62 (t, J = 7.2, 1H), 7.63 (d, J = 7.2, 1H), 7.73 (t, J = 7.2, 1H), 7.93, (d, J = 7.3, 1H).

6.2.2. Reaction of DMAD, PhCOOH and [Ru(PhCOO)(CO)$_2$PPh$_3$]$_2$ (6)

A solution of DMAD (142 mg, 1 mmol), benzoic acid (122 mg, 1 mmol), and **6** (270 mg 0.25 mmol) in toluene (10 ml) was refluxed under nitrogen for 3 h, then cooled to room temperature and triphenylphosphine (262 mg, 1 mmol) was added. The mixture was separated as described in the previous experiment to give starting material **6** (140 mg, 52%), dimethyl α-(benzoyloxy)maleate, dimethyl α-(benzoyloxy)fumarate, and dicarbonyldibenzoate bis(triphenylphosphine) ruthenium(II) (**7a**) (60 mg, 13%), followed by triphenylphosphine oxide.

6.2.3. Reaction of 4-octyne and [Ru(PhCOO)(CO)$_2$-PhCOOH]$_2$ (5a)

A solution of **5a** (100 mg, 0.125 mmol) and 4-octyne (77 mg, 0.7 mmol) in toluene (5 ml) was refluxed under nitrogen for 3 h then cooled to room temperature, and triphenylphosphine (130 mg, 0.5 mmol) was added. The residue obtained after evaporation of solvent was chromatographed on silica to give **6** with methylene chloride-petroleum ether (1:3) as eluent and (*E*)-4-(benzoyloxy)-4-octene with methylene chloride-petroleum ether (1:1) as eluent. Further elution of the column with methylene chloride followed by a solution of methanol (3%) in methylene chloride gave a mixture of **7a** and **8a**. This mixture was separated by rechromatography on silica to give **7a** with 2% methanol in methylene chloride as eluent and **8a** with a 4% solution, followed by traces of triphenylphosphine oxide.

6.2.4. Reaction of DMAD and [Ru(4-Me-C$_6$H$_4$COO)(CO)$_2$(4-Me-C$_6$H$_4$COOH)]$_2$ (5b)

A solution of DMAD (0.71 g, 5 mmol) and **5b** (1.07 g, 1.25 mmol) in toluene (10 ml) was refluxed under nitrogen for 2 h. The mixture was cooled to room temperature and triphenylphosphine (1.31 g, 5 mmol) was added. The residue obtained after evaporating the toluene *in vacuo* was chromatographed on a silica column. The following substances were obtained by eluting the column with solutions of methylene chloride in petroleum ether of increasing concentrations: a. [Ru(4-MeC$_6$H$_4$COO)(CO)$_2$PPh$_3$]$_2$, 330 mg (22%); b. crude **8b**, crystallized from methylene chloride–cyclohexane to give yellow crystals, 18 mg; c. dimethyl α-(4-methylbenzoyloxy) maleate, 225 mg (39%), ^{1}H NMR: δ 2.37 (s, 3H), 3.75 (s, 3H), 3.80 (s, 3H), 6.19 (s, 1H), 7.23 (d, J = 8, 2H), 7.92 (d, J = 8, 2H). ^{13}C-NMR: 22.1q, 52.6q, 53.2q, 115.7d, 128.9d, 130.1s, 131.2d, 146.0s, 148.6s, 162.4 (s, CO_2), 164.3s, 164.9s. IR: 1730, 1670 cm^{-1}; d. dimethyl α-(4-methylbenzoyloxy) fumarate, 225 mg (39%), ^{1}H NMR: δ 2.37 (s, 3H), 3.75 (s, 3H), 3.80 (s, 3H), 6.80 (s, 1H), 7.26 (d, J = 8.1, 2H), 7.98 (d, J = 8.1, 2H); e. **9b**, 20 mg (2%), ^{1}H NMR: δ 2.44 (s, 3H), 3.73 (s, 3H), 3.80 (s, 3H), 3.84 (s, 6H), 6.229 (s, 1H), 6.232 (s, 1H), 7.23 (s, 1H), 7.33 (d, J = 7.8, 1H), 7.99 (d, J = 7.8, 1H). ^{13}C-NMR: 22.1 (q, Me), 52.8 (q, 2Me), 53.1 (q, Me), 53.5 (q, Me), 116.1 (d, =CH), 128.6d, 130.2s, 130.6d, 132.3d, 132.4d, 138.6s, 142.9s, 145.6s, 147.9s, 162.2 (s, CO_2), 164.1s, 165.0s, 166.2s, 166.7s. MS (EI): m/z 278 ([M^+ –(MeOOC)$_2$C$_2$], 6%), 260 (100%); f. triphenylphosphine oxide; g. complex **7b**, crystallized from methylene chloride-cyclohexane solution, 740 mg (31%). IR (KBr): 2045, 1988, 1610, 1570, 1485, 1435, 1345 cm^{-1} (for ^{1}H NMR and ^{13}C-NMR spectral data see text); h. complex **8b** was eluted from the column with a 3% solution of methanol in methylene chloride, and crystallized from benzene-cyclohexane solution, 82 mg (3.9%). Anal. Found: C, 66.16; H, 4.15. $C_{46}H_{36}O_4P_2Ru \cdot H_2O$ calcd.: C, 66.27; H, 4.56% (for ^{1}H NMR and ^{13}C-NMR spectral data see text).

Complex **8b** (25 mg, 3 mmol) in a toluene solution of *p*-toluic acid (0.008 M, 0.8 ml) was unchanged after 1 h at ambient temperature. Heating the above solution (1 h) under reflux gave **7b** quantitatively (IR, TLC).

Complex **7b** (0.13 M solution in toluene) was refluxed for 3 h; no change in TLC and IR could be detected.

6.3 Preparative scale reactions

6.3.1. Addition of acetic acid to diphenylacetylene

Diphenylacetylene (8.7 g; 0.05 mol), acetic acid (12 g; 0.2 mol) and $Ru_3(CO)_{12}$ (0.1056 g; 2.165 mmol) were heated under nitrogen at 110°C for 21.5 h. Solid (55 mg) separated upon cooling, acetic acid was evaporated off *in vacuo*, and the residue flash-chromatographed on silica to give diphenylacetylene (0.5 g) and α-acetoxystilbene (7.5 g; 64%).

6.3.2. Addition of acetic acid to DMAD

DMAD (14.2 g; 0.1 mol), acetic acid 6.0 g; 0.1 mol) and $Ru_3(CO)_{12}$ (215 mg; 0.33 mmol) were heated at 110°C under nitrogen for 22 h. The mixture was distilled, b.p. 64–82°C/0.2 mmHg. 7.4 g, 37% of product was identified as a mixture of α-acetoxy maleate and fumarate of *ca.* 90% purity.

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