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Ruthenium carboxylate complexes as easily prepared and efficient catalysts for the synthesis of β-oxopropyl esters

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ABSTRACT

The easily prepared complex *cis*-[Ru(κ^2-O_2CMe)$_2$(PPh_3)$_2$] is an effective catalyst for the addition of carboxylic acids to propargyl alcohols to afford β-oxopropyl esters. The reaction is tolerant to a range of functional groups on the propargyl alcohol and is effective in the case of the steroid ethisterone. An investigation into the ruthenium-containing products from the reaction involving benzoic acid revealed that rapid exchange between coordinated acetate and benzoate ligands occurs. The synthesis of crystallographically characterised *cis*-[Ru(κ^2-O_2CPh)$_2$(PPh_3)$_2$] was developed. This benzoate-substituted complex was shown to react with HC≡CPh and HC≡CC(OH)PhH to give [Ru(κ^2-O_2CPh)(κ^1-O_2CPh)(=C=CPhH)(PPh_3)$_2$] and [Ru(κ^2-O_2CPh)(κ^1-O_2CPh)(=C=CC{OH}PhH)(PPh_3)$_2$] respectively. Reaction of *cis*-[Ru(κ^2-O_2CPh)$_2$(PPh_3)$_2$] with CO affords [Ru(κ^2-O_2CPh)(κ^1-O_2CPh)(CO)(PPh_3)$_2$] or [Ru(κ^2-O_2CPh)$_2$(CO)$_2$(PPh_3)$_2$] depending on the conditions employed. Related carbonyl compounds are thought to be the ruthenium-containing products from the catalytic reactions and [Ru(κ^2-O_2CMe)(κ^1-O_2CMe)(CO)(PPh_3)$_2$] was also shown to be a competent catalyst.

1. Introduction

Alkynes are versatile substrates for the construction of elaborate organic architectures. The high degree of unsaturation of these substrates allows for the possibility of two formal addition processes across the carbon–carbon triple bond and, crucially, addition-type reactions offer the possibility of a highly atom-efficient method of functionalization. Due to the constraints of orbital symmetry, formal [2+2] additions to alkynes are forbidden and addition reactions such as hydrobromination, halogenation, hydroboration proceed *via* sequential electrophilic-nucleophilic attack. There is a clear requirement in these uncatalysed reactions for the presence of a strong electrophile (H^+, Br^+, HBR_2) to perform the initial step in the reaction, however, in their absence such addition reactions are prohibited. In order therefore to circumvent these issues a suitable catalyst may be employed which will allow for the atom-efficient addition of less activated substrates [1].

One crucial issue over the addition of unsymmetrical substrates to alkynes is the control of the regiochemistry of the reaction. Considering, for example, the hydration of terminal alkynes (Scheme 1) [2], the metal-promoted Markovnikov addition to yield methyl ketones is common and this outcome may simply be explained by coordination of the alkyne to an electrophilic metal centre in an η^2-binding mode which, in turn, activates the triple bonds towards nucleophilic attack by water at the substituted carbon atom [2,3]. In contrast, in certain ruthenium-catalysed examples, the addition of water may result in anti-Markovnikov addition to afford aldehydes. This change in regiochemistry may be rationalised by considering that nucleophilic attack occurs at the α-carbon of a vinylidene ligand which has been formed from the alkyne substrate [4–12]. Ruthenium complexes have been shown to catalyse the addition of a range of substrates containing E–H (E = O, N, P) groups across the triple bonds of terminal alkynes and, depending on the catalyst, substrate and reaction conditions employed, it is possible to generate products of Markovnikov or anti-Markovnikov addition [9,13–15].

We have recently demonstrated that *cis*-[Ru(κ^2-O_2CMe)$_2$(PPh_3)$_2$], **1a**, is a highly selective precursor for the formation of complexes containing vinylidene ligands [16]. Reaction with, for example, HC≡CPh, **2**, results in the rapid formation of [Ru(κ^2-O_2CMe)(κ^1-O_2CMe)(=C=CHPh)(PPh_3)$_2$], **3a**. Treatment of **1a** with propargyl alcohols HC≡CC(OH)RR^1 (**4a** R = R^1 = Ph; **4b** R = R^1 = Me) afforded long-lived hydroxyl-substituted vinylidene complexes [Ru(κ^2-O_2CMe)(κ^1-O_2CMe)(=C=CHC{OH}RR^1}(PPh_3)$_2$], (**5a** R = R$^{1\prime}$ = Ph; **5b** R = R^1 = Me). This reaction occurs under extremely mild conditions and the key step in alkyne/vinylidene tautomerisation appears to be the ability of an acetate ligand to participate in a ligand-assisted proton shuttle (LAPS) mechanism (Scheme 2) [17]. Here the acetate

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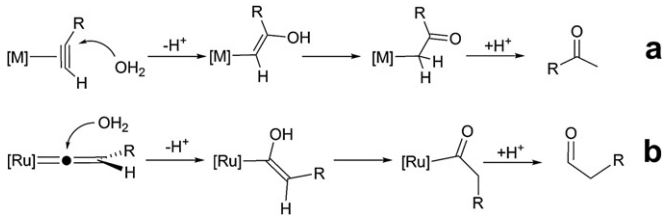


Scheme 1. General mechanisms for the hydration of alkynes (a) Markovnikov pathway (b) anti-Markovnikov.

initially acts as an intramolecular base to deprotonate the coordinated alkyne and in a second step reprotonation occurs to afford the final vinylidene complex.

As complex **1a** may be easily prepared from $RuCl_3 \cdot xH_2O$ in two high yielding steps and it reacts readily with alkynes to form vinylidene complexes we anticipated that it would act as a versatile catalyst for a range of transformations involving terminal alkynes. We now report that **1a**, and its benzoate-substituted analogue *cis*-[Ru(κ^2-O_2CPh)$_2$(PPh_3)$_2$], **1b**, are able to promote the atom-efficient formation of β-oxopropyl esters from propargyl alcohols and carboxylic acids.

2. Results and discussion

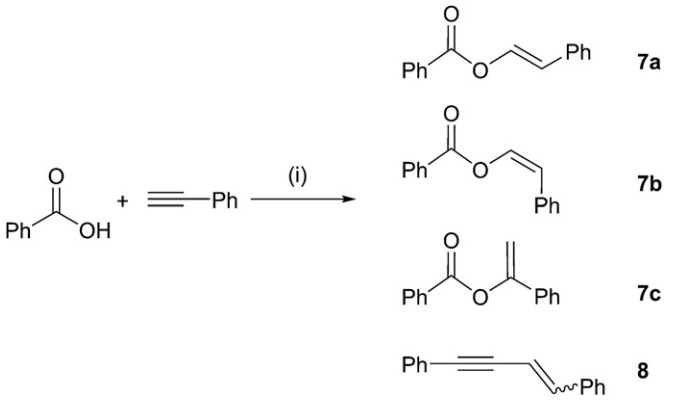
2.1. Reaction of HC≡CPh, 2, with $PhCO_2H$, 6b

Ruthenium [18–22] and rhodium [23] complexes may facilitate the addition of carboxylic acids to terminal alkynes to prepare alk-1-en-1-yl esters. We were therefore interested to discover if **1a** could act as a catalyst for this reaction. Heating a toluene solution of **2** and benzoic acid, **7b**, in the presence of **1a** (5 mol%) at 60 °C for 16 h resulted in a mixture of products. In addition to unreacted **7b**, a small amount of the desired ester **7a** (Scheme 3) was observed, however the major product was the eneyne **8** arising from the ruthenium-mediated dimerisation of **2** [24–31]. Repeating the reaction at 120 °C led to consumption of the starting materials, but now four products **7a**, **7b**, **7c** and **8** were obtained in a 6:1:10:1 ratio, as shown by ^{1}H NMR spectroscopy.

It was evident from these results that whilst at low temperatures **1a** was able to catalyse the anti-Markovnikov addition reaction of the carboxylic acid, this process did not compete favourably with the dimerisation of the alkyne. At higher temperature Markovnikov addition is preferred, although selectivity was not high.

2.2. Reaction of propargyl alcohols with carboxylic acids

Our previous studies have demonstrated that, in contrast to its behaviour with **2**, **1a** was an inefficient catalyst for the dimerisation of propargyl alcohols. It was therefore reasoned that the addition of carboxylic acids to this class of substrate may be more competitive than the corresponding dimerisation. This indeed proved to be the case. Reaction of phenylpropargyl alcohol, HC≡CCH(OH)Ph, **4e**, with benzoic acid, **6b**, at 120 °C in toluene solution for 16 h in the



Scheme 3. (i) **1a** (5 mol %), toluene, 60 °C or 110 °C, 16 h.

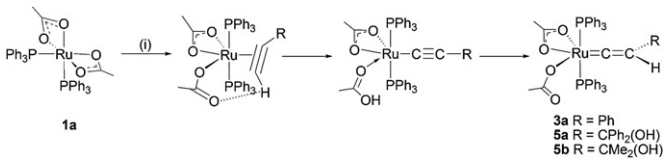
presence of **1a** (5 mol%) resulted in the formation of β-oxopropyl ester **9eb** (Scheme 4, Table 1). A study of the crude reaction mixture by ^{1}H NMR spectroscopy demonstrated that conversion was essentially quantitative and that the product could be isolated in good yield by column chromatography.

Attempts to optimise the reaction conditions demonstrated that employing 1 mol % of **1a** did not result in a significant decrease in the yield of the product. In addition, repeating the reaction in the absence of **1a** did not result in the formation of any **9eb**, indicating that the ruthenium complex was essential for the reaction.

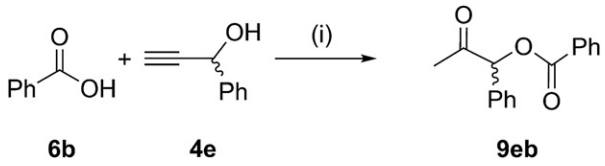
A range of propargyl alcohols and carboxylic acids were screened in order to assess the scope of the reaction and the results are presented in Table 1. Pleasingly, for the majority of substrates employed, conversion to the β-oxopropyl esters occurred in essentially quantitative yield as shown by the NMR spectra of the crude reaction mixtures and the products could be isolated in good to excellent yields. The reaction was unsuccessful when alcohol **4a** was employed as substrate which may simply be a result of the steric hindrance caused by the presence of two phenyl groups on the γ-carbon of the substrate.

Reaction of the biologically active propargyl alcohol ethisterone, **4h**, with benzoic acid was also successful and the desired ester, **9hb**, was isolated in 53% as a single diastereoisomer. In this instance, some **4h** was also recovered and small amounts of an impurity, thought to be an α,β-unsaturated vinyl aldehyde arising from a Meyer–Schuster-type reaction [32]. It should be noted that related aldehyde products were often observed as trace components of crude reaction mixtures.

These results demonstrate that **1a** is a versatile catalyst for the conversion of propargyl alcohols to β-oxopropyl esters even in the presence of a functionalised substrate such as **4h**. A number of ruthenium-based catalysts have been shown to be able to facilitate this reaction. For example, Mitsudo et al. [34] demonstrated that a system based on *bis*(η^5-cyclooctadienyl)ruthenium, PBu_3 and maleic anhydride was able to generate β-oxo esters in yields of between 54 and 51%, whereas Bruneau and Dixneuf have employed [$RuCl_2$(*p*-cymene)(PR_3)] (R = Me, Ph) [33] and [Ru(μ-O_2CH)(CO)$_2$(PPh_3)]$_2$ [35]. More recently, Bauer has shown that half-sandwich ruthenium



Scheme 2. (i) + HC≡CR.



Scheme 4. (i) **1a** (5 mol %), toluene, 110 °C, 16 h.

Table 1

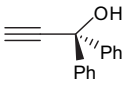
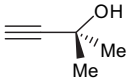
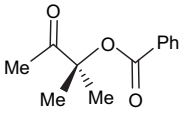
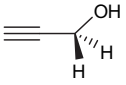
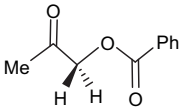
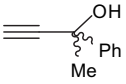
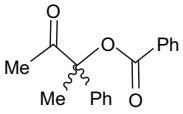
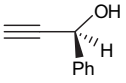
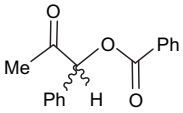
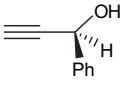
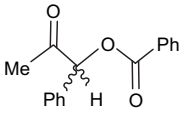
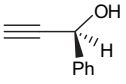
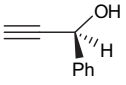
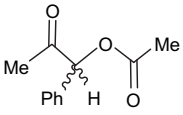
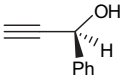
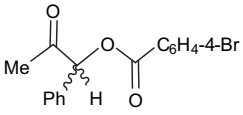
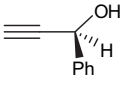
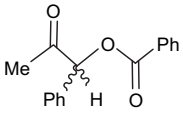
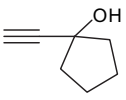
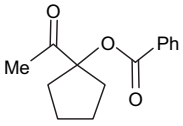
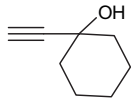
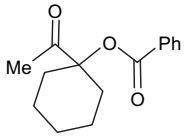
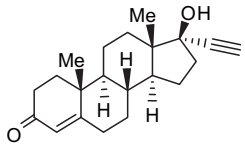
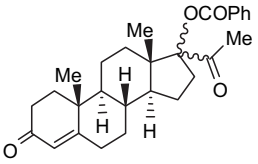
Entry	Alkyne		Acid	Catalyst	Product		Yield/%
1		**4a**	**6b**	**1a**	–		0
2		**4b**	**6b**	**1a**		**9bb**	79
3		**4c**	**6b**	**1a**		**9cb**	77
4		**4d**	**6b**	**1a**		**9db**	72
5		**4e**	**6b**	**1a**		**9eb**	81
6		**4e**	**6b**	**10a**		**9eb**	81
7		**4e**	**6b**	–	–	–	0
8		**4e**	**6a**	**1a**		**9da**	79
9		**4e**	**6c**	**1a**		**9dc**	51
10		**4e**	**6b**	**1b**		**9eb**	68
11		**4f**	**6b**	**1a**		**9fb**	89

Table 1 (*continued*)

Entry	Alkyne		Acid	Catalyst	Product		Yield/%
12		**4g**	**6b**	**1a**		**9gb**	78
13		**4h**	**6b**	**1a**		**9hb**	53

complexes containing phosphoramidite ligands may be used to prepare β-oxo esters in yields of up to 95% [36], Cadierno et al. have shown that the incorporation of water-solubilising phosphine ligands enables the formation of β-oxo esters to be performed in aqueous solution [37] and Yi and Gao have shown that [RuClH(CO)(P^iPr_3)$_3$] may also act a catalyst precursor [22]. The performance of **1a** is generally comparable to these catalyst systems and is both easy to prepare and handle.[1]

2.3. Stoichiometric studies

In order to gain insight into the mechanism of this reaction, the crude reaction mixture was studied by $^{31}P\{^1H\}$ NMR spectroscopy and mass spectrometry to identify the ruthenium-containing products from the reaction.

The mass spectra of the crude reaction mixtures showed a peak at $m/z = 803.1$ which appeared to correspond to a complex [Ru(κ^2-O_2CMe)$(CO)_2(PPh_3)_2]^+$. In order to ascertain if this suggestion was indeed correct, the reaction between **4e** and 4-bromobenzoic acid, **5c**, using **1a** as catalyst was performed. The expected product **9ec** was obtained (Table 1, entry 9) and an examination of the crude reaction mixture by mass spectrometry revealed the presence of ions centred at $m/z = 881.0$ as expected for a complex [Ru(κ^2-O_2C–C_6H_4-4-Br)$(CO)_2(PPh_3)_2]^+$. The correct isotope pattern for the incorporation of a bromine atom was observed.

As no evidence for any acetate ligands coordinated to the ruthenium was obtained in these studies, it was presumed that a rapid exchange of acetate and benzoate ligands was occurring within the reaction mixture. In order to verify this hypothesis a toluene-d_8 solution of **1a** was treated with two equivalents of benzoic acid. A $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture exhibited two very broad resonances in the region δ 66, at a chemical shift similar to that observed for pure **1a** and for *cis*-[Ru(κ^2-O_2CPh)$_2(PPh_3)_2$], **1b** (*q.v.*). Related complexes possessing mutually trans-phosphine ligand typically exhibit resonances in the $^{31}P\{^1H\}$ spectrum between δ 40 and 30 [16,17]. We therefore concluded that rapid exchange of acetate and benzoate ligands was occurring, even at room temperature.

Given the large excess of benzoic acid (when compared to ruthenium) it was considered that the actual catalytic species did not contain acetate, but rather benzoate ligands.

In order to support this argument, *cis*-[Ru(κ^2-O_2CPh)$_2(PPh_3)_2$], **1b**, was prepared from the reaction of [$RuCl_2(PPh_3)_3$] with sodium benzoate. The $^{31}P\{^1H\}$ NMR spectrum of **1b** exhibited a resonance at δ 63.1, similar to that for **1a**. As well as the expected resonances in the ^1H and ^{13}C NMR spectra, the structure of **1b** was confirmed by single crystal X-ray diffraction. An ORTEP representation of the structure is shown in Fig. 1, selected bond lengths and angles for all structures reported in Table 2 and details of the data collection and structure refinement in Table 3.

As expected on the basis of the NMR data, **1b** exhibits a similar distorted octahedral coordination geometry to **1a** with the two PPh_3 ligands occupying mutually *cis* sites. However, in contrast to **1a**, the two Ru–P bonds lengths are significantly different (Ru–P(1) 2.2467(5) Å, Ru–P(2) 2.2463(5) Å for **1a**; Ru–P(1) 2.2425(6) Å, Ru–P(2) 2.2664(5) Å for **1b**) and this may be a result of a π-stacking interaction between the benzoate ligand and the phenyl groups of the PPh_3 ligand containing P(2).

The chemistry exhibited by **1b** is also reminiscent of **1a**. For example, **1b** was able to catalyse the reaction between **4e** with **5b** to give β-oxopropyl ester **9eb** (Table 1, entry 10). The reaction of **1b** with **2** or **4d** resulted in the formation of [Ru(κ^2-O_2CPh)(κ^1-O_2CPh)(=C=CHPh)$(PPh_3)_2$], **3b** and [Ru(κ^2-O_2CPh)(κ^1-O_2CPh)(=C=CHC{OH}PhH)$(PPh_3)_2$], **5c** respectively. The NMR spectra of **3b** and **5c** display the expected features, most notable, the presence of the vinylidene ligands was confirmed by low field resonances in the $^{13}C\{^1H\}$ NMR spectra at δ 358.16 (t, $J = 16.8$ Hz) for **3b** and δ 347.26 (t, $J = 16.0$ Hz) for **5c**. The $^{13}C\{^1H\}$ NMR spectra also showed the presence of a single carbonyl resonance for the O_2CPh groups, consistent with exchange of κ^1- and κ^2- bound benzoate which is fast on the NMR timescale. A similar observation was made for the acetate-containing analogues [16].

The structure of **3b** was confirmed by a single crystal X-ray diffraction experiment. A representation of the structure is shown in Fig. 2. The structure determination demonstrated that the complex crystallised with two molecules of CH_2Cl_2 and that the κ^2-O_2CPh and vinylidene ligand were disordered between their respective sites in a 55:45 ratio. Although the majority of the bond metrics with the two different forms of **3b** are similar, in the major form a CH_2Cl_2 of crystallisation is located above the phenyl ring of the κ^2-O_2CPh ligand – in the minor form it is over the phenyl ring of the vinylidene group, presumably indicating C–H–π interactions (Major form C59···C(5) distance 3.1557(1) Å; minor form C59···C(20a) 3.4224(2) Å). The other significant difference between the two forms of **3b** is in the orientation of the vinylidene ligand. In the major form of **3b** the vinylidene lies significantly out of the plane containing the two benzoate ligands (angle between mean plane

[1] Solid sample of Complex **1a** may be stored and handled in air for prolonged period with no obvious evidence of decomposition.

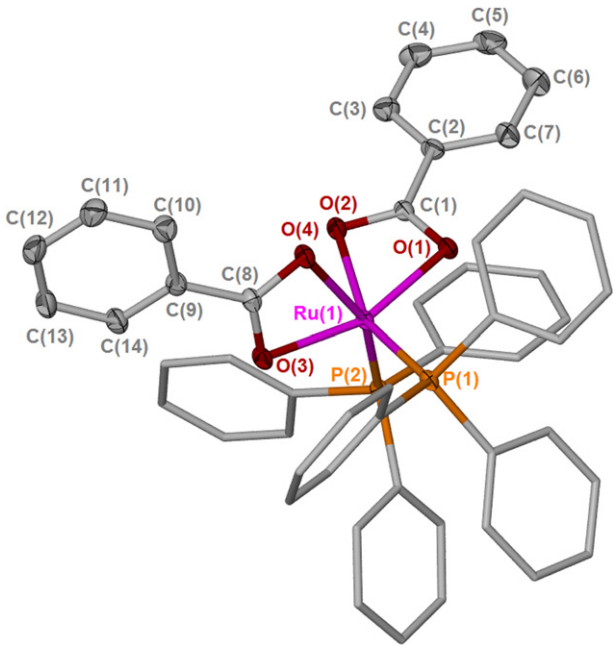


Fig. 1. Molecular structure of **1b**. Thermal ellipsoids (where shown) are at the 50% probability level. Hydrogen atoms omitted for clarity.

Ru–O(1)–O(2)–O(3) and plane Ru–C(15)–C(16)–H(16)–C(17) = 32.54°). In the minor form the deviation from the plane is less (corresponding angle 19.33°). However, in both cases there is a marked difference from the acetate complex **3a** in which OAc ligands and the vinylidene are essentially co-planar (angle between relevant planes 9.64°). These differences may simply reflect the more significant steric bulk of the benzoate ligand when compared to acetate and/or the presence of the CH_2Cl_2 of crystallisation interacting with the phenyl groups in the complex.

Table 2
Selected bond lengths (Å) and angles (°) for the structures determined.

Metric	**1b**	**3c** major	**3c** minor	**11**
Ru–P(1)	2.2424(5)	2.4031(6)	–	2.4026(5)
Ru–P(2)	2.2664(5)	2.3925(6)	–	2.4247(5)
Ru–O(1)	2.1016(12)	2.110(3)	2.110(4)	2.0954(13)
Ru–O(2)	2.2278(13)	2.313(4)	2.243(7)	–
Ru–O(3)	2.1017(12)	2.0464(18)	–	2.0883(13)
Ru–O(4)	2.2272(12)	–	–	–
Ru–C(15)	–	1.794(9)	1.787(8)	1.8797(19)
Ru–C(16)	–	–	–	1.8794(19)
C(15)–C(16)	–	1.312(10)	1.331(9)	–
C(15)–O(5)	–	–	–	1.143(2)
C(16)–O(6)	–	–	–	1.144(2)
P(1)–Ru–P(2)	104.046(17)	178.08(2)	–	177.876(17)
O(1)–Ru–P(1)	97.82(4)	82.30(7)	97.25(10)	91.86(4)
O(2)–Ru–P(1)	156.91(4)	92.66(13)	89.7(2)	–
O(3)–Ru–P(1)	94.92(4)	95.12(5)	–	83.94(4)
O(4)–Ru–P(1)	91.37(4)	–	–	–
O(1)–Ru–P(2)	91.35(4)	97.36(8)	83.87(10)	86.30(4)
O(2)–Ru–P(2)	86.34(4)	85.56(13)	92.2(2)	–
O(3)–Ru–P(2)	100.06(4)	84.75(5)	–	94.71(4)
O(4)–Ru–P(2)	156.85(4)	–	–	–
C(15)–Ru–O(1)	–	97.1(3)	100.5(3)	96.92(7)
C(15)–Ru–O(2)	–	155.3(3)	160.1(4)	–
C(15)–Ru–O(3)	–	96.6(3)	110.7(3)	175.83(6)
Ru–C(15)–C(16)	–	176.9(8)	171.6(7)	–
C(16)–Ru–O(1)	–	–	–	175.83(6)
C(16)–Ru–O(3)	–	–	–	95.42(7)
C(16)–Ru(1)–C(15)	–	–	–	86.67(8)

An independent synthesis was sought of $[Ru(\kappa^2\text{-}O_2CPh)(CO)_2(PPh_3)_2]^+$, the proposed ruthenium-containing product from the catalytic reactions. Treatment of **1b** with gaseous CO in MeOH solution results in the formation of a pale yellow precipitate identified as $[Ru(\kappa^2\text{-}O_2CPh)(\kappa^1\text{-}O_2CPh)(CO)(PPh_3)_2]$, **10b**, related to the corresponding acetate complex $[Ru(\kappa^2\text{-}O_2CMe)(\kappa^1\text{-}O_2CMe)(CO)(PPh_3)_2]$, **10a**. Treatment of either complexes **1a** or **1b** with gaseous CO in CH_2Cl_2 solution for 24 h resulted in a mixture of products. When the reactions were monitored by IR spectroscopy a band due to the monocarbonyl complexes **10** were observed, as were two bands for at 2049 and 1987 cm^{-1} characteristic of a *cis* dicarbonyl species, proposed to be $[Ru(\kappa^1\text{-}O_2CR)_2(CO)_2(PPh_3)_2]$, (R = Me, **11a**, R = Ph, **11b**). Prolonged carbonylation did not result in an increase in the intensity of the bands due to this dicarbonyl species.

In an attempt to form the desired cationic complex, one equivalent of $AgBF_4$ was added to the appropriate reaction mixtures. This resulted in the formation of two new bands in the IR spectrum of the mixture (2070 and 2015 cm^{-1} R = Me; 2069 and 2014 cm^{-1} R = Ph), the change in frequency being consistent with the formation of cationic complexes, such as $[Ru(\kappa^2\text{-}O_2CR)(CO)_2(PPh_3)_2]^+$. In the case of the benzoate-substituted complex this cationic complex was the only species present after 48 h; in the case of the acetate complex the reaction was far slower and trace quantities of **11a** were still present after 5 days.

Attempts to isolate these cationic complexes by filtration through celite resulted in some unusual behaviour. In the case of both acetate and benzoate-substituted complexes, examination of the filtrate by IR spectroscopy demonstrated that the bands due to the cationic complex had significantly decreased in intensity and the bands for complex **11** had reappeared. The relative amounts of the two species did not change on standing. However, addition of NaOAc to a solution generated in this manner resulted in the smooth conversion to the dicarbonyl complexes assigned as to **11a**. These results led to us conclude that addition of silver salts to the carbonyl complexes resulted in formation of cationic dicarbonyl and, after filtration, any residual carboxylate salts present in the filtrate react with the cationic complex to reform **11**.

It proved possible to isolate crystals of complex **11b** from these reaction mixtures and the infra-red spectrum of the complex was consistent with κ^1-coordination of the benzoate ligands with bands being observed at 1347 cm^{-1} (OCO sym) and 1609 cm^{-1} (OCO-asym) ($\Delta\nu$ 262 cm^{-1}) [38]. The structure of **11b** was also confirmed by single crystal X-ray diffraction, an ORTEP representation of the structure is shown in Fig. 3. As expected, the complex essentially possesses an octahedral geometry with mutually *cis* carbonyl ligands and two κ^1-benzoate ligands.

It is well-known that either hydrolysis [39] or oxidation [40] of transition metal vinylidene ligands results in the formation of the corresponding carbonyl derivatives. In addition, we have also demonstrated that hydroxy-substituted vinylidene complexes such as **5b** convert to $[Ru(\kappa^2\text{-}O_2CMe)(\kappa^1\text{-}O_2CMe)(CO)(PPh_3)_2]$, **10a** and $H_2C{=}CMe_2$ which provides an alternative source of CO in the reaction mixture [16]. These pathways are all plausible routes to the observed carbonyl complexes obtained from the catalytic reaction mixtures. In addition, complex $[Ru(\kappa^2\text{-}O_2CMe)(\kappa^1\text{-}O_2CMe)(CO)(PPh_3)_2]$, **10a**, is also a viable catalyst for the addition of benzoic acid to **4e** (Table 1, Entry 6). The product, **9eb** was obtained in essentially identical yield to the reaction when **1a** was employed, thus indicating that complexes containing carbonyl ligands are also competent catalysts for this reaction.

2.4. Mechanistic considerations

The generally accepted mechanism for the ruthenium-mediated formation of β-oxopropyl esters from propargyl alcohols and

Table 3
Crystallographic data for complexes **1b**, **3b**.2CH_2Cl_2 and **11**.

	1b	**3b**·2CH_2Cl_2	**11**
Empirical formula	$C_{50}H_{40}O_4P_2Ru$	$C_{60}H_{50}Cl_4O_4P_2Ru$	$C_{52}H_{40}O_6P_2Ru$
Formula weight	867.83	1139.81	923.85
Temperature (K)	110(2)	110(2)	110(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P−1	P2(1)/n	P2(1)/n
a (Å)	11.0473(8)	14.3833(9)	12.0033(6)
b (Å)	12.7076(9)	23.7659(15)	18.5525(9)
c (Å)	16.3350(12)	15.4674(10)	18.5525(9)
α (°)	81.0710(10)	90	90
β (°)	71.7110(10)	101.3350(10)	102.1410(10)
γ (°).	67.4420(10)	90	90
Volume ($Å^3$)	2009.2(3)	5184.1(6)	4192.3(4)
Z	2	4	4
Density (calculated) (Mg/m^3)	1.434	1.460	1.464
Absorption coefficient (mm^{-1})	0.517	0.619	0.504
F(000)	892	2336	1896
Crystal size (mm)	0.36 × 0.15 × 0.13	0.23 × 0.13 × 0.05	0.17 × 0.10 × 0.06
Theta range for data collection (°)	1.74 to 28.31	1.59 to 28.31	1.54 to 30.03
Index ranges	−14 ⇐ h ⇐ 14 −16 ⇐ k ⇐ 16 −21 ⇐ l ⇐ 21	−19 ⇐ h ⇐ 19 −31 ⇐ k ⇐ 31 −20 ⇐ l ⇐ 20	−16 ⇐ h ⇐ 16 −25 ⇐ k ⇐ 26 −27 ⇐ l ⇐ 26
Reflections collected	20754	53205	47456
Independent reflections	9874 [R(int) = 0.0187]	12882 [R(int) = 0.0368]	12136 [R(int) = 0.0416]
Completeness to theta	98.7 (to 28.31°)	99.9 (to 28.31°)	98.9 (to 30.03°)
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.936 and 0.761	0.970 and 0.784	0.970 and 0.826
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	9874/0/514	12882/0/805	12136/0/550
Goodness-of-fit on F^2	1.064	1.026	1.034
Final R indices [I > 2sigma(I)]	*R*1 = 0.0317 wR2 = 0.0825	*R*1 = 0.0407 wR2 = 0.0995	*R*1 = 0.0348 wR2 = 0.0778
R indices (all data)	*R*1 = 0.0364 wR2 = 0.0861	*R*1 = 0.0571 wR2 = 0.1081	*R*1 = 0.0551 wR2 = 0.0862
Largest diff. peak and hole (e $Å^{-3}$)	1.071 and −0.988	0.615 and −0.922	1.065 and −0.399

carboxylic acids is shown in Scheme 6a [22,33,36,41]. Here, addition of a carboxylate nucleophile to a coordinated alkyne ligand proceeds in a Markovnikov fashion, this is followed by an intramolecular transesterification reaction. The observation of a Markovnikov-type addition is consistent with our observations that the addition of benzoic acid to phenyl acetylene at 120 °C affords **7c** as the major product.

An attempted catalytic reaction between HC≡$CCH_2(O_2CPh)$ with water to give **9bc** only resulted in the isolation of the starting material, which appears to preclude an alternative mechanism involving esterification at the hydroxyl–vinylidene complex. A similar observation has been made by Dixneuf et al. [33]. In addition, reaction of phenyl propargyl ether HC≡$CCH_2(OPh)$, **12**, with benzoic

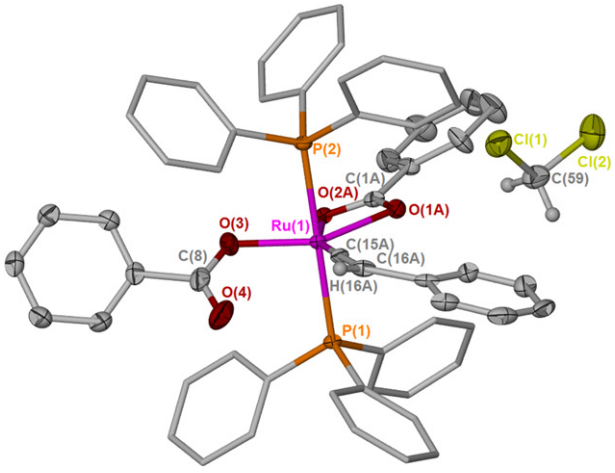


Fig. 2. Molecular structure of the major form of complex **3b**. Thermal ellipsoids (where shown) are at the 50% probability level. Hydrogen atoms, except H(16A), H(59A) and H(59B), and a CH_2Cl_2 of crystallisation omitted for clarity.

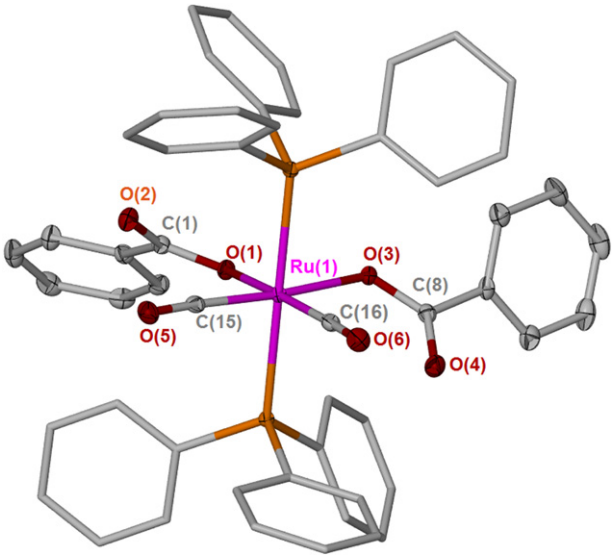
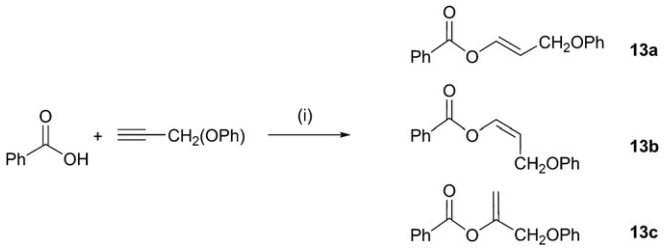


Fig. 3. Molecular structure of **11**. Thermal ellipsoids (where shown) are at the 50% probability level. Hydrogen atoms omitted for clarity.



Scheme 5. (i) **1a** (5 mol %), toluene, 120 °C, 16 h.

acid in the presence of **1a** (1 mol%) results in the formation of three products, **13a**–**c** in a 0.7:1:1.6 ratio (**13a**:**13b**:**13c**), Scheme 5. Clearly this product distribution arises from the Markovnikov (**13c**) and anti-Markovnikov (**13a**–**b**) addition reactions to the alkyne and demonstrates the importance of the propargyl alcohol group in the formation of β-oxopropyl esters.

In the reaction between benzoic acid to phenyl acetylene, lower temperatures appear to favour anti-Markovnikov addition to give **7a**. These products are thought to arise *via* intramolecular attack of a coordinated carboxylate ligand onto the α-carbon of a vinylidene ligand (Scheme 6b) [22,42]. In related studies, we have demonstrated that the acetate ligand in complexes of type **3** may undergo facile nucleophilic attack at the α-carbon of the vinylidene ligand to give isolable metallo-enol esters **11** (Scheme 6c) [17]. Indeed, in stoichiometric studies we have shown that protonation of **11** with acetic acid affords **7a** and **10a** [43].

In summary we have demonstrated that the easily prepared ruthenium carboxylate complexes *cis*-[Ru(κ^2-O_2CR)$_2$(PPh$_3$)$_2$], (R = Me, Ph) are effective catalysts for the addition of carboxylic acids to propargyl alcohols to give β-oxopropyl esters.

3. Experimental section

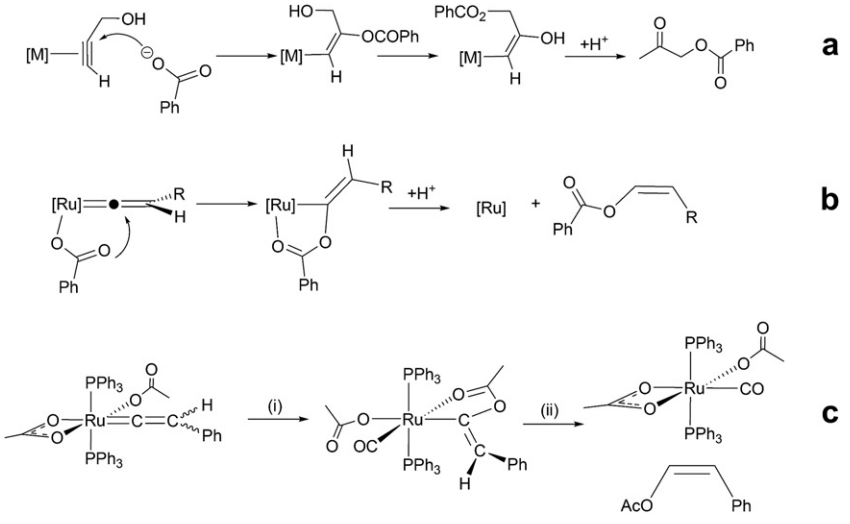
All experimental procedures were performed under an inert atmosphere of dinitrogen or argon using standard Schlenk line and glovebox techniques. An Innovative Technologies anhydrous solvent engineering system was used for purification of dichloromethane, n-pentane, n-hexane and toluene. All other solvents were AR grade and either used without further purification or degassed by purging with dinitrogen where stated. $CDCl_3$ used for NMR spectroscopy, alkynes, propargyl alcohols and carboxylic acids were supplied by Aldrich Chemicals and used without any further purification. The CD_2Cl_2 used for NMR spectroscopy was dried over CaH_2 and degassed with three freeze-pump-thaw cycles. NMR spectra were acquired on the following instruments: Bruker AMX 300 (operating frequencies ^{1}H 300.13 MHz, ^{31}P 121.40 MHz, ^{13}C 76.98 MHz), Bruker AVANCE 500 (operating frequencies ^{1}H 500.23 MHz, ^{31}P 202.50 MHz, ^{13}C 125.77 MHz), Jeol ECX-400 (operating frequencies ^{1}H 400 MHz, ^{31}P 161.80 MHz, ^{13}C 100.60 MHz), Jeol EX-270 (operating frequencies ^{1}H 270 MHz, ^{31}P 109.6 MHz, ^{13}C 67.9 MHz). ^{31}P and ^{13}C spectra were recorded with proton decoupling. Chemical shifts are quoted as parts per million. Mass spectra were recorded on a Thermo-Electron Corp LCQ Classic instrument (ESI). IR spectra were recorded using either CsCl solution cells or KBr discs on a Mattson Research Series spectrometer. Flash column chromatography was carried out using Fluka Silica Gel. Complex **1a** [16] and [$RuCl_2(PPh_3)_3$] [44] were prepared according to literature procedures.

3.1. Synthesis of *cis*-[Ru(κ^2-O_2CPh)$_2$(PPh$_3$)$_2$], **1b**

NaO_2CPh (7.5 g, 52.15 mmol) was added to a solution of [$RuCl_2(PPh_3)_3$] (5.0 g, 5.215 mmol) in deoxygenated ^{t}BuOH. The mixture was heated at reflux for 1 h, after which time a colour change from black to orange-red was observed. When cool, the solid was isolated by filtration and washed with 80 mL of H_2O, 60 mL of CH_3OH, and 50 mL of Et_2O. The orange powder was dried *in vacuo*. Crystals suitable for X-ray diffraction were obtained from a CH_2Cl_2/n-pentane solution. Yield: 3.01 g (67%). NMR Spectra ($CDCl_3$): ^{1}H: δ_H 7.64 (ad, 7.36 Hz, 4H, ***Ph***), 7.29 (at, 7.43 Hz, 2H, ***Ph***), 7.23–7.15 (22H, ***Ph***), 7.03 (at, 7.43 Hz, 12H, ***Ph***). ^{31}P{^{1}H}: δ_P 63.1 (s, ***P***Ph$_3$). ^{13}C{^{1}H}: δ_C 183.09 (s, ***C***O_2Ph), 135.02 (m, $^1J_{PC} + {}^3J_{PC} = 44.2$ Hz, P***Ph***$_3$-***C***$_1$), 134.48 (t, 9.3 Hz, P***Ph***$_3$-***C***$_2$), 132.66 (s, O_2C***Ph***-***C***$_1$), 131.36 (s, O_2C***Ph***-***C***$_4$), 129.07 (s, P***Ph***$_3$-***C***$_4$), 128.46 (s, O_2C***Ph***-***C***$_2$), 127.56 (t, 9.4 Hz, P***Ph***$_3$-***C***$_3$), 127.38 (s, O_2C***Ph***-***C***$_3$). IR (DCM): 1425 cm^{-1} (κ^2-OCOsym), 1433 cm^{-1} (P-Ph$_3$), 1482 cm^{-1} (P-Ph$_3$), 1505 cm^{-1} (κ^2-OCOasym), Δν(chelate) 80 cm^{-1}. MS (ESI): 869 *m*/*z* ([M]$^+$), 788 *m*/*z* ([$Ru(O_2CPh)(PPh_3)_2(CNCH_3)$]$^+$), 747 *m*/*z* ([$Ru(O_2CPh)(PPh_3)_2$]$^+$). Elemental Analysis: (calc %) C 69.19, H 4.58; (found %) C 68.90, H 4.59.

3.2. Synthesis of [Ru(κ^2-O_2CPh)(κ^1-O_2CPh)(PPh$_3$)$_2$(=C=CHPh)], (***3b***)

Phenylacetylene (13 μL, 0.11 mmol) was added to a solution of **1b** (100 mg, 0.11 mmol) in 25 mL of CH_2Cl_2 and the reaction mixture



Scheme 6. (i) + CO.

was stirred for 1 h. The volume was reduced slightly *in vacuo* before addition of 30 mL of n-pentane, which resulted in the formation of a pink-red precipitate. The solid was isolated by filtration, washed with 2 × 20 mL portions of n-pentane, and dried under vacuum. Crystals suitable for X-ray diffraction were obtained from a CH_2Cl_2/n-pentane solution. Yield: 84 mg, (75%). NMR Spectra ($CDCl_3$): ^{1}H: δ_H 7.54 (m, 12H, ***Ph***), 7.27–7.14 (26H, ***Ph***), 7.06 (at, 7.74 Hz, 4H, ***Ph***), 6.89 (3H, ***Ph***), 5.44 (t, $^4J_{PH}$ = 3.8 Hz, 1H, [Ru]=C=C***H***Ph). ^{31}P{^{1}H}: δ_P 33.45 (s, ***P***Ph$_3$). ^{13}C{^{1}H}: δ_C 358.16 (t, $^2J_{PC}$ = 16.8 Hz, [Ru]=***C***), 174.81 (s, O$_2$***C***Ph), 134.90 (t, $^2J_{PC}$ + $^4J_{PC}$ = 11.1 Hz, P***Ph***$_3$-***C***$_2$), 134.49 (t, $^4J_{PC}$ = 4.63 Hz, CH***Ph***-***C***$_1$), 133.58 Hz (s, O$_2$C***Ph***-***C***$_1$), 130.27 (s, O$_2$C***Ph***-***C***$_4$), 129.78 (s, P***Ph***$_3$-***C***$_4$), 129.36 (t, $^1J_{PC}$ + $^3J_{PC}$ = 43.2 Hz, P***Ph***$_3$-***C***$_1$), 128.56 (s, O$_2$C***Ph***-***C***$_2$), 127.88 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.5 Hz, P***Ph***$_3$-***C***$_3$), 126.73 (s, O$_2$C***Ph***-***C***$_3$), 125.01 (s, CH***Ph***-***C***$_2$/***C***$_3$), 123.65 (s, CH***Ph***-***C***$_4$), 112.82 (t, $^3J_{PC}$ = 4.6 Hz, [Ru]=C=***C***) IR (DCM): 1339 cm^{-1} (κ^1-OCOsym), 1417 cm^{-1} (κ^2-OCO-sym), 1434 cm^{-1} (P-Ph$_3$), 1491 cm^{-1} (κ^2-OCO-sym), 1594 cm^{-1} (κ^1-OCO-asym), Δν(uni) 255 cm^{-1}, Δν(chelate) 74 cm^{-1}. MS (ESI): 993 *m*/*z* ([M]Na$^+$), 971 *m*/*z* ([M]$^+$), 890 *m*/*z* ([M − CCPh]Na$^+$).

3.3. Synthesis of [Ru(κ^2-OCOPh)(κ^1-OCOPh)(PPh$_3$)$_2$(=C=CH-C{OH}PhH)] (**5c**)

Phenylpropynol (14 μL, 0.11 mmol) was added to a solution of **1b** (100 mg, 0.11 mmol) in 25 mL of CH_2Cl_2 and the reaction mixture was stirred for 1 h. The volume was reduced slightly *in vacuo* before addition of 30 mL of n-pentane, resulting in the formation of an orange-yellow precipitate. The solid was isolated by filtration, washed with 2 × 20 mL portions of n-pentane, and dried under vacuum. Yield: 97 mg (84%). NMR Spectra ($CDCl_3$): ^{1}H: δ_H 7.54 (m, 12H, ***Ph***), 7.16 (24H, ***Ph***), 7.12 (m, 3H, ***Ph***), 7.04 (at, 7.68 Hz, 4H, ***Ph***), 6.87 (ad, 7.14 Hz, 2H, ***Ph***), 5.47 (d, 1H, $^3J_{HH}$ = 7.8 Hz, C***H***(OH)Ph), 4.60 (aq, *J* = 3.84 Hz, [Ru]=C=C***H***), 1.87 (s, 1H, CH(O***H***)Ph). ^{31}P{^{1}H}: δ_P 34.25 (s, ***P***Ph$_3$) ^{13}C{^{1}H}: δ_C 347.26 (t, $^2J_{PC}$ = 16.0 Hz, [Ru]=***C***), 174.82 (s, O$_2$***C***Ph), 144.90 (s, CH(OH)***Ph***-***C***$_1$),134.90 (t, $^2J_{PC}$ + $^4J_{PC}$ = 10.8 Hz, P***Ph***$_3$-***C***$_2$), 133.41 (s, O$_2$C***Ph***-***C***$_1$), 130.29 (s, O$_2$C***Ph***-***C***$_4$), 129.99 (s, P***Ph***$_3$-***C***$_4$), 129.42 (t, $^1J_{PC}$ + $^3J_{PC}$ = 43.1 Hz, P***Ph***$_3$-***C***$_1$), 128.46 (s, O$_2$C***Ph***-***C***$_2$), 128.09 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.3 Hz, P***Ph***$_3$-***C***$_3$), 127.95 (s, O$_2$C***Ph***-***C***$_3$), 126.71 (s, C(OH)H***Ph***-***C***$_2$), 126.62 (s, C(OH)H***Ph***-***C***$_4$), 126.22 (s, C(OH)H***Ph***-***C***$_3$), 112.53 (t, $^3J_{PC}$ = 4.6 Hz, [Ru]=C=***C***), 67.24 (s, ***C***(OH)HPh). IR (DCM): 1340 cm^{-1} (κ^1-OCO-sym), 1407 cm^{-1} (κ^2-OCO-sym), 1433 cm^{-1} (P-Ph$_3$), 1482 cm^{-1} (P-Ph$_3$), 1492 cm^{-1} (κ^2-OCO-asym), 1594 cm^{-1} (κ^1-OCO-asym), 1621 cm^{-1} (C=C), Δν(uni) 254 cm^{-1}, Δν (chelate) 85 cm^{-1}. MS (ESI): 983 *m*/*z* ([M − OH]$^+$).

3.4. Benzoic acid 1-dimethyl-2-oxo-propyl ester, **9bb**

2-methyl-3-butyn-2-ol (171 mg, 2.03 mmol) and benzoic acid (248 mg, 2.03 mmol) were added to a solution of **1a** (15 mg, 0.02 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt$_3$ (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase of dichloromethane). Isolated yield: 330 mg (79%). NMR Spectra ($CDCl_3$): ^{1}H: δ_H 8.01 (2H, ***Ph***), 7.54 (1H, ***Ph***), 7.41 (2H, ***Ph***), 2.12 (s, 3H, C***H***$_3$C=O), 1.56 (s, 6H, C{C***H***$_3$}$_2$). ^{13}C{^{1}H}: δ_C 206.61 (s, ***C***=O), 165.62 (s, ***C***O$_2$), 133.23 (s, ***Ph***), 129.61 (s, ***Ph***), 128.31 (s, ***Ph***), 84.09 (s, ***C***{CH$_3$}$_2$), 23.43 (s, ***C***H$_3$) 23.27 (s, ***C***H$_3$). IR (DCM): 1715 cm^{-1} (CH$_3$C=O), 1721 cm^{-1} (CO$_2$). MS (ESI): *m*/*z* 229.0835 ([M] + Na$^+$ expected for $C_{12}H_{15}NaO_3$ 229.0835), *m*/*z* 207.1018 ([M]$^+$H$^+$ expected for $C_{12}H_{15}O_3$ 207.1016).

3.5. Benzoic acid 2-oxo-propyl ester, **9cb**

Prop-2-yn-1-ol (114 mg, 2.03 mmol) and benzoic acid (248 mg, 2.03 mmol) were added to a solution of **1a** (15 mg, 0.02 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt$_3$ (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase in the concentration of dichloromethane). Isolated yield: 280 mg (77%). NMR Spectra ($CDCl_3$): ^{1}H: δ_H 8.00–7.97 (m, 2H, ***Ph***), 7.50–7.45 (m, 1H, ***Ph***), 7.36–7.32 (m, 2H, ***Ph***), 4.77 (s, 2H, OC***H***$_2$), 2.10 (s, 3H, C***H***$_3$). ^{13}C: δ_C 202.23 (s, ***C***=O), 166.01 (s, ***C***O$_2$), 133.55 (s, ***Ph***), 129.92 (s, ***Ph***), 129.25 (s, ***Ph***), 128.56 (s, ***Ph***), 68.47 (s, O***C***H$_2$), 25.67 (s, ***C***H$_3$). IR (DCM): 1726 cm^{-1} (CH$_3$C=O), 1741 cm^{-1}. MS (ESI): *m*/*z* 201.0526 ([M] + Na$^+$, expected for $C_{10}H_{10}NaO_3$ 201.0522).

3.6. Benzoic acid 1-methyl-2-oxo-1-phenyl-propyl ester, **9db**

2-Phenyl-3-butyn-2-ol (297 mg, 2.03 mmol) and benzoic acid (248 mg, 2.03 mmol) were added to a solution of **1a** (15 mg, 0.02 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt$_3$ (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase in the concentration of dichloromethane). Isolated yield: 390 mg (72%). NMR Spectra ($CDCl_3$): ^{1}H: δ_H 8.11 (m, 2H, ***Ph***), 7.41 (m, 8H ***Ph***), 1.91 (s, 3H, C***H***$_3$), 1.88 (s, 3H, C***H***$_3$). ^{13}C{^{1}H}: δ_C 203.57 (s, ***C***=O), 165.37 (s, ***C***O$_2$), 138.79 (s, ***Ph***), 133.61 (s, ***Ph***), 129.79 (s, ***Ph***), 129.68 (s, ***Ph***), 128.80 (s, ***Ph***), 128.60 (s, ***Ph***), 128.16 (s, ***Ph***), 124.71 (s, ***Ph***), 87.87 (s, ***C***Me), 23.64 (s, ***C***H$_3$), 22.95 (s, ***C***H$_3$). IR (DCM): 1717 cm^{-1} (CH$_3$C=O), 1724 cm^{-1} (OC=O). MS (ESI): *m*/*z* 291.0995 *m*/*z* ([M] + Na$^+$ expected for $C_{17}H_{16}NaO_3$ 291.0992), *m*/*z* 147.0808 ([M] − PhCO$_2^+$ expected for $C_{10}H_{11}O$ 147.0804).

3.7. Benzoic acid 2-oxo-1-phenyl-propyl ester, **9eb**

Phenylpropyn-1-ol (269 mg, 2.03 mmol) and benzoic acid (248 mg, 2.03 mmol) were added to a solution of **1a** (15 mg, 0.02 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt$_3$ (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase in the concentration of dichloromethane). Isolated yield: 420 mg (81%). NMR Spectra ($CDCl_3$): ^{1}H: δ_H 8.12 (m, 2H, ***Ph***), 7.46 (m, 8H, ***Ph***), 6.21 (s, 1H, C***H***Ph), 2.17 (s, 3H, ***C***H$_3$). ^{13}C: δ_C 201.52 (s, ***C***=O), 165.53 (s, ***C***O$_2$), 133.24 (s, ***Ph***), 129.66 (s, ***Ph***), 129.13 (s, ***Ph***), 127.70 (s, ***Ph***), 81.10 (s, ***C***HPh), 25.84 (s, ***C***H$_3$). IR (DCM): 1720 cm^{-1} (CH$_3$C=O), 1736 cm^{-1} (OC=O). MS (ESI): *m*/*z* 277.0832 ([M] + Na$^+$, expected for $C_{16}H_{14}NaO_3$ 277.0835), *m*/*z* 133.0646 ([CH$_3$COPhCH]$^+$, expected for C_9H_9O 133.0648).

Compound **9eb** was also prepared in an identical fashion using **1b** (17.7 mg, 0.02 mmol, isolated yield of **9eb** 68%) or **10a** (16.0 mg, 0.02 mmol, isolated yield of **9eb** 81%) in place of **1a**. The spectroscopic data matched those given above in both cases.

3.8. Acetic acid 2-oxo-1-phenyl-propyl ester, **9ea**

Phenylpropyn-1-ol (269 mg, 2.03 mmol) and acetic acid (122 mg, 2.03 mmol) were added to a solution of **1a** (15 mg, 0.02 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt$_3$ (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase in the concentration of dichloromethane). Isolated yield: 310 mg (79%). NMR Spectra ($CDCl_3$): ^{1}H: δ_H 7.29 (5H, ***Ph***), 5.86 (s, 1H, C***H***Ph), 2.04 (s, 3H, C***H***$_3$CO), 1.97 (s, 3H, CH$_3$CO$_2$). ^{13}C: δ_C 201.48 (s, ***C***=O), 169.99 (s, ***C***O$_2$), 132.94 (s, ***Ph***), 129.12 (s, ***Ph***), 128.83 (s, ***Ph***), 127.81 (s, ***Ph***), 80.69 (s, ***C***HPh), 25.79 (s, ***C***H$_3$), 20.39 (s, ***C***H$_3$). IR (DCM): 1731 cm^{-1} (CH$_3$C=O), 1745 cm^{-1} (OC=O). MS

(ESI): *m/z* 215.0677 ([M] + Na^+ expected for $C_{11}H_{12}NaO_3$ 215.0677), *m/z* 133.0647 ([M] − $MeCO_2^+$ expected for C_9H_9O 133.0647), *m/z* 102.1277 ([M] − $MeCO_2^+$ expected for C_9H_9O 133.0647)

3.9. 4-Bromobenzoic acid 2-oxo-1-phenyl-propyl ester, **9ec**

Phenylpropyn-1-ol (269 mg, 2.034 mmol) and 4-bromobenzoic acid (409 mg, 2.034 mmol) were added to a solution of **1a** (15 mg, 0.02 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt_3 (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase in the concentration of dichloromethane). Isolated yield: 345 mg (51%). NMR Spectra ($CDCl_3$): ^1H: δ_H 7.95 (m, 2H, ***Ph***), 7.60–7.41 (6H, ***Ph***), 6.17 (s, 1H, C***H***Ph), 2.17 (s, 3H, C***H***$_3$). $^{13}C\{^1H\}$: δ_C 201.31 (s, ***C***=O), 165.07 (s, ***C***O_2), 133.05 (s, ***Ph***), 131.79 (s, ***Ph***), 131.38 (s, ***Ph***), 129.49 (s, ***Ph***), 129.16 (s, ***Ph***), 128.63 (s, ***Ph***), 128.15 (s, ***Ph***), 128.02 (s, ***Ph***), 81.44 (s, ***C***HPh), 26.15 (s, ***C***H_3). IR (DCM): 1721 cm^{-1} (C=O). MS (ESI): *m/z* 354.9932 ([M] + Na^+ expected for for $C_{16}H_{13}^{79}BrNaO_3$ 354.9940), *m/z* 333.0107 ([M] + H^+ expected for for $C_{16}H_{14}^{79}BrO_3$ 333.0121), *m/z* 279.0924 ([M] − Br^+ expected for for $C_{16}H_{14}^{79}BrO_3$ 333.0121) *m/z* 133.0646 ($MeCOCHPh^+$ expected for C_9H_9O 133.0648).

3.10. Benzoic acid 1-acetyl-cyclopentyl ester, **9fb**

1-Ethynylcyclopentanol (224 mg, 2.03 mmol) and benzoic acid (248 mg, 2.03 mmol) were added to a solution of **1a** (15 mg, 0.02 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt_3 (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase in the concentration of dichloromethane). Isolated yield: 420 mg (89%). NMR Spectra ($CDCl_3$): ^1H: δ_H 7.96 (m, 2H, ***Ph***), 7.49 (m, 1H, ***Ph***), 7.36 (m, 2H, ***Ph***), 2.22 (m, 2H, C***H***$_2$), 2.06 (s, 3H, C***H***$_3$), 1.96 (m, 2H, C***H***$_2$), 1.70 (m, 4H, C***H***$_2$). $^{13}C\{^1H\}$: δ_C 205.7 (s, ***C***=O), 166.2 (s, ***C***O_2), 133.4 (s, ***Ph***), 129.7 (s, ***Ph***), 128.4 (s, Ph), 94.4 (s, ***C***), 35.7 (s, ***C***H_2), 24.9 (s, ***C***H_2), 24.5 (s, ***C***H_3CO). IR (DCM): 1716 cm^{-1} (CH_3C=O), 1719 cm^{-1} (OC=O). MS (ESI): 255.0992 ([M] + Na^+ expected for $C_{14}H_{16}NaO_3$ 255.0992), 178 *m/z* ([M − Ph] + Na^+), 150 *m/z* ([M − PhCO]Na^+).

3.11. Benzoic acid 1-acetyl-cyclohexyl ester, **9gb**

1-Ethynyl-1-cyclohexanol (0.253 g, 2.034 mmol) and benzoic acid (0.248 g, 2.034 mmol) were added to a solution of *cis*-Ru(κ^2-$OCOCH_3)_2(PPh_3)_2$ (0.0151 g, 0.020 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt_3 (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase of dichloromethane). Isolated yield: 0.390 g, 78%. NMR Spectra ($CDCl_3$): ^1H: δ_H 8.01 (m, 2H, ***Ph***), 7.51 (m, 1H, ***Ph***), 7.39 (m, 2H, ***Ph***), 2.13 (d, J_{HH} = 12.5 Hz, 2H, C***H***$_2$), 2.05 (s, 3H, C***H***$_3$), 1.70–1.48 (8H, C***H***$_2$). $^{13}C\{^1H\}$: δ_C 207.12 (s, ***C***=O), 165.32 (s, ***C***O_2), 133.27 (s, ***Ph***), 129.67 (s, ***Ph***), 129.61 (s, ***Ph***), 128.39 (s, Ph), 85.53 (s, ***C***), 30.75 (s, ***C***H_2), 24.96 (s, ***C***H_2), 23.54 (s, CH_3), 21.27 (s, ***C***H_2). IR (DCM): 1717 cm^{-1}(C=O). MS (ESI): *m/z* 269.1139 *m/z* ([M] + Na^+ expected for $C_{15}H_{18}NaO_3$ 269.1148), *m/z* 247.1322 ([M] + H^+ expected for $C_{15}H_{19}O_3$ 247.1329).

3.12. Benzoic acid 1-acetyl-ethisterone ester, **9hb**

Ethisterone (636 mg, 2.03 mmol) and benzoic acid (248 mg, 2.03 mmol) were added to a solution of **1a** (15 mg, 0.02 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt_3 (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase in the concentration of dichloromethane). Isolated yield: 465 mg (53%). NMR Spectra ($CDCl_3$) ^1H: δ_H 8.03 (m, 2H, ***Ph***), 7.55 (m, 1H, ***Ph***), 7.43 (m, 2H, ***Ph***), 5.67 (s, 1H, C=C***H***), 2.45–2.19 (m, C***H***/C***H***$_2$), 2.03 (s, 3H, $COCH_3$), 1.97–1.30 (m, C***H***/C***H***$_2$), 1.16–1.01 (m, C***H***, C***H***$_2$, C***H***$_3$), 0.92–0.82 (m, C***H***, C***H***$_2$, C***H***$_3$). $^{13}C\{^1H\}$: δ_C 207.88 (s, CH_3***C***=O), 199.24 (s, ***C***=O), 170.66 (s, ***C***=CH),), 166.44 (s, ***C***O_2Ph), 133.40 (s, Ph), 129.75 (s, ***Ph***), 129.67 (s, ***Ph***), 129.54 (s, ***Ph***), 128.46 (s, ***Ph***), 128.36 (s, ***Ph***), 123.82 (s, C=***C***H), 96.27 (s, ***C***), 52.81 (s, ***C***H), 47.31 (s, ***C***H), 46.92 (s, ***C***), 38.32 (s, ***C***), 35.52 (s, ***C***H_2), 35.47 (s, ***C***H_2), 33.72 (s, ***C***H_2), 32.85 (s, ***C***H_2), 32.56 (s), 26.95 (s, ***C***H), 24.52 (s, ***C***H_2), 20.50 (s, ***C***H_2), 17.22 (s, ***C***H_3), 15.22 (s, 13.55 (s, ***C***H_3). IR (DCM): 1716 cm^{-1}, 1668 cm^{-1} (C=O). MS (ESI) *m/z* ([M]$^+$) 435.2527 (expected for $C_{28}H_{35}O_4$ 435.2530, [M-OCOPh]$^+$).

3.13. Synthesis of [Ru(κ^2-OCOPh)(κ^1-OCOPh)$(PPh_3)_2$(CO)], **10b**

Complex **1b** (200 mg, 0.230 mmol) was suspended in 20 mL of deoxygenated MeOH in a Schlenk tube equipped with a stirrer bar. The reaction mixture was then placed under an atmosphere of CO and stirred for 10 min. Over the course of this time the suspension changed colour from red to pale yellow. The product was isolated by filtration and washed with 10 mL of MeOH and 10 mL of Et_2O and dried *in vacuo*. Yield: 95 mg (52%). NMR ($CDCl_3$): ^1H: δ_H 7.47 (m, 12H, P***Ph***$_3$), 7.11 (m, 18H, ***Ph***), 7.04 (m, 6H, P***Ph***$_3$), 6.88 (at, 7.68 Hz, 4H, O_2C***Ph***). $^{31}P\{^1H\}$: δ_P 38.71 (s, ***P***Ph_3). $^{13}C\{^1H\}$: δ_C 206.85 (t, $^2J_{PC}$ = 13.9 Hz, Ru***C***O), 176.39 (s, O_2***C***Ph), 134.56 (t, $^2J_{PC}$ + $^4J_{PC}$ = 12.3 Hz, P***Ph***$_3$-***C***$_2$), 133.39 (s, O_2C***Ph***-***C***$_1$), 129.92 (s, O_2C***Ph***-***C***$_4$) 129.83 (s, P***Ph***$_3$-***C***$_4$), 129.59 (m, P***Ph***$_3$-***C***$_1$), 128.07 (s, O_2C***Ph***-***C***$_2$), 127.96 (t, $^3J_{PC}$ + $^5J_{PC}$ = 9.3 Hz, P***Ph***$_3$-***C***$_3$), 126.35 (s, O_2C***Ph***-***C***$_3$). IR (DCM): 1350 cm^{-1} (κ^1-OCO-sym), 1444 cm^{-1} (κ^2-OCO-sym), 1434 cm^{-1} (P-Ph_3), 1483 cm^{-1} (P-Ph_3), 1505 cm^{-1} (κ^2-OCO-asym), 1616 cm^{-1} (κ^1-OCOasym), 1947 cm^{-1} (CO). Δν(uni) 266 cm^{-1}, Δν (chelate) 61 cm^{-1}. MS (ESI): 816 *m/z* ([Ru$(O_2CPh)(PPh_3)_2$(CO)(MeCN)]$^+$), 788 *m/z* ([Ru$(O_2CPh)(PPh_3)_2$(MeCN)]$^+$).

3.14. Reaction of complexes **1a** and **1b** with CO

Complex **1b** (75 mg, 86.4 μmol) was dissolved in 10 mL CH_2Cl_2 under an atmosphere of N_2. The N_2 atmosphere was removed *in vacuo* and replaced with CO. After stirring for 15 min the solution had changed from a dark red-brown to a dark blue-green. The solution was stirred for 24 h under CO before the flask was protected from the light with aluminium foil and $AgBF_4$ (18.0 mg, 92.4 μmol) added. The mixture was allowed to stir under an atmosphere of CO for 3 days; at this point the solution had turned dark brown and a precipitate was observed. The CO atmosphere was removed *in vacuo* and replaced with N_2 and the mixture filtered through a short Celite column.

The reaction using **1a** was carried out in an identical fashion using 64.8 mg (87.1 μmol) Ru(κ^2-$OAc)_2(PPh_3)_2$ and 17.0 mg (87.3 μmol) $AgBF_4$. IR spectroscopy demonstrated that after 5 days that only trace amounts of **11a** remained at which the point the reaction mixture was filtered through celite. The filtrate was divided into two approximately equal portions and 0.5 equivalent NaOAc was added (5.5 mg, 67.0 μmol).

3.15. Synthesis of [Ru(κ^1-$O_2CPh)_2(PPh_3)_2(CO)_2$], **11b**

Complex **1b** (200 mg, 0.230 mmol) was dissolved in 20 mL CH_2Cl_2 and CO gas bubbled through the solution until a colour change from orange to green was observed. $AgBF_4$ (45 mg, 0.230 mmol) was then added and the mixture stirred under an atmosphere of CO for 24 h,

after which a dark brown solution and a precipitate were observed. The product was isolated by filtration through celite. Crystals suitable for X-ray diffraction were obtained from a CD_2Cl_2/n-pentane solution. NMR Spectra exhibited resonances for a minor carbonyl-containing impurity. Resonance for **11b** (CD_2Cl_2) ^{1}H: δ_H 7.76 (m, 12H, P***Ph***$_3$), 7.61 (m, 4H, O_2C***Ph***) 7.47 (m 6H P***Ph***$_3$), 7.28 (m, 18H, P***Ph***$_3$ and O_2C***Ph***). ^{31}P{^{1}H}: δ_P 29.57 (s, ***P***Ph$_3$). ^{13}C{^{1}H}: δ_C 197.70 (t, $^2J_{PC}$ = 11.5 Hz, Ru***C***O), 172.20 (s, O_2***C***Ph), 136.22 (s, O_2C***Ph***-***C***$_4$), 134.57 (m, P***Ph***$_3$-***C***$_2$), 130.96 (s, P***Ph***$_3$-***C***$_4$), 130.44 (s, O_2C***Ph***-***C***$_{2/3}$), 130.76 (s, s, O_2C***Ph***-***C***$_1$) 129.84 (s, O_2C***Ph***-***C***$_{2/3}$), 128.72 (m, P***Ph***$_3$-***C***$_3$), 127.44 (br, P***Ph***$_3$-***C***$_1$). IR (DCM): 1347 cm^{-1} (κ^1-OCOsym), 1434 cm^{-1} (P-Ph$_3$), 1484 cm^{-1} (P-Ph$_3$), 1609 cm^{-1} (κ^1-OCO-asym) 1987 cm^{-1} (CO) 2049 cm^{-1} (CO) Δν(uni) 262 cm^{-1}. MS (ESI): 803.1046 *m*/*z* (Expected for $C_{45}H_{35}O_4P_2Ru$ 803.1049, [Ru(κ^2-OCOPh)(PPh$_3$)$_2$(CO)$_2$]$^+$).

3.16. Reaction of HC≡CCH$_2$(OPh) with benzoic acid

Phenyl propargyl ether (258 mg, 1.95 mmol) and benzoic acid (238 mg, 1.95 mmol) were added to a solution of **1a** (14.5 mg, 0.02 mmol) in 20 mL toluene and heated at 120 °C for 16 h. The product was purified by flash column chromatography. The column was doped with NEt_3 (5% in n-hexane) and then n-hexane/dichloromethane used as the eluent (starting with n-hexane and a gradual increase in the concentration of dichloromethane). The three isomers, which could not be separated by column chromatography, were obtained in a ratio of 1:0.7:1.6 (**13a**:**13b**:**13c**). Isolated yield 160 mg (32%). NMR spectra (CD_2Cl_2): ^{1}H δ_H 4.61 (dd, $^3J_{HH}$ = 6.67 Hz, $^4J_{HH}$ = 1.28 Hz, 2H, C***H***$_2$, **13b**), 4.71 (br s, 2H, C***H***$_2$, **13c**), 4.85 (dd, $^3J_{HH}$ = 6.67 Hz, $^4J_{HH}$ = 1.56 Hz, 2H, C*H*$_2$, **13a**), 5.18 (m, 1H, C=C***H***$_a$H$_b$, **13c**), 5.24 (m, 1H, C=CH$_a$***H***$_b$, **13c**), 5.35 (aq, $^3J_{HH}$ = 6.55 Hz, $^3J_{HH}$ = 6.55 Hz, 1H, =C***H***, **13b**), 5.91 (dt, $^3J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 6.77 Hz, 1H, =C***H***, **13a**) 6.93–7.01 (m, ***Ph***), 7.20–7.33 (m, ***Ph***), 7.42–7.72 (m, ***Ph***, =C***H***, **13b** and =C***H***, **13a**), 8.07–8.24 (m, Ph); ^{13}C δ_C 164.6 (s, Ph***C***O$_2$, **13c**),163.4 (s, O_2***C***Ph, **13b**),163.0 (s, O_2***C***Ph, **13a**),158.6 (s, O_2C***Ph***-***C***$_1$, **13c**),158.5 (s, O_2C***Ph***-***C***$_1$, **13a**),158.3 (s, O_2C***Ph***-***C***$_1$, **13b**),151.6 (s, *C*=CH$_2$, **13c**),139.4 (s, =***C***H, **13b**),136.4 (s, =O_2C***Ph***-***C***$_1$H, **13a**)133.7,133.6,130.1,130.0,129.9,(s, Ph-***C***H),129.7 (s, Ph-***C***),129.6,129.5,129.5,(s, Ph-***C***H),129.4 (s, Ph-***C***),128.9 (s, Ph-***C***),128.8, 128.7,128.6,121.9,121.4,121.0,120.9,114.9,114.8,114.7, (s, Ph-***C***H),110.3 (s, =***C***H, **13a**),109.8 (s, =***C***H, **13b**),103.9 (s, C=***C***H$_2$, **13c**),66.7 (s,***C***H$_2$OPh, **13a**),64.7 (s,***C***H$_2$OPh, **13c**),61.6 (s, ***C***H$_2$OPh, **13a**); EI-MS: 254.0937 ([M]$^+$expected for $C_{16}H_{14}O_3$254.0937).

4. Details of X-ray diffraction analysis

Details of the collection and refinement are presented in Table 3. Diffraction data were collected at 110 K on a Bruker Smart Apex diffractometer with Mo-Kα radiation (λ = 0.71073 Å) using an SMART CCD camera. Diffractometer control, data collection, and initial unit-cell determination was performed using SMART [45]. Frame integration and unit-cell refinement software was carried out with SAINT+ [46]. Absorption corrections were applied by SADABS (v2.03, Sheldrick). Structures were solved by direct methods using SHELXS-97 [47] and refined by full-matrix least-squares using SHELXL-97 [48]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions with the exception of the hydrogen atom attached to the vinylidene carbon atom in **2b** were located by difference map.

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Appendix A. Supplementary material

CCDC 784238, 784239 and 784240 contain the supplementary crystallographic data for complexes **1b**, **3c** and **11** respectively. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

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