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Cyclopentadienyl-ruthenium and -osmium chemistry

Part XXXIV *. Reactions of 1-alkynes with σ -vinyl-ruthenium complexes. X-ray structures

of $\text{Ru}\{\eta^3\text{-CH}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{C}=\text{CHPh}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$
 and $\text{Ru}(\eta\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_3(\text{CO}_2\text{Me})_3\text{CHC}^t\text{BuCH}(\text{CO}_2\text{Me})\}$

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Abstract

Reactions between HC_2R ($\text{R} = \text{Ph}$, ^tBu) and the chelate vinyl ester complex $\text{Ru}\{\text{C}(\text{CO}_2\text{Me})=\text{CHC}(\text{O})\text{OMe}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ have given η^3 -allyl derivatives $\text{Ru}\{\eta^3\text{-CH}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{C}=\text{CHR}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$, as shown by an X-ray structure of the phenyl derivative. Similarly, the reaction between HC_2Ph and $\text{Ru}\{\text{C}(\text{OMe})=\text{CH}(\text{CO}_2\text{Me})\}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ gave $\text{Ru}\{\eta^3\text{-CH}(\text{CO}_2\text{Me})\text{C}(\text{OMe})\text{C}=\text{CHPh}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$. These reactions probably proceed via displacement of the ester carbonyl group or PPh_3 by the 1-alkyne, which isomerises to the corresponding vinylidene before a formal insertion into the $\text{Ru-C}(sp^2)$ bond. Complexes containing cyclic adducts of the 1-alkyne and the butadienyl ligand, namely $\text{Ru}(\eta\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_3(\text{CO}_2\text{Me})_3\text{CHCR}^t\text{CH}(\text{CO}_2\text{Me})\}$, were obtained from $\text{Ru}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})=\text{CH}(\text{CO}_2\text{Me})\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ and HC_2R ($\text{R} = \text{Ph}$, ^tBu), as shown by an X-ray structure of the *t*-butyl derivative. A small amount of an η^5 -vinylcyclohexadienyl complex was also obtained from the reaction with HC_2Ph . In these reactions, the 1-alkyne does not isomerise, probably for steric reasons; the first step may involve replacement of PPh_3 by the alkyne, rather than formation of an η^1 -butadienyl complex.

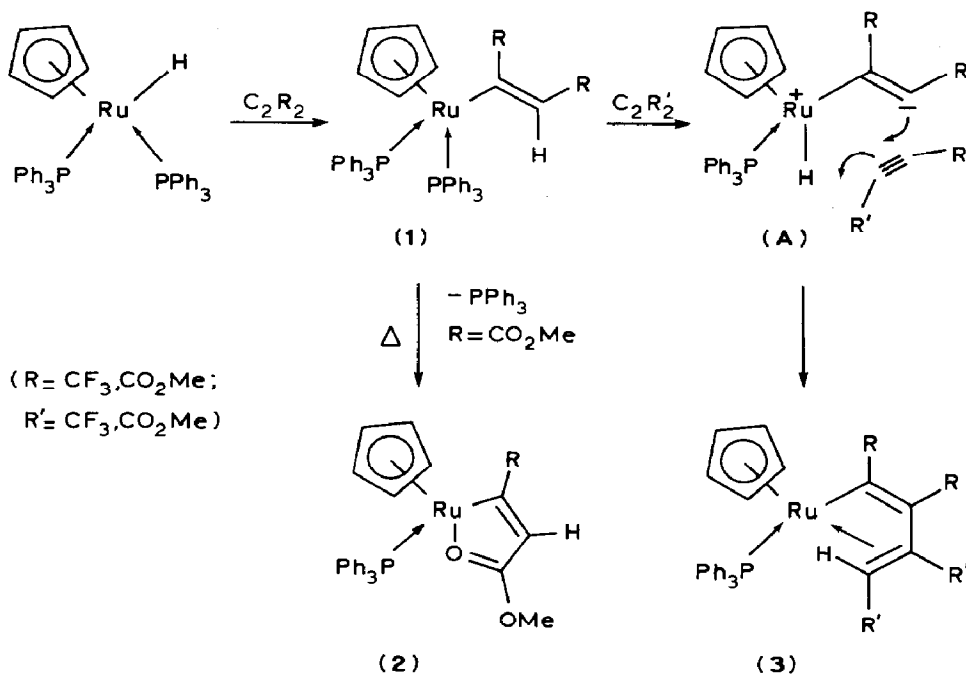
* For Parts XXXII and XXXIII see ref. 1.

Introduction

Insertion reactions of alkynes into metal-hydride and metal-alkyl bonds have been known for many years and generally give complexes containing substituted vinyl groups σ -bonded to the metal [2]. Subsequent reactions may follow. Thus, in the case of $\text{RuH}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$, initial insertion into the Ru-H bond gave $\text{Ru}(\text{CR}=\text{CHR})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ (Scheme 1; **1**, $\text{R} = \text{CO}_2\text{Me}$, CF_3). For $\text{R} = \text{CO}_2\text{Me}$, ready displacement of PPh_3 by the ester carbonyl group gave $\text{Ru}\{\text{C}(\text{CO}_2\text{Me})=\text{CHC}(\text{O})\text{OMe}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**2**). With excess alkyne, the butadienyl complexes $\text{Ru}(\text{CR}=\text{CRCR}'=\text{CHR}')(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**3**, $\text{R} = \text{R}' = \text{CO}_2\text{Me}$, CF_3 ; $\text{R} = \text{CO}_2\text{Me}$, $\text{R}' = \text{CF}_3$) were obtained, the second molecule of alkyne apparently inserting into a C-H bond, a reaction which has been rationalised by a dipolar intermediate (A) (Scheme 1) [3,4]. Other studies of several other alkynes revealed that the first formed σ -vinyl complex could undergo several further reactions to form unusual ligands [5].

In some cases, such as the 1-alkynes HC_2R ($\text{R} = \text{Ph}$, C_6H_5 , CO_2Me), the alkyne is sufficiently strong an acid to displace the hydride in $\text{RuH}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ as H_2 , with concomitant formation of the σ -acetylide, $\text{Ru}(\text{C}_2\text{R})(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ [6].

Reactions of ruthenium alkyl complexes $\text{RuR}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$ ($\text{R} = \text{Me}$, CH_2Ph) have also given a plethora of complexes, the formation of which can be explained by a combination of reactions involving insertion of the alkyne into the Ru-C(sp^3) bond, elimination of the alkyl as alkane (in reactions with 1-alkynes), and further elaboration of the vinyl ligands [6].



Scheme 1

Our interest in the reactivity of complexes containing $M-C(sp)$ and $M-C(sp^2)$ bonds has recently concentrated on the former [7], but the ready availability of a range of derivatives containing σ -vinyl and σ -buta-1,3-dien-2-yl groups has prompted us to examine further the reactivity of these compounds [3]. This paper describes some reactions between 1-alkynes, HC_2R ($R = Ph$ or tBu) and complexes **2**, **3** ($R = CO_2Me$), and $Ru\{C(OMe)=CH(CO_2Me)\}(PPh_3)_2(\eta-C_5H_5)$ (**4**), which is formed by deprotonation of the methoxycarbene cation $[Ru\{C(OMe)(CH_2-CO_2Me)\}(PPh_3)_2(\eta-C_5H_5)]^+$ [8]. The molecular structures of two major products are also reported.

Results

Reactions of 1-alkynes with $Ru\{C(CO_2Me)=CHC(O)OMe\}(PPh_3)(\eta-C_5H_5)$ (**2**)

The reactions between HC_2R ($R = Ph$ or tBu) and **2** were carried out in 1,2-dimethoxyethane (dme) under nitrogen in a small autoclave to achieve the necessary temperature ($120^\circ C$) for optimum conversion. By this method, good yields of the 1/1 adducts **5** and **6** were obtained.

These complexes form air-stable yellow crystalline solids, which were characterised by elemental microanalyses and from their spectroscopic properties. In their electron impact (EI) mass spectra, the molecular ions found centred on m/z 673 and 653, respectively, fragmented either by elimination of the organic ligand (for **5**), or by the expected loss of Me, OMe and CO_2Me groups (for **6**); loss of Me from $[M - PPh_3]^+$ was also found for **5**. There were no ions formed by loss of the alkyne moiety. In the 1H NMR spectra, the two CO_2Me groups are magnetically inequivalent. Two single protons resonated at δ 1.59 and 6.07 (for **5**) and 1.43 and 4.94 ppm (for **6**); both showed coupling to the ^{31}P nucleus of ca. 13–16 and 3–4 Hz,

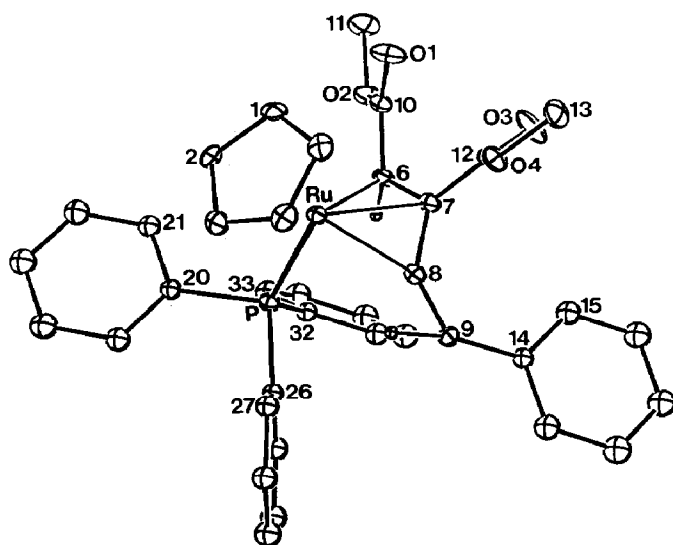


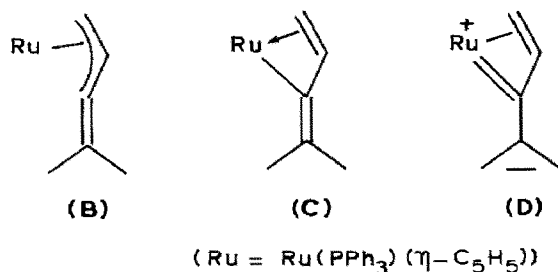
Fig. 1. ORTEP view of $Ru\{\eta^3-CH(CO_2Me)C(CO_2Me)C=CHPh\}(PPh_3)(\eta-C_5H_5)$ (**5**) showing atom-labelling scheme. Atoms not otherwise indicated are carbons. For clarity only the ipso carbon atoms of the PPh_3 ligand are shown.

Table 1

Selected bond distances (Å) and angles (deg) for $\text{Ru}\{\eta^3\text{-CH}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{C}=\text{CHPh}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**5**)

<i>Bond distances</i>			
Ru–P(1)	2.310(2)	Ru–C(6)	2.190(5)
Ru–C(7)	2.108(6)	Ru–C(8)	2.061(6)
C(6)–C(7)	1.432(8)	C(6)–C(10)	1.463(8)
C(7)–C(8)	1.431(8)	C(7)–C(12)	1.500(8)
C(8)–C(9)	1.335(8)	C(9)–C(14)	1.477(7)
<i>Bond angles</i>			
Ru–C(6)–C(10)	116.9(4)	Ru–C(7)–C(6)	73.7(3)
Ru–C(7)–C(8)	68.2(3)	Ru–C(7)–C(12)	128.1(4)
Ru–C(8)–C(7)	71.7(3)	Ru–C(8)–C(9)	146.2(4)
P(1)–Ru–C(6)	89.5(1)	P(1)–Ru–C(7)	105.8(2)
P(1)–Ru–C(8)	84.0(2)	C(10)–C(6)–C(7)	119.8(5)
C(6)–C(7)–C(8)	116.6(5)	C(6)–C(7)–C(12)	122.2(5)
C(8)–C(7)–C(12)	121.2(5)	C(7)–C(8)–C(9)	141.8(6)
C(8)–C(9)–C(14)	128.3(5)		

respectively. In the ^{13}C NMR spectrum of **5**, the skeletal carbons were found at δ 36.1, 61.3, 123.6 and 164.9 ppm; other resonances are listed in the Experimental section. The ^1H resonance for the butadienyl proton in **3** ($\text{R} = \text{R}' = \text{CO}_2\text{Me}$) was recently reported at δ 2.22 [4].



Molecular structure of 5. We carried out an X-ray structure determination on the phenylethyne adduct to determine the mode of addition of the alkyne to the vinyl ligand. Figure 1 shows a plot of the molecule, and reveals that these complexes are not butadienyls but allylic derivatives. Table 1 summarises important bond distances and angles. The ruthenium has distorted octahedral coordination, with the C_5H_5 group (Ru–C 2.212–2.247(6), av. 2.232 Å) occupying one octahedral face, and the PPh_3 ligand (Ru–P 2.310(2) Å) one of the remaining three positions. These distances are within the normal limits found previously on many occasions for these compounds [9].

The remaining ligand has been formed by combination of the substituted vinyl group in **2** with phenylvinylidene to give an η^3 -methylene-allyl moiety. The metal–carbon separations (Ru–C(6) 2.190(5), Ru–C(7) 2.108(6), Ru–C(8) 2.061(6) Å) are similar to those found in other complexes containing related ligands, such as $\text{Ru}\{\eta^3\text{-C}(\text{CN})_2\text{CPhC}=\text{C}(\text{CN})_2\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ [10]. The angle at the central allylic carbon, C(6)–C(7)–C(8), is 116.6(5)° and C(7)–C(8)–C(9) is 141.8(6)°. Within the allylic group, the two C–C separations are identical at 1.432(8) and 1.431(8) Å,

Table 2

Selected bond distances (Å) and angles (deg) for $\text{Ru}(\eta\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_3(\text{CO}_2\text{Me})_3\text{CHC}^1\text{BuCH}(\text{CO}_2\text{Me})\}$ (**9**)

<i>Bond distances</i>			
Ru–C(9)	2.179(7)	Ru–C(12)	2.123(6)
Ru–C(15)	2.173(7)	Ru–C(18)	2.169(6)
Ru–C(19)	2.254(7)	C(6)–C(7)	1.51(1)
C(6)–C(9)	1.52(1)	C(6)–C(19)	1.531(9)
C(9)–C(10)	1.49(1)	C(9)–C(12)	1.46(1)
C(12)–C(13)	1.49(1)	C(12)–C(15)	1.43(1)
C(15)–C(16)	1.49(1)	C(15)–C(18)	1.41(1)
C(18)–C(19)	1.411(9)	C(19)–C(20)	1.53(1)
<i>Bond angles</i>			
Ru–C(9)–C(6)	98.1(4)	Ru–C(9)–C(10)	115.1(5)
Ru–C(9)–C(12)	68.1(4)	Ru–C(12)–C(9)	72.2(4)
Ru–C(12)–C(13)	123.9(5)	Ru–C(12)–C(15)	72.5(4)
Ru–C(15)–C(12)	68.7(4)	Ru–C(15)–C(16)	129.8(5)
Ru–C(15)–C(18)	71.0(4)	Ru–C(18)–C(15)	71.2(4)
Ru–C(18)–C(19)	74.7(4)	Ru–C(19)–C(6)	94.5(4)
Ru–C(19)–C(18)	68.2(4)	Ru–C(19)–C(20)	125.5(5)
C(7)–C(6)–C(9)	112.7(5)	C(7)–C(6)–C(19)	114.5(5)
C(9)–C(6)–C(19)	101.7(5)	C(6)–C(9)–C(10)	122.4(6)
C(6)–C(9)–C(12)	116.5(6)	C(10)–C(9)–C(12)	119.2(6)
C(9)–C(12)–C(13)	120.9(6)	C(9)–C(12)–C(15)	116.3(6)
C(13)–C(12)–C(15)	122.7(6)	C(12)–C(15)–C(16)	119.5(6)
C(12)–C(15)–C(18)	118.9(6)	C(16)–C(15)–C(18)	121.4(6)
C(15)–C(18)–C(19)	120.5(6)	C(18)–C(19)–C(20)	121.9(6)
C(18)–C(19)–C(6)	114.4(6)	C(6)–C(19)–C(20)	119.1(6)

*Molecular structure of $\text{Ru}(\eta\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_3(\text{CO}_2\text{Me})_3\text{CHC}^1\text{BuCH}(\text{CO}_2\text{Me})\}$ (**9**).* A computer-generated plot of a molecule of **9** is shown in Fig. 2, and important bond distances and angles are given in Table 2. The ruthenium is coordinated to a C_5H_5 ligand (Ru–C 2.174(8)–2.199(9), av. 2.187 Å) and a highly substituted η^5 -cyclohexadienyl ligand formed by combination of the alkyne with the butadienyl ligand present in **3** (R = R' = CO_2Me). The metal is attached to five carbons bearing CO_2Me , H and ^1Bu substituents, with the ring being completed by C(6), bearing *endo*-H and *exo*- CO_2Me substituents. The Ru–C distances may be compared with those found for the substituted C_5 ring in $\text{Ru}(\eta\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}$ (2.157–2.178(2) Å) [11], and also with the Rh–C separations found for the $\eta^4\text{-C}_5\text{H}_3(\text{CO}_2\text{Me})_3$ ligand in $\text{Rh}\{\eta^4\text{-C}_5\text{H}_3(\text{CO}_2\text{Me})_3\}\{\eta^5\text{-C}_5\text{H}_2(\text{CO}_2\text{Me})_3\}$ (2.14 Å) [12]. The five metal-bonded carbons of the cyclohexadienyl ligand are closely coplanar (maximum deviation, C(15) – 0.039(8) Å).

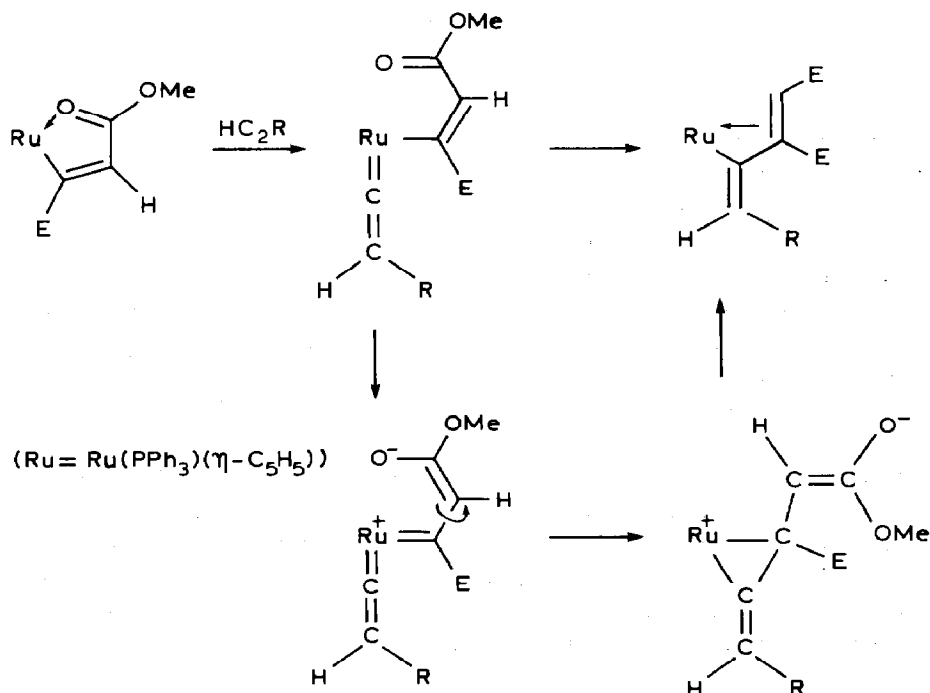
In the ^1H NMR spectrum, protons attached to C(6) and C(18) are coupled together ($J(\text{HH})$ ca. 1 Hz); the latter are found at δ ca. 6, i.e. with chemical shifts comparable to the *endo* proton found at δ 6.3 in $\text{Rh}\{\eta^4\text{-C}_5\text{H}_3(\text{CO}_2\text{Me})_3\}\{\eta^5\text{-C}_5\text{H}_2(\text{CO}_2\text{Me})_3\}$ [12]. Four CO_2Me resonances and the C_5H_5 signal are present in each spectrum; for **9**, the CMe_3 protons are found at δ 1.09. In the FAB mass spectra, fragment ions include those formed by the usual loss of Me, OMe or CO_2Me groups.

A small amount of a second product (**10**) was isolated from the reaction between **3** (R = R' = CO_2Me) and HC_2Ph . This complex exhibited a molecular ion at m/z

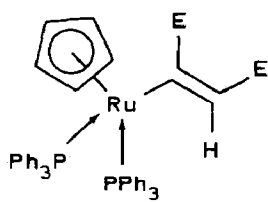
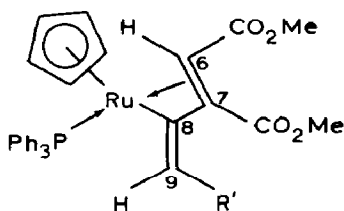
656, corresponding to the addition of two molecules of phenylethyne and the loss of the PPh_3 ligand. The ^1H NMR spectrum contained four CO_2Me resonances in positions similar to those found for the mono-adduct (**8**). Fragment ions included those formed by loss of OMe , CO_2Me and HC_2Ph groups. No crystallographically suitable crystals were obtained, but on the basis of related work in which the complex $\text{Ru}(\eta\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_8\text{H}(\text{CO}_2\text{Me})_8\}$ has been fully characterised [13] as the vinylcyclohexadienyl derivative **11**, it is likely that **10** has a similar structure. The precise pattern of substitution is not certain, but the ready loss of 2 HC_2Ph from the molecular ion to give an ion at m/z 451, formulated as $[\text{Ru}\{\text{HC}_4(\text{CO}_2\text{Me})_4\}(\eta\text{-C}_5\text{H}_5)]^+$ suggests that the second alkyne is incorporated as the *exo* vinyl substituent.

Discussion

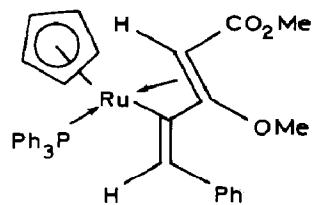
Our previous studies [5,6] had led to the expectation that reactions between **2** and 1-alkynes would result in the formation of butadienyl complexes of type **3**. As we have shown above, the products obtained from HC_2R ($\text{R} = \text{Ph}$, ^tBu) have the isomeric allylic structures **5** and **6**. The formation of these complexes is envisaged to proceed by isomerisation of the 1-alkyne to vinylidene as it coordinates to the metal atom [14]. This is followed by migration of the vinyl group to the coordinated vinylidene, also with isomerisation (*cis* \rightarrow *trans*) [3], to give the new C_4 ligand (Scheme 2). The formation of vinylidenes from 1-alkynes is well documented [15], and recent studies have described their subsequent reactions either to give complexes, such as $\text{Mn}\{\text{C}=\text{C}(\text{CN})_2\}\text{P}(\text{O})(\text{OR})_2\}\{\text{CO}\}\{\text{P}(\text{OR})_3\}\{\text{dppe}\}$ [16], or organic



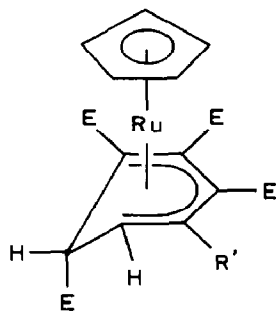
Scheme 2

(4) (E = CO₂Me)

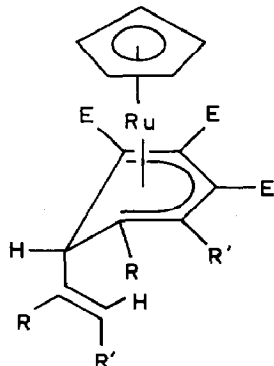
(5) R' = Ph

(6) R' = ^tBu

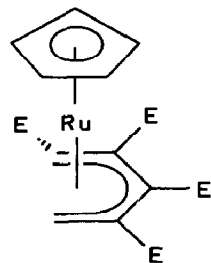
(7)

(E = CO₂Me)

(8) R' = Ph

(9) R' = ^tBu(E = CO₂Me)

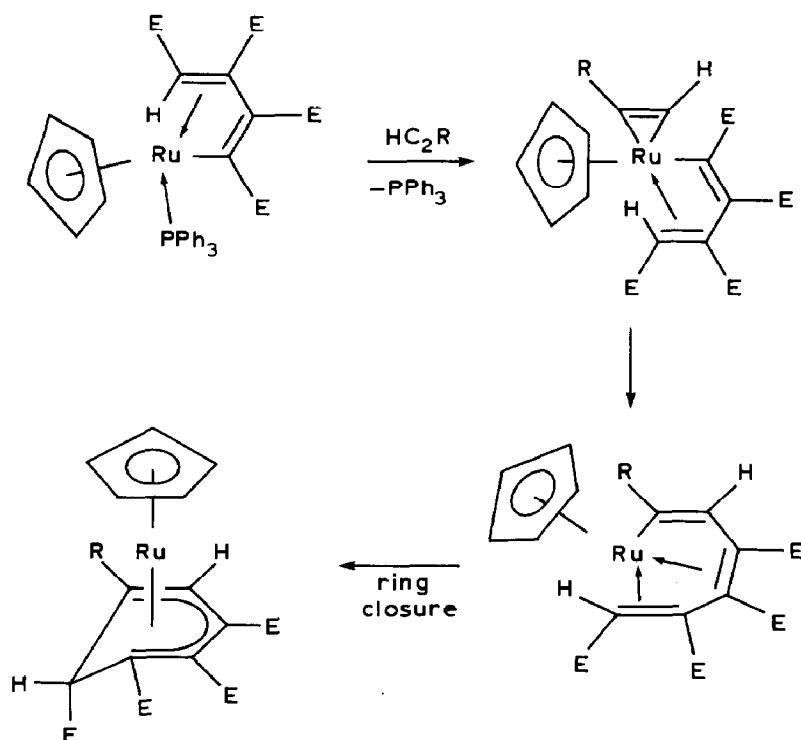
(10) R, R' = H, Ph

(11) R, R' = H, ^tBu(12) (E = CO₂Me)

compounds, such as methylenecyclopentenediones [17], in which a recognisable vinylidene fragment is present.

The unsaturated allylic ligand has several precedents, including [Fe(CO)₃{η³-C(CO₂Me)₂CHC=O}]⁻, whose structure was inferred from spectroscopic data [18], the molybdenum complex Mo{OC(O)C₃F₇}(CO)₂(bpy){η³-CH₂C(CONHMe)C=CH₂} [19], as well as a multitude of derivatives earlier described by us and formed by subsequent chelation of the buta-1,3-dien-2-yl ligand generated by ring-opening reactions of σ-cyclobutenyl complexes, themselves obtained by formal [2 + 2] cycloaddition reactions between metal acetylides and electron-deficient alkenes [20–23].

As pointed out on previous occasions, representation of the allyl-ruthenium system as depicted in the classical form **B** is at variance with the ¹³C NMR parameters, particularly the chemical shift of the metal-bonded carbon, which is usually around δ 200 ppm. The M–C separation for this carbon is also short, indicating some degree of multiple bonding. In **5**, the geometry around C(8), with the large C(7)–C(8)–C(9) angle (141.8(6)°), and the distinct bending of the C=C double bond out of the C(7)–C(8)–Ru plane (torsion angle C(6)–C(7)–C(8)–C(9) 128.4°), also suggest the carbenic nature of C(8). Thus, although an ene-yl formulation such as **C** might appear more appropriate than **B**, being supported also by



Scheme 3

nearly equal C–C distances within the allyl group, we are now inclined to suggest that ligands of this type have a considerable contribution from the dipolar form **D**. Formally, this may be considered to be a chelating vinylcarbene ligand, and the low-field shift of the σ -bonded carbon is in accord with this description [24]. A precise understanding of the bonding in these interesting complexes must await a theoretical study.

These ligands, which may be considered as $\eta^3(4e)$ -allyls, join the steadily growing cohort of carbon ligands which are attached to Second-Row and Third-Row transition metals of Groups 5–8 by $M=C(sp^2)$ multiple bonds. Examples include $\eta^2(3e)$ -vinyl [25], $\eta^3(4e)$ -allylidene [26], $\eta^4(5e)$ -butadienyl ligands [27], and metalla-cyclopentatriene complexes, which may be folded [28,29] or planar [30], depending on d electron count. Extended Hückel MO calculations [31] have suggested that backbonding from the metal into the unsaturated systems is particularly favourable in these compounds.

Formation of the η^5 -cyclohexadienyl ligands in **8** in **9** can be achieved as shown in Scheme 3. Displacement of the coordinated C=C double bond from the metal in butadienyl complexes of type **3**, for example, by CO, CNR or PR₃, generally requires forcing conditions [4]. We suggest coordination of the entering 1-alkyne occurs by displacement of the PPh₃ ligand, which process is followed by C–C bond formation to give a hexatrienyl ligand before isomerisation to the vinylidene can occur. Coordination of the 5e-dienyl system is followed by cyclisation and H-migration to generate the η^5 -cyclohexadienyl ligands found in **8** and **9**. We recall that a related H-shift occurs in the formation of the acyclic η^5 -pentadienyl ligand in **12** by

thermolysis of $\overline{\text{Ru}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})=\text{CMe}(\text{CO}_2\text{Me})\}}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$, the methyl analogue of **3** ($\text{R} = \text{R}' = \text{CO}_2\text{Me}$) [6].

Formation of **10** may occur by incorporation of a second molecule of HC_2Ph into an alternative conformer of the penultimate intermediate shown in Scheme 3; these reactions will be discussed in more detail elsewhere. It is interesting to note that the formation of the cyclic ligands does not involve isomerisation of the 1-alkyne to the vinylidene, in contrast with the reactions leading to complexes **5** and **6**. The origins of these differences are not clear at present; it may be relevant that the sterically demanding PPh_3 ligand is not eliminated in the latter case, so that the vacant coordination site to be occupied by the alkyne/vinylidene is smaller.

Experimental

General. All reactions were carried out under dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. Pressure reactions were carried out in a stainless steel laboratory autoclave (Carl R oth, Karlsruhe), internal volume 100 ml, equipped with a glass liner. Elemental analyses were by the Canadian Microanalytical Service, New Westminster, B.C., Canada V3M 1S3.

Spectroscopic measurements. Infrared spectra (in nujol) were recorded using a Perkin-Elmer 683 double-beam spectrophotometer with NaCl optics. NMR spectra were obtained with Bruker WP80 (^1H , at 80 MHz; ^{13}C , at 20.1 MHz) or CXP300 (^1H , at 300 MHz; ^{13}C , at 75.47 MHz) spectrometers. EI mass spectra were obtained with a GEC-Kratos MS3074 mass spectrometer (70 eV ionising energy, 4 kV accelerating potential). FAB mass spectra were recorded with a VG ZAB 2HF instrument (exciting gas Ar, source pressure 10^{-6} mbar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 8 kV). The matrix was 3-nitrobenzyl alcohol. Peaks are recorded as: m/z , assignment, relative intensity.

Chromatography. Column chromatography was on alumina or Florisil (20×2 cm), initially packed in light petroleum (b.p. $40\text{--}60^\circ\text{C}$). Thin layer chromatography (TLC) was on glass plates (20×20 cm) coated with Merck GF₂₅₄ silica gel (0.5 mm).

Starting materials. Complexes **2** [7], **3** ($\text{R} = \text{R}' = \text{CO}_2\text{Me}$) [7] and **4** [8] were prepared by the literature methods.

Reactions of $\overline{\text{Ru}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{O})\text{Me}\}}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**2**)

(i) *With phenylethyne.* A solution containing **2** (450 mg, 0.78 mmol) and HC_2Ph (90 mg, 0.84 mmol) in 1,2-dimethoxyethane (50 ml) was heated in a small autoclave (120°C , 16 h, 35 atm N_2). After cooling and venting, evaporation of solvent gave a yellow oil which was recrystallised (Et_2O) as bright yellow crystals of $\text{Ru}\{\eta^3\text{-CH}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{C}=\text{CHPh}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (**5**) (320 mg, 61%), m.p. $205\text{--}206^\circ\text{C}$. Anal. Found: C, 65.1, H, 4.92; M (mass spectrometry), 673. $\text{C}_{37}\text{H}_{33}\text{O}_4\text{PRu}$ calcd.: C, 65.96; H, 4.94%; M , 673. Infrared (Nujol): $\nu(\text{CO})$ 1715s; $\nu(\text{CO} + \text{C}=\text{C})$ 1698(br), 1595w; other bands at 1300 m, 1191m, 1095m, 1088(sh), 805m, 750m, 692m cm^{-1} . ^1H NMR: $\delta(\text{CDCl}_3)$ 1.59, d, $J(\text{HP})$ 15.9 Hz, 1H, $=\text{CH}$; 3.56, 3.70, s, 3H each, OMe; 4.68, s, 5H, C_5H_5 ; 6.07, d, $J(\text{HP})$ 3.8 Hz, 1H, CHPh ; 7.33, m, 20H, Ph. ^{13}C NMR: $\delta(\text{CDCl}_3)$ 36.07, d, $J(\text{CP})$ 2.9 Hz, C(6); 51.00, 52.24, $2 \times$ s, OMe; 61.32, d, $J(\text{CP})$ 2.9 Hz, C(7); 86.71, s, C_5H_5 ; 123.55, d, $J(\text{CP})$ 7.4 Hz, C(9); 125.3–138.6, m, Ph; 164.60, d, $J(\text{CP})$ 19.1, C(8); 172.68, d, $J(\text{CP})$ 2.9 Hz,

C(6)CO₂Me; 175.90, s, C(7)CO₂Me. EI MS: 673, [M]⁺, 10; 429, [Ru(PPh₃)-(C₅H₅)⁺, 34; 411, [M - PPh₃]⁺, 11; 396, [411 - Me]⁺, 31; 381, [M - 2Me]⁺, 7; 352, [Ru(PPh₂)(C₅H₅)⁺, 10; 334, [411 - Ph]⁺, 10; 262, [PPh₃]⁺, 100; 243, [RuPh-(C₅H₅)⁺, 4.

(ii) *With 3,3-dimethylbut-1-yne.* A solution containing **2** (270 mg, 0.47 mmol) and HC₂^tBu (40 mg, 0.49 mmol) in 1,2-dimethoxyethane (50 ml) was heated in an autoclave (120 °C, 16 h, 30 atm N₂). After cooling and venting, removal of solvent and crystallisation of the resulting yellow oil (Et₂O/dme) gave yellow-green microcrystals of Ru{η³-CH(CO₂Me)C(CO₂Me)=CH^tBu}(PPh₃)(η-C₅H₅) (**6**) (250 mg, 82%), m.p. 183–185 °C. Anal. Found: C, 64.04; H, 5.57; *M* (mass spectrometry), 653. C₃₅H₃₇O₄PRu calcd.: C, 64.31; H, 5.71%; *M* 653. Infrared (Nujol): ν(CO) 1720m, 1210s; ν(CO + C=C) 1708(br); other bands at 1290m, 1145m, 1112m, 1107(sh), 810m, 700m cm⁻¹. ¹H NMR: δ(CDCl₃) 1.43, d, *J* 13.1 Hz, 1H, =CH; 3.67, 3.73, s, 3H each, OMe; 4.56, s, 5H, C₅H₅; 4.94, d, *J* 2.9 Hz, 1H, =CH^tBu; 7.35, m, 15H, Ph. ¹³C NMR: δ(CDCl₃) 30.15, s, CMe₃; 35.30, d, *J* 4.4 Hz, C(6); 35.85, s, CMe₃; 50.78, 52.02, 2 × s, OMe; 59.63, s, C(7); 86.49, s, C₅H₅; 132.04, d, *J* 7.4 Hz, C(9); 127.6–137.3, m, Ph; 152.74, d, *J* 16.2 Hz, C(8); 174.51, 176.05, 2 × s, CO₂Me. EI MS: 653, [M]⁺, 28; 622, [M - OMe]⁺, 2; 594, [M - CO₂Me]⁺, 3; 443, [RuMe(PPh₃)(C₅H₅)⁺, 15; 429, [Ru(PPh₃)(C₅H₅)⁺, 75; 391, [M - PPh₃]⁺, 88; 376, [391 - Me]⁺, 13; 361, [391 - 2Me]⁺, 13; 262, [PPh₃]⁺, 100; 243, [RuPh(C₅H₅)⁺, 13.

*Reaction between Ru{C(OMe)=CH(CO₂Me)}(PPh₃)₂(η-C₅H₅) (**4**) and HC₂Ph*

A solution of **4** (200 mg, 0.25 mmol) and HC₂Ph (51 mg, 1.23 mmol) in tetrahydrofuran (30 ml) was heated in an autoclave (120 °C, 20 h, 40 atm N₂). The resulting dark yellow solution was evaporated to dryness and the residue was dissolved in the minimum amount of CH₂Cl₂. Preparative TLC (1/1 CH₂Cl₂/light petroleum) gave the major product as a yellow band (*R_f* 0.21). Extraction with acetone and crystallisation (Et₂O/light petroleum) gave yellow crystals of Ru{η³-CH(CO₂Me)C(CO₂Me)C=CHPh}(PPh₃)(η-C₅H₅) (**7**) (15 mg, 9%), m.p. 192 °C. Anal. Found: C, 66.35; H, 5.11; *M* (mass spectrometry), 646. C₃₆H₃₃O₃PRu calcd.: C, 66.97; H, 5.15%; *M*, 646. Infrared (Nujol): ν(CO) 1720m, 1699m; other bands at 1310m, 1267m, 1212m, 1158s, 1125s, 1095s, 1088s, 1050s, 1028s, 1000w, 930w, 880w, 830w, 810w, 750s, 722s, 699s cm⁻¹. ¹H NMR: δ(CDCl₃) 1.66, d, *J*(HP) 4.7 Hz, 1H, =CH; 3.15, s, 3H, OMe; 3.74, s, 3H, OMe; 4.52, s, 5H, C₅H₅; 6.16, d, *J*(HP) 3.3 Hz, 1H, CH; 7.26, m, 20H, Ph. ¹³C NMR: δ(CDCl₃) 35.78, s, C(6); 50.60, 53.33, 2 × s, OMe; 83.21, s, C₅H₅; 112.77, s, C(7); 125.0–135.4, m, Ph; 138.59, s, C(8); 155.67, s, C(8); 175.4, s, CO₂Me. FAB MS: 646, [M]⁺, 35.7; 630, [M - Me]⁺, 1.6; 615, [M - OMe]⁺, 15.7; 587, [M - CO₂Me]⁺, 2.3; 569, [M - Ph]⁺, 3.3; 429, [Ru(PPh₃)(C₅H₅)⁺, 100; 383, [M - PPh₃]⁺, 7.2; 368, [M - Me - PPh₃]⁺, 28.6; 352, [Ru(PPh₂)(C₅H₅)⁺, 10.7.

*Reactions of Ru{C(CO₂Me)=C(CO₂Me)C(CO₂Me)=CH(CO₂Me)}(PPh₃)(η-C₅H₅) (**3**, R = R' = CO₂Me)*

(i) *With phenylethyne.* A solution containing **3** (R = R' = CO₂Me) (215 mg, 0.30 mmol) and HC₂Ph (123 mg, 1.21 mmol) in 1,2-dimethoxyethane (30 ml) was heated in an autoclave (120 °C, 16 h, 35 atm N₂). After cooling, venting and removal of solvent, the resulting yellow oil was purified by preparative TLC (silica gel; 30/70

acetone/light petroleum). Two yellow bands were separated: band 1 (R_f 0.33) gave yellow microcrystals (from Et₂O) of Ru(η -C₅H₅){ η^5 -C₃(CO₂Me)₃CHCPhCH(CO₂Me)} · 0.25 CH₂Cl₂ (**8**) (57 mg, 34%), m.p. 183–187 °C. Anal. Found: C, 52.97; H, 4.34; M (mass spectrometry), 554. C₂₅H₂₄O₈Ru · 0.25CH₂Cl₂ calcd.: C, 52.77; H, 4.30%; M , 554. Infrared (Nujol): ν (CO) 1735s(br), 1230s(br); ν (CO + C=C) 1715(sh), 1600m; other bands at 1581 w, 1502m, 1410m, 1395m, 1340s, 1302s, 1204s, 1150s, 1104m, 1078s, 1030m, 1003s, 990s, 950m, 850w, 821s, 800s, 771s, 760m, 750m, 702s, 683m cm⁻¹. ¹H NMR; δ (CDCl₃) 3.51, 3.76, 3.84, 3.88, 4 × s, 3H each, OMe; 4.69, d, J 1.22 Hz, 1H, CH; 4.72, s, 5H, C₅H₅; 6.15, d, J 1.22 Hz, 1H, =CH; 7.45, m, 5H, Ph. FAB MS: 554, [M]⁺, 5; 539, [M - Me]⁺, 1; 524, [M - OMe]⁺, 22; 511, [M - COMe]⁺, 3; 495, [M - CO₂Me]⁺, 100; 480, [495 - Me]⁺, 3; 465, [495 - 2Me]⁺, 1; 451, [Ru{C₄H(CO₂Me)₄}(C₅H₅)]⁺, 1; 437, [M - 2CO₂Me]⁺, 6; 378, [M - 3CO₂Me]⁺, 4; 242, [RuPh(C₅H₅)]⁺, 4. Band 2 (R_f 0.39) gave yellow crystals (from Et₂O/light petroleum) of Ru(η -C₅H₅){ η^5 -C₈H₃Ph₂(CO₂Me)₄} · CH₂Cl₂ (**10**) (11 mg, 6%), m.p. 145 °C. Anal. Found: C, 54.72; H, 4.45; M (mass spectrometry), 656. C₃₃H₃₀O₈Ru · CH₂Cl₂ calcd.: C, 55.14; H, 4.36%; M , 656. Infrared (Nujol): ν (CO) 1752s, 1725m(sh), 1716s, 1245s, 1231s; other bands at

Table 3

Crystallographic data for compounds Ru(η^3 -CH(CO₂Me)C(CO₂Me)C=CHPh)(PPh₃)(η -C₅H₅) (**5**) and Ru(η -C₅H₅){ η^5 -C₃(CO₂Me)₃CHC^tBuCH(CO₂Me)} (**9**)

	5	9
formula	C ₃₇ H ₃₃ O ₄ PRu	C ₂₃ H ₂₈ O ₈ Ru
fw	673.7	533.5
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a , Å	12.337(2)	8.192(2)
b , Å	11.472(3)	33.961(2)
c , Å	22.639(7)	8.819(1)
β , deg	101.66(2)	112.73(1)
V , Å ³	3138(3)	2263(2)
Z	4	4
D_{calcd} , g/cm ³	1.426	1.566
$F(000)$	1384	1096
crystal dimensions, mm	0.15 × 0.15 × 0.34	0.26 × 0.16 × 0.28
scan mode	$\omega : 2\theta$	
data collected	4852	3330
$2\theta_{\text{max}}$, deg	55	55
$h k l$ space explored	$\pm h, + k, + l$	
μ (Mo- K_α), cm ⁻¹	5.45	6.91
transmission factors	0.931–0.887	0.893–0.791
unique reflections	4104	2964
R_{int}	0.024	0.049
reflections with $I \geq 2.5\sigma(I)$	3019	2023
no. of variables	221	292
R	0.043	0.042
R_w	0.047	0.045
k	2.03	1.18
g	0.0004	0.0006
residual density, e/Å ³	-0.47 to +0.71	-0.64 to +0.55

1603w, 1500w, 1349s, 1318s, 1301m, 1290m, 1281m, 1191m, 1170m, 1150s, 1120s, 1072m, 971s, 949w, 880w, 832w, 820m, 801m, 778s, 770m, 740m, 722w, 704s cm^{-1} .
 ^1H NMR: $\delta(\text{CDCl}_3)$ 3.56, 3.61, 3.78, 3.88, $4 \times \text{s}$, 3H each, OMe; 4.44, 4.96, 5.61, $3 \times \text{s}$, 1H each, ring protons; 5.03, s, 5H, C_5H_5 ; 5.30, s, 2H, CH_2Cl_2 ; 7.18, m, 10H, Ph. FAB MS: 656, $[\text{M}]^+$, 5; 625, $[\text{M} - \text{OMe}]^+$, 1; 597, $[\text{M} - \text{CO}_2\text{Me}]^+$, 7; 553,

Table 4

Fractional atomic coordinates ($\times 10^5$ for Ru; $\times 10^4$ for others) for $\text{Ru}\{\eta^3\text{-CH}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{-C}=\text{CHPh}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ (5)

Atom	x	y	z
Ru	42988(4)	8470(4)	16283(2)
P(1)	3103(1)	2142(1)	1046(1)
O(1)	5447(4)	1271(4)	3173(2)
O(2)	4615(4)	2999(4)	3126(2)
O(3)	7448(4)	1871(5)	2656(2)
O(4)	7186(3)	319(4)	2074(2)
C(1)	4154(6)	-615(5)	2260(3)
C(2)	3109(5)	-428(5)	1887(3)
C(3)	3215(5)	-639(5)	1279(3)
C(4)	4322(6)	-979(5)	1285(3)
C(5)	4912(6)	-959(5)	1899(3)
C(6)	4976(5)	2279(5)	2231(2)
C(7)	5781(5)	1776(5)	1931(3)
C(8)	5495(5)	1723(5)	1287(3)
C(9)	5878(5)	2002(5)	794(3)
C(10)	5062(5)	2089(5)	2877(3)
C(11)	4656(7)	2919(8)	3774(3)
C(12)	6868(5)	1318(5)	2271(3)
C(13)	8249(5)	-131(6)	2390(3)
C(14)	6831(3)	2750(4)	748(1)
C(15)	7474(3)	3297(4)	1249(1)
C(16)	8363(3)	4000(4)	1180(1)
C(17)	8609(3)	4155(4)	610(1)
C(18)	7966(3)	3607(4)	109(1)
C(19)	7077(3)	2905(4)	178(1)
C(20)	1650(3)	1811(4)	1071(1)
C(21)	1353(3)	1792(4)	1634(1)
C(22)	280(3)	1480(4)	1679(1)
C(23)	-496(3)	1187(4)	1162(1)
C(24)	-199(3)	1206(4)	600(1)
C(25)	874(3)	1518(4)	554(1)
C(26)	3094(3)	2109(3)	235(2)
C(27)	3313(3)	1058(3)	-28(2)
C(28)	3242(3)	990(3)	-650(2)
C(29)	2951(3)	1974(3)	-1009(2)
C(30)	2732(3)	3025(3)	-747(2)
C(31)	2804(3)	3093(3)	-125(2)
C(32)	3227(3)	3722(3)	1215(2)
C(33)	2437(3)	4300(3)	1469(2)
C(34)	2591(3)	5468(3)	1636(2)
C(35)	3534(3)	6059(3)	1548(2)
C(36)	4324(3)	5481(3)	1294(2)
C(37)	4171(3)	4313(3)	1128(2)

$[M - HC_2Ph]^+$, 63; 538, $[553 - Me]^+$, 7; 522, $[553 - OMe]^+$, 9; 512, $[553 - COMe]^+$, 6; 495, $[553 - CO_2Me]^+$, 100; 451, $[Ru(HC_4(CO_2Me)_4)(C_5H_5)]^+$, 4; 438, $[553 - 2CO_2Me]^+$, 21.

(ii) *With 3,3-dimethylbut-1-yne.* A solution of **3** ($R = R' = CO_2Me$) (100 mg, 0.14 mmol) and HC_2^1Bu (35 mg, 0.42 mmol) in toluene (30 ml) was heated in a small autoclave (120 °C, 16 h, 35 atm N_2). After cooling, venting and removal of solvent, the resulting yellow oil was purified by preparative TLC (silica gel; 30/70 acetone/light petroleum). The yellow band (R_f 0.36) gave yellow crystals (from Et_2O /light petroleum) of $Ru(\eta-C_5H_5)\{\eta^5-C_3(CO_2Me)_3CHC^1BuCH(CO_2Me)\} \cdot 0.25CH_2Cl_2$ (**9**) (16 mg, 21%), m.p. 185 °C. Anal. Found: C, 50.13; H, 5.18; M (mass spectrometry), 533. $C_{23}H_{28}O_8Ru \cdot 0.25CH_2Cl_2$ calcd.: C, 50.34; H, 5.18%; M , 533. Infrared (Nujol): $\nu(CO)$ 1753m, 1723s, 1705s, 1234s; other bands at 1366w, 1288m, 1267m, 1203m, 1122m, 1150m, 1088m, 1041m, 1009m, 992w, 955m, 908w, 831m, 800m, 780w, 720m cm^{-1} . 1H NMR: $\delta(CDCl_3)$ 1.09, s, 9H, CMe_3 ; 3.50, 3.74, 3.80, 3.85, $4 \times s$, 3H each, OMe; 4.16, d, J 1.0 Hz, 1H, CH; 4.86, s, 5H, C_5H_5 ; 5.73, d, J 1.2 Hz, 1H, $=CH$.

Table 5

Fractional atomic coordinates ($\times 10^5$ for Ru; $\times 10^4$ for others) for $Ru(\eta-C_5H_5)\{\eta^5-C_3(CO_2Me)_3-CHC^1BuCH(CO_2Me)\}$ (**9**)

Atom	x	y	z
Ru	51291(7)	85246(2)	-5910(7)
O(1)	622(7)	9365(2)	-864(7)
O(2)	2219(6)	9465(2)	1792(6)
O(3)	6148(7)	8566(2)	3844(7)
O(4)	6670(7)	9180(2)	3300(6)
O(5)	4046(8)	7847(2)	1893(7)
O(6)	2448(7)	8278(2)	2676(6)
O(7)	705(7)	7900(2)	-986(7)
O(8)	372(7)	8151(2)	-3432(6)
C(1)	7642(12)	8543(3)	-912(15)
C(2)	7955(11)	8394(3)	585(13)
C(3)	7006(12)	8042(3)	416(12)
C(4)	6098(10)	7983(3)	-1296(12)
C(5)	6502(11)	8299(3)	-2106(11)
C(6)	3759(9)	9216(2)	246(8)
C(7)	2013(9)	9355(2)	284(8)
C(8)	635(12)	9594(3)	1995(11)
C(9)	4427(9)	8836(2)	1225(8)
C(10)	5803(9)	8836(2)	2911(9)
C(11)	8144(11)	9192(3)	4864(11)
C(12)	3352(8)	8491(2)	627(8)
C(13)	3357(10)	8164(2)	1776(9)
C(14)	2408(14)	8001(3)	3889(11)
C(15)	2317(8)	8477(2)	-1094(8)
C(16)	1088(9)	8143(2)	-1789(9)
C(17)	-877(10)	7840(2)	-4236(10)
C(18)	2582(8)	8772(2)	-2126(8)
C(19)	3669(8)	9098(2)	-1440(8)
C(20)	4092(9)	9407(2)	-2512(8)
C(21)	3969(11)	9228(2)	-4155(9)
C(22)	2776(10)	9747(2)	-2870(10)
C(23)	5951(10)	9576(3)	-1635(10)

FAB MS: 533, $[M]^+$, 2; 519, $[M - CH_4]^+$, 1; 503, $[M - 2Me]^+$, 13; 488, $[M - 3Me]^+$, 2; 474, $[M - CO_2Me]^+$, 100; 459, $[474 - Me]^+$, 8; 445, $[474 - Me - OMe]^+$, 3; 401, $[474 - CH_2CO_2Me]^+$, 3; 342, $[401 - CO_2Me]^+$, 1; 300, $[RuC_6H_2(CO_2Me)]^+$, 3.

X-ray crystallographic analyses of 5 and 9

The crystallographic data summarized in Table 3 were measured, at room temperature, on an Enraf-Nonius CAD4 diffractometer fitted with Mo- K_α (graphite monochromator) radiation, $\lambda = 0.7107 \text{ \AA}$. Three check reflections were monitored throughout the data collections and indicated that no decomposition of either crystal occurred during the measurements. Data were corrected for Lorentz and polarization effects [32] and for absorption employing an analytical procedure [33]. The structures were determined by Patterson methods and refined by full-matrix least-squares methods on F , $w = k/[\sigma^2(F) + g|F|^2]$, with scattering factors for neutral Ru (corrected for f' and f'') from ref. 34 (remaining atoms from ref. 33) and anisotropic thermal parameters; H atoms were placed in calculated positions (C-H 0.97 Å) and were not refined.

Atomic positional parameters are given in Tables 4 and 5, selected bond lengths and angles in Tables 1 and 2 and the numbering schemes used shown in Figs. 1 and 2 which were drawn with ORTEP [35] (15% probability ellipsoids).

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Supplementary material available

Tables of thermal parameters, hydrogen atom parameters, bond lengths, bond angles and listings of the structure factor amplitudes for 5 and 9.

References

- 1 Part XXXII: M.I. Bruce, M.P. Cifuentes, M.R. Snow and E.R.T. Tiekink, *J. Organomet. Chem.*, 359 (1989) 379; Part XXXIII: M.I. Bruce, T.W. Hambley, M.I. Liddell, A.G. Swincer and E.R.T. Tiekink, *Organometallics*, in press.
- 2 J.P. Collman, L.S. Hegeudus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd Ed., University Science Books, Mill Valley, CA, 1987, Chap. 6.
- 3 T. Blackmore, M.I. Bruce and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1974) 106.
- 4 M.I. Bruce, A. Catlow, M.G. Humphrey, G.A. Koutsantonis, M.R. Snow and E.R.T. Tiekink, *J. Organomet. Chem.*, 338 (1988) 59.
- 5 M.I. Bruce, R.C.F. Gardner, J.A.K. Howard, F.G.A. Stone, M. Welling and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1977) 62.
- 6 M.I. Bruce, R.C.F. Gardner and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1979) 906.
- 7 M.I. Bruce, *Pure Appl. Chem.*, 58 (1986) 553.
- 8 M.I. Bruce, D.N. Duffy, M.G. Humphrey and A.G. Swincer, *J. Organomet. Chem.*, 282 (1985) 383.
- 9 M.I. Bruce, M.G. Humphrey, M.R. Snow and E.R.T. Tiekink, *J. Organomet. Chem.*, 314 (1986) 213.
- 10 M.I. Bruce, J.R. Rodgers, M.R. Snow and A.G. Swincer, *J. Chem. Soc., Chem. Commun.*, (1981) 271.
- 11 M.I. Bruce, R.C. Wallis, M.L. Williams, B.W. Skelton and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1983) 2183.

- 12 M.I. Bruce, P.A. Humphrey, J.K. Walton, B.W. Skelton and A.H. White, *J. Organomet. Chem.*, 333 (1987) 393.
- 13 M.I. Bruce, G.A. Koutsantonis and E.R.T. Tiekink, unpublished results.
- 14 J. Silvestre and R. Hoffmann, *Helv. Chim. Acta.*, 68 (1985) 1461.
- 15 M.I. Bruce and A.G. Swincer, *Adv. Organomet. Chem.*, 22 (1983) 59.
- 16 M.G. Newton, N.S. Pantaleo, R.B. King and S.P. Diefenbach, *J. Chem. Soc., Chem. Commun.*, (1979) 55.
- 17 L.S. Liebeskind and R. Chidambaram, *J. Am. Chem. Soc.*, 109 (1987) 5025.
- 18 K. Nakatsu, Y. Inai, T. Mitsudo, Y. Watanabe, H. Nakanishi and Y. Takegami, *J. Organomet. Chem.*, 159 (1978) 111.
- 19 B.J. Brisdon, A.G.W. Hodson, M.F. Mahon and K.C. Molloy, *J. Organomet. Chem.*, 334 (1988) C8.
- 20 M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, *Organometallics*, 4 (1985) 494.
- 21 M.I. Bruce, T.W. Hambley, M.R. Snow and A.G. Swincer, *Organometallics*, 4 (1985) 501.
- 22 M.I. Bruce, M.J. Liddell, M.R. Snow and E.R.T. Tiekink, *Organometallics*, 7 (1988) 343.
- 23 M.I. Bruce, T.W. Hambley, M.J. Liddell, M.R. Snow, A.G. Swincer and E.R.T. Tiekink, unpublished results.
- 24 S.G. Feng, A.S. Gamble and J.L. Templeton, *Organometallics*, 8 (1989) 2024.
- 25 M. Green, N.C. Norman and A.G. Orpen, *J. Am. Chem. Soc.*, 103 (1981) 1267; S.R. Allen, R.G. Beevor, M. Green, N.C. Norman, A.G. Orpen and I.D. Williams, *J. Chem. Soc., Dalton Trans.*, (1985) 435; J.L. Davidson, W.F. Wilson, L. Manojlovic-Muir and K.W. Muir, *J. Organomet. Chem.*, 254 (1983) C6; L. Carlton, J.L. Davidson, J.C. Miller and K.W. Muir, *J. Chem. Soc., Chem. Commun.*, (1984) 11; J.L. Davidson, *J. Chem. Soc., Dalton Trans.*, (1987) 5715.
- 26 W.A. Herrmann, R.A. Fischer and E. Herdtweck, *Angew. Chem.*, 99 (1987) 1286; *Angew. Chem., Int. Ed. Engl.*, 26 (1987) 1263.
- 27 G.C. Conole, M. Green, M. McPartlin, C. Reeve and C.M. Woolhouse, *J. Chem. Soc., Chem. Commun.*, (1988) 1310.
- 28 W. Hirpo and M.D. Curtis, *J. Am. Chem. Soc.*, 110 (1988) 5218.
- 29 J.L. Kerschner, P.E. Fanwick and I.P. Rothwell, *J. Am. Chem. Soc.*, 110 (1988) 8235.
- 30 M.O. Albers, P.J.A. de Waal, D.C. Liles, D.J. Robinson, E. Singleton and M.B. Wiege, *J. Chem. Soc., Chem. Commun.*, (1986) 1680.
- 31 M.D. Curtis, unpublished work cited in ref. 28.
- 32 PREABS and PROCES, Data Reduction Programs for CAD4 Diffractometer, University of Melbourne, Victoria, Australia, 1981.
- 33 G.M. Sheldrick, SHELX76, Program for Crystal Structure Determination, University of Cambridge, Cambridge, England, 1976.
- 34 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol. IV (1974) 99.
- 35 Johnson, C.K., ORTEPII, Report ORNL-3794, Oak Ridge National Laboratory, Tennessee, U.S.A., 1971.