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Cyclopentadienyl-ruthenium and -osmium chemistry

XXXVII *. Oligomerisation of $C_2(CO_2Me)_2$ at a cyclopentadienyl-ruthenium centre: X-ray structures of $RuI\{\eta^4\text{-}CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\eta\text{-}C_5H_5)$, $Ru(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_6H(CO_2Me)_6\}$ and $Ru(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_6[C(CO_2Me)=CH(CO_2Me)](CO_2Me)_6\}$

Michael I. Bruce, George A. Koutsantonis, Edward R.T. Tiekink
*Department of Physical and Inorganic Chemistry, University of Adelaide,
Adelaide, South Australia 5001 (Australia)*

and Brian K. Nicholson
Department of Chemistry, University of Waikato, Hamilton (New Zealand)

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Abstract

Reactions between $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ ($X = Cl, I$) and $C_2(CO_2Me)_2$ in MeOH in the presence of NH_4PF_6 have given three types of complex, which have been fully characterised by X-ray studies. These are the η^4-diene complexes $RuX\{\eta^4\text{-}CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ (**1**, X = Cl; **2**, X = I) and the η^5-cyclohexadienyl derivatives $Ru(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_6H(CO_2Me)_6\}$ (**4**) and $Ru(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_6[C(CO_2Me)=CH(CO_2Me)](CO_2Me)_6\}$ (**5**). The three complexes are formed by di-, tri- and tetra-merisation of the alkyne at the mononuclear ruthenium centre; the last reaction is unprecedented. Possible mechanisms are discussed.

Introduction

Reactions between alkynes and metal hydrides generally afford σ-vinyl-metal complexes in reactions which proceed by *cis* addition of the M–H unit to the C≡C triple bond [1]. It has been known for many years that alkynes containing electron withdrawing substituents (CO_2Me, CF_3, etc) afford products which often react further with C–C bond formation. This added reactivity has been attributed to the addition of dipolar character into the η-alkyne-metal intermediate by the sub-

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* For Part XXXVI see ref. 41.

stituents [2]. We have used this concept to rationalise the formation of a variety of unusual ligands (butadienyl, cumulenyl, etc) in the reactions of Ru–H bonds with activated alkynes [3].

More recently others have shown that formal insertion of such alkynes into metal–halogen bonds can also occur, examples being seen in the reactions of $PtCl_2(CO)_2$ [4], *trans*-$PtClMe(PMe_2Ph)_2$ [5], PtIMe(bpy) [6] or *trans*-$RuCl_2(CO)_2L_2$ (L = PMe_2Ph, $AsMe_2Ph$) [7]. The ready ionisation of halide from $RuX(PR_3)_2(\eta\text{-}C_5H_5)$ in polar solvents [8] prompted us to examine the reactions of these complexes with $C_2(CO_2Me)_2$. Initial studies were not promising, but we found that addition of NH_4PF_6 to the reaction mixture resulted in the formation of three types of complex, containing di-, tri- and tetra-mers of the alkyne in combination with one or two H atoms. This paper describes this work and includes crystallographic studies of the three title complexes.

Results

Reactions of dimethyl acetylenedicarboxylate with $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ (X = Cl, I)

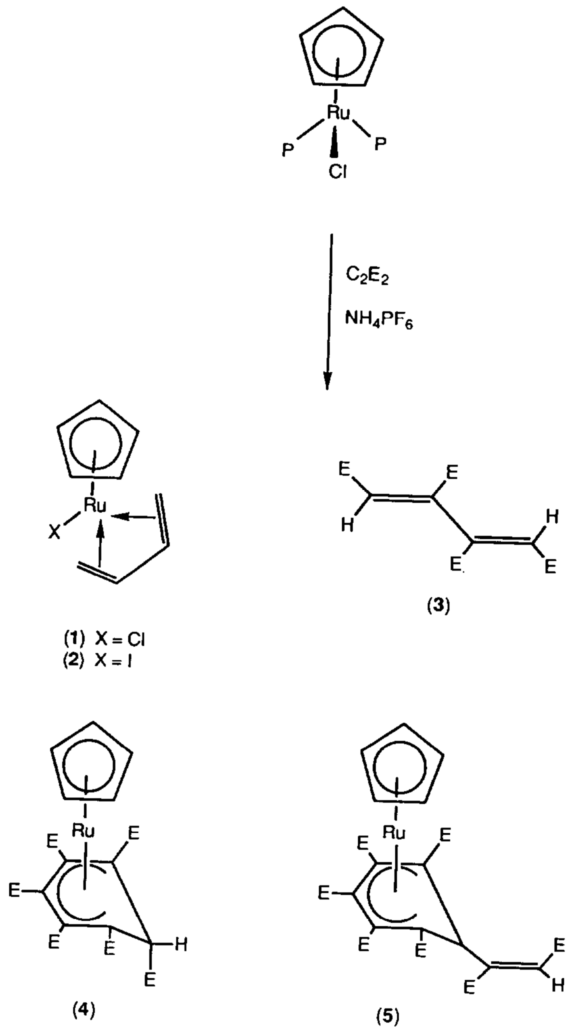
Heating a suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and dimethyl acetylenedicarboxylate (dmad) in the presence of NH_4PF_6 in refluxing methanol for ca. one hour gave a complex mixture of products. Chromatography allowed the isolation of one metal-containing compound, identified by the usual spectroscopic and microanalytical techniques as $RuCl\{\eta^4\text{-}CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ (**1**). This complex was also obtained in 60% yield from the reaction between $RuCl(\eta^4\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$ and tetramethyl *Z*,*Z*-1,3-butadiene-1,2,3,4-tetracarboxylate in MeOH at 60 °C.

The corresponding iodo complex (**2**) was isolated from the reaction between $C_2(CO_2Me)_2$, $RuI(PPh_3)_2(\eta\text{-}C_5H_5)$ and NH_4PF_6, together with the free diene, *Z*,*Z*-$CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)$ (**3**) and the complexes $Ru(\eta\text{-}C_5H_5)\{HC_n(CO_2Me)_n\}$ ($n = 6$ (**4**) and 8 (**5**); Scheme 1). The molecular structures of **2**, **4** and **5** were determined by X-ray crystallography.

(i) Molecular structure of $RuI\{\eta^4\text{-}CH(CO_2Me)=C(CO_2Me)\text{-}C(CO_2Me)=CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ (2)

A plot of the structure of **2** is shown in Fig. 1; Table 1 collects relevant bond distances and angles. The ruthenium atom has distorted octahedral coordination, with the C_5H_5 group occupying three facial positions (Ru–C(cp) 2.14–2.27(3) Å; av. 2.20 Å). The other three coordination sites are filled by I (Ru–I 2.727(2) Å) and the η^4-*E*,*E*-$CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)$ ligand (Ru–C 2.15–2.22(3) Å, av. 2.18 Å). The Ru–C(cp) distances are unexceptional [9,10] and the Ru–I separation is similar to that found in $RuI(CO)(PPh_3)(\eta\text{-}C_5H_4R)$ (R = neomenthyl) (2.708(1) Å) [11].

The C_4 carbons C(6)–C(9) are coplanar, and the dihedral angle between the C_4 and C_5 planes is 20.4°. The Ru–C(diene) distances are similar to the Ru–C(sp^2) separations in $Ru\{\eta^3\text{-}C(CO_2Me)=C(CO_2Me)C(CF_3)=CH(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)$ (**6**) (2.171, 2.185(6) Å) [12]. The C–C separations have a short-long-short pattern (C(6)–C(7) 1.39(3), C(7)–C(8) 1.48(3), C(8)–C(9) 1.37(3) Å), with angles at C(7) and C(8) of 118(2), 116(2)°, respectively, the whole being consistent with localised geometry in the η^4-diene. Only the CO_2Me group attached to C(9) is essentially



Scheme 1

coplanar with the C_4 moiety; elsewhere we have described the random orientations of CO_2Me groups found in poly-CO_2Me hydrocarbon ligands, such as $C_5(CO_2Me)_5$, attached to transition metals [13]. There are no exceptional features in the geometry of the four CO_2Me groups.

(ii) Molecular structures of $Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_6H(CO_2Me)_6\}$ *(4) and* $Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_8H(CO_2Me)_8\}$ *(5)*

The molecular structures of complexes **4** and **5** are shown in Figs. 2 and 3, respectively. Relevant interatomic parameters for both complexes are collected in Table 2. The two structures are closely related, the ruthenium atoms in both being coordinated to η-C_5H_5 and η^5-cyclohexadienyl ligands; in **4**, the latter has an *endo*-H and six CO_2Me substituents, while in **5**, the *endo*-H is replaced by a

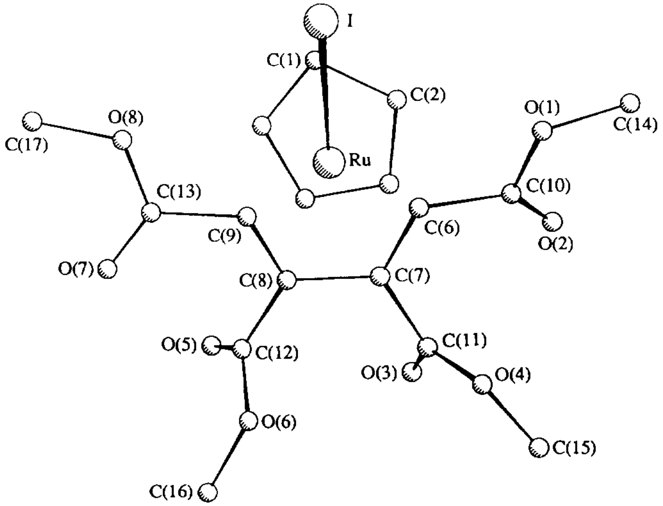


Fig. 1. Molecular structure and crystallographic numbering scheme for $RuI\{\eta^4\text{-}CH(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ (**2**).

trans-$C(CO_2Me){=}CH(CO_2Me)$ unit. The complexes result from tri- and tetramerisation of $C_2(CO_2Me)_2$ at the ruthenium centre (see below).

Individual Ru–C(cp) and Ru–C_6 distances are similar in the two complexes. Least squares planes through the C_5H_5 rings in complexes **4** and **5** are 1.83 and 1.84 Å distant from their respective ruthenium atoms. The planes bonded by C(6)–C(10) in the coordinated portions of the η^5-C_6 ligands in **4** and **5** are found somewhat closer to the ruthenium (1.66 and 1.65 Å, respectively). The acute dihedral angles between the planes defined by C(6)–C(10) and C(6)C(11)C(10) within the cyclohexadienyl ligands of **4** and **5**, are 47.6 and 55.2 °, respectively. In addition the dihedral angles between the C_5 and η^5-C_6 planes in **4** and **5** are 2.1

Table 1

Selected bond distances (Å) and angles (deg.) for $RuI\{\eta^4\text{-}CH(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ (**2**)

Distances			
Ru–I	2.727(2)	Ru–C(8)	2.15(2)
Ru–C(1)	2.27(3)	Ru–C(9)	2.22(3)
Ru–C(2)	2.20(2)	C(6)–C(7)	1.39(3)
Ru–C(3)	2.23(3)	C(7)–C(8)	1.48(3)
Ru–C(4)	2.17(2)	C(8)–C(9)	1.37(3)
Ru–C(5)	2.14(3)	C(6)–C(10)	1.52(3)
Ru–C(cp) (av.)	2.20	C(7)–C(11)	1.51(3)
Ru–C(6)	2.20(2)	C(8)–C(12)	1.47(3)
Ru–C(7)	2.15(2)	C(9)–C(13)	1.53(3)
Angles			
C(7)–C(6)–C(10)	112(3)	C(7)–C(8)–C(9)	116(2)
C(6)–C(7)–C(8)	118(2)	C(7)–C(8)–C(12)	123(2)
C(6)–C(7)–C(11)	128(2)	C(9)–C(8)–C(12)	121(2)
C(8)–C(7)–C(11)	115(2)	C(8)–C(9)–C(13)	118(2)

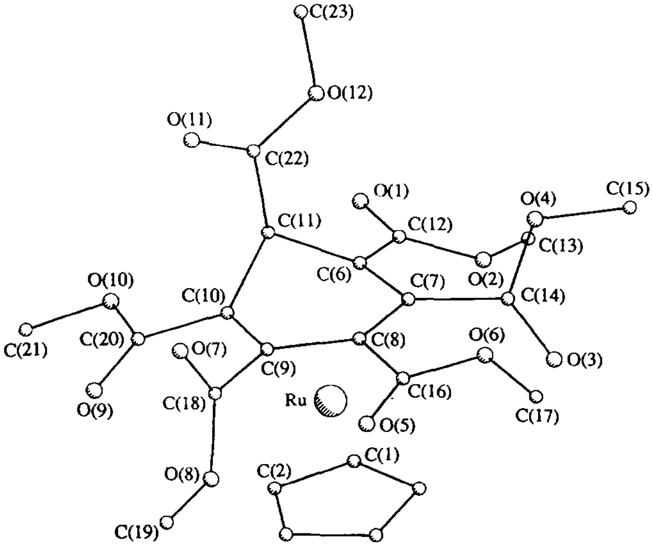


Fig. 2. Molecular structure and crystallographic numbering scheme for $Ru(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_6H(CO_2Me)_6\}$ (4).

and 7.2°. The larger angles in **5** are probably a result of steric interaction of the pendant bis(methoxycarbonyl)vinyl group attached to C(11) with the rest of the molecule. These latter dihedral angles may be compared with those in ruthenocene

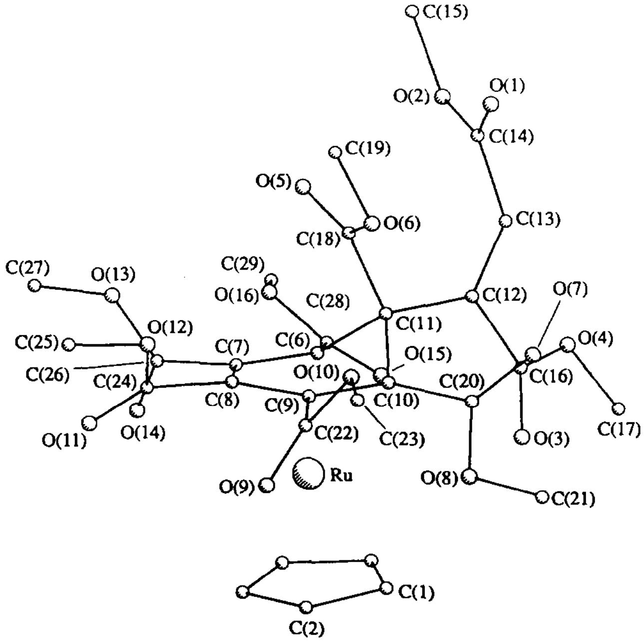


Fig. 3. Molecular structure and crystallographic numbering scheme for $Ru(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_6[C(CO_2Me)=CH(CO_2Me)](CO_2Me)_6\}$ (5).

Table 2

Selected bond distances (Å) and angles (deg.) for Ru(η^5-C_5H_5){η^5-$C_6H(CO_2Me)_6$} (4) and Ru(η^5-C_5H_5){η^5-$C_6[C(CO_2Me)=CH(CO_2Me)](CO_2Me)_6$} (5)

	4	**5**
Distances		
Ru–C(1)	2.201(3)	2.207(2)
Ru–C(2)	2.202(3)	2.231(3)
Ru–C(3)	2.186(3)	2.216(3)
Ru–C(4)	2.174(3)	2.183(2)
Ru–C(5)	2.181(3)	2.178(2)
Ru–C(cp) (av.)	2.189	2.203
Ru–C(6)	2.193(2)	2.154(3)
Ru–C(7)	2.138(2)	2.125(3)
Ru–C(8)	2.181(2)	2.178(2)
Ru–C(9)	2.148(2)	2.146(3)
Ru–C(10)	2.183(3)	2.189(3)
Ru–C(C_6) (av.)	2.169	2.158
C(6)–C(7)	1.429(3)	1.422(4)
C(7)–C(8)	1.444(3)	1.437(4)
C(8)–C(9)	1.451(4)	1.429(4)
C(9)–C(10)	1.425(4)	1.440(4)
C(6)–C(11)	1.511(3)	1.552(4)
C(10)–C(11)	1.514(3)	1.529(4)
Angles		
C(7)–C(6)–C(11)	119.2(2)	115.7(2)
C(6)–C(7)–C(8)	117.4(2)	117.3(2)
C(7)–C(8)–C(9)	118.2(2)	118.4(3)
C(8)–C(9)–C(10)	118.4(2)	118.3(3)
C(9)–C(10)–C(11)	117.5(2)	114.6(2)
C(6)–C(11)–C(10)	101.8(2)	97.9(2)
Dihedral planes		
C(1)–C(5)/C(6)–C(10)	2.1	7.2

(0.0 °) [14] and Ru(η-C_5H_5){η-$C_5(CO_2Me)_5$} (1.5 °) [15]. In the latter complex the $C_5(CO_2Me)_5$ ring is closer to the ruthenium than the C_5H_5 moiety (1.796 vs 1.817 Å). This phenomenon was also observed in the structure of **2**, in which the plane bonded by the butadiene carbons is 0.15 Å closer to the ruthenium than the plane of the C_5 ring. A possible reason for the closer approach of the C_6 ligands in **4** and **5** is that in the ligands containing electron-withdrawing CO_2Me groups, compensation for loss of electron density is made by stronger Ru–ligand back donation thereby shortening the bonds between the metal and the η^5-C_6 ligands.

Intra-ring C–C distances in the C_5H_5 ligand in **4** (1.383–1.429(5) Å) are similar to those in ruthenocene (1.428–1.438 Å); the C–C separations in the η^5-bonded portion of the cyclohexadienyl ligands are more comparable (1.422–1.451(4) Å). The C(sp^2)–C(sp^3) separations are 1.511, 1.514(3) Å in **4** and 1.529, 1.552(4) Å in **5**.

The ester group attached to C(11) in **4** occupies the exocyclic position; in **5** there is an *endo-trans*-bis(methoxycarbonyl)vinyl group. The vinyl proton, attached to C(13) in **5**, was located in the structure determination. The vinyl moiety also carries the two CO_2Me groups in a mutually *trans* configuration with the C=C distance (C(12)–C(13) 1.333(5) Å) comparable to that found in PtH{Z-$C(CO_2Me)$=$CH(CO_2Me)$}$(P^nBu^tBu_2)_2$ (**6**) (1.37(2) Å) [16]. The angle C(12)–C(13)–C(14) in **5** is 132.5(3)° (cf. 124.8(8)° in **6**). None of the CO_2Me groups exhibits any anomalous structural feature.

Spectroscopic data

The various IR, ^1H and ^{13}C NMR spectra, and FAB MS data obtained for the three complexes are in accord with their molecular structures described above. Thus, the IR spectra contain strong to medium intensity bands between 1700–1760 cm^{-1} (ν(C=O)) and 1160–1280 cm^{-1} (ν(C–O)). In **5**, a weak ν(C=C) band occurs at 1640 cm^{-1}. The ^1H NMR spectra contain sharp singlets in the appropriate regions for the OMe and C_5H_5 protons; the *endo*-H in **4** resonated at δ 4.54, while the vinyl proton in **5** was found at δ 6.63. The two diene protons in **2** occured at δ 2.07.

The skeletal diene carbons in **2** resonated at δ 47.9 (terminal) and 92.8 (inner). For **4** and **5**, the uncoordinated ring carbons resonate around δ 42.4, while the other carbons were found between δ 87–95. Other signals between δ 51–53 (OMe), 85–90 (C_5H_5) and 165–172 (CO_2Me) were characteristic of these groups.

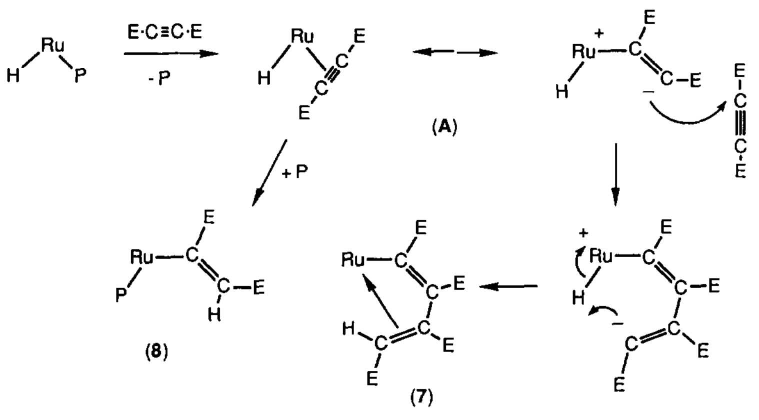
In the FAB mass spectra, the molecular ions fragmented by loss of halogen (if present), OMe and CO_2Me groups as expected. In the spectrum of **4** sequential loss of four $C_2H_2O_2$ fragments from $[Ru(C_5H_5)\{C_6H_2(CO_2Me)_4\}]^+$ gave $[Ru(C_5H_5)(C_6H_6)]^+$ (*m/z* 244); this series of ions can be formulated as stable 18e arene-cyclopentadienyl-Ru cations. A similar feature has been observed in the spectrum of $Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_5(CO_2Me)_5\}$, leading in this case to the formation of $[Ru(C_5H_5)_2]^+$ [17]. Strong metal-free ions in **2** correspond to $[H_2C_4(CO_2Me)_4]^+$ and others formed by loss of OMe and CO_2 groups from this ion.

Discussion

The three types of complex formed in the reactions between $C_2(CO_2Me)_2$ and $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$ are formed by di-, tri- and tetra-merisation of the alkyne at the ruthenium centre, followed by addition of one or two hydrogen atoms to the resulting organic species. The reactions are unusual extensions of alkyne-ruthenium chemistry, and the formation of the tetrameric ligand in **5** is without precedent. The precise mechanisms of the reactions leading to the formation of these complexes are unclear, but it is possible to indicate possible routes to them. Further, since **2** does not react with $C_2(CO_2Me)_2$ to give either **4** or **5**, at least two reaction paths are being followed.

Our previous studies [18] have demonstrated the dimerisation of $C_2(CO_2Me)_2$ in the reaction with $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$, which afforded the η^3-1,3,4-butadienyl Ru{$C(CO_2Me)$=$C(CO_2Me)C(CO_2Me)$=$CH(CO_2Me)$}$(PPh_3)(\eta\text{-}C_5H_5)$ (**7**, Scheme 2). It was suggested that displacement of PPh_3 by the alkyne afforded the dipolar η-alkyne intermediate A. This could then react further, either by hydrogen migration from the metal to the β-carbon and addition of the displaced PPh_3 to the metal centre to give the vinyl **8**, or by attack on a second molecule of alkyne to give the butadienyl ligand, which chelates via the C=C double bond to give **7**.

Although we have not been able to convert **7** to an η^4-diene complex, for example, by addition of acid, we suggest that reactions which are similar to that

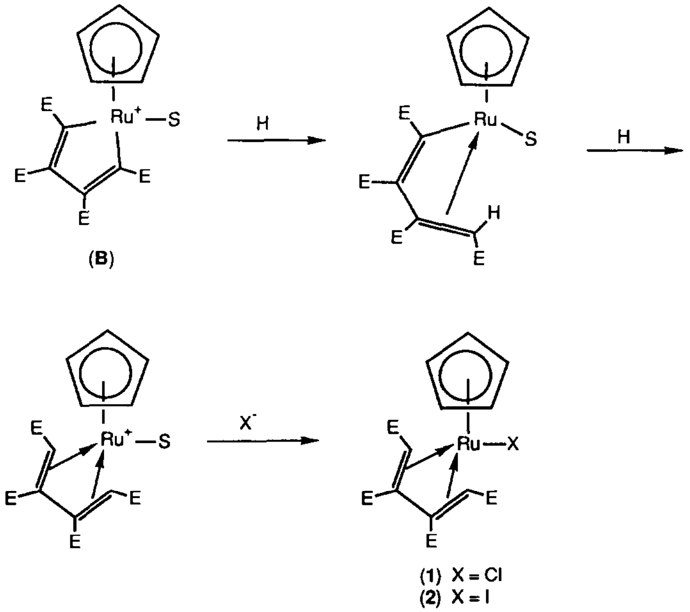


Ru = Ru(PPh$_3$)(η-C$_5$H$_5$)

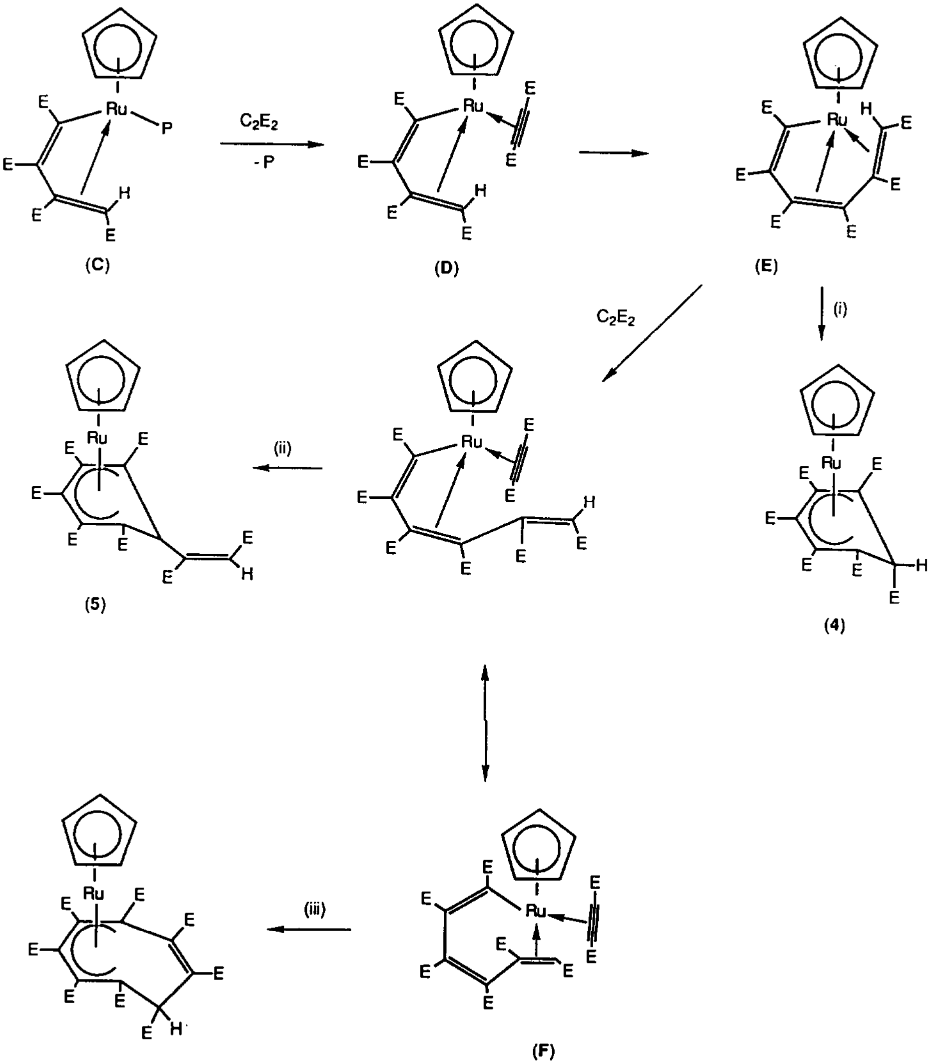
Scheme 2

forming **7** occur in our system. The essential difference is the ionic displacement of X^- to give a weakly solvated intermediate **B** (Scheme 3), which is followed by addition of H (from NH_4PF_6) to form the diene and final substitution of solvent by X^- to give **1** or **2**. Ample precedents for these reactions have been described previously.

The reaction sequence leading to **4** and **5** is related to the formation of $Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_3(CO_2Me)_3CHCRCH(CO_2Me)\}$ ($R = {}^tBu$, Ph) (**9**) that we reported recently [19]. These complexes were obtained from reactions of 1-alkynes with the butadienyl complex **7**. We suggest that, in the present case, formation of



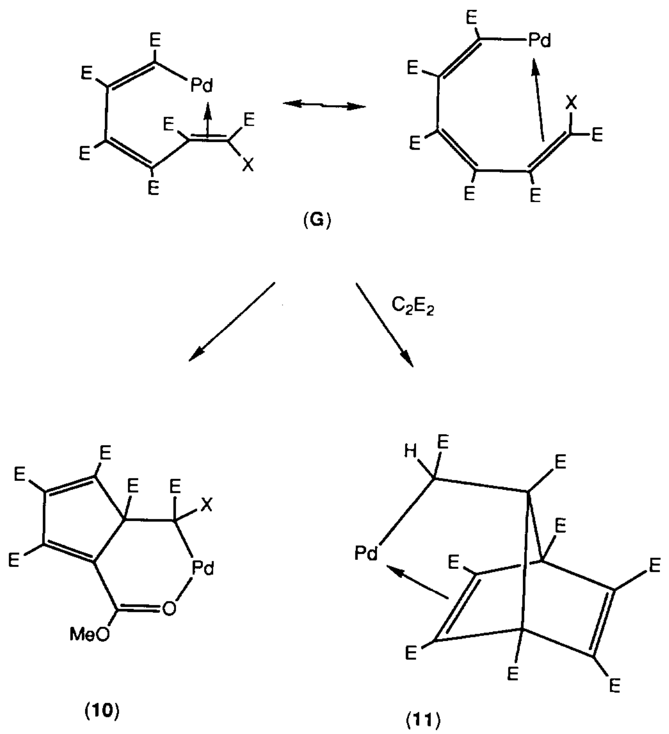
Scheme 3



Scheme 4

the dienyl by addition of one H to intermediate **B**, to give **C** (Scheme 4), is followed by displacement of PPh_3 and coordination of a third molecule of alkyne **D**. The displaced PPh_3 may combine with excess $C_2(CO_2Me)_2$ to give a phosphole [20]. Further coupling of the dienyl ligand with the coordinated alkyne (in **D**) generates a C–C bond (**E**); since no PPh_3 remains coordinated to ruthenium, ring-closure of the resulting η^5-dienyl occurred to give the η^5-cyclohexadienyl ligand (step i).

In the presence of an excess of $C_2(CO_2Me)_2$, coordination of a fourth molecule of the alkyne would give intermediate (**F**). There are two possible consequences: (a) ring-closure as before to give a 6-membered ring bearing an exocyclic vinyl ligand, as found in **5** (step ii), or (b) C–C bond formation between the terminal C atoms to give an 8-membered cyclic ligand (step iii). The choice is determined by

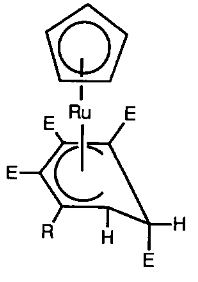


Scheme 5

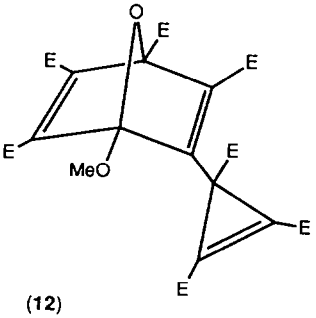
the conformation of the 6-carbon ligand in intermediate **F**; the observed formation of **5** shows that the former path is favoured.

In these reactions, the source of the H is considered to be the ammonium cation, which is known to protonate complexes containing the basic $Ru(PR_3)(\eta\text{-}C_5H_5)$ moiety. An alternative H precursor might be the binuclear derivative $[\{Ru(L)(PPh_3)(\eta\text{-}C_5H_5)\}_2(\mu\text{-}H)]^+$ (L = alkyne, for example), similar to the binuclear carbonyl [21] and isonitrile-tertiary phosphine derivatives [22] reported by others.

It is interesting, at this stage, to relate our findings to the well-known tri- and tetra-merisation of $C_2(CO_2Me)_2$ on palladium centres, described by Maitlis and coworkers nearly 20 years ago [23]. Their proposed mechanism (Scheme 5) also featured stepwise addition of acetylene molecules and provided a route to tri- and tetramers. The extent of the reaction is governed by the size of the acetylenic substituents. Bulky substituents, e.g. phenyl, cause the reaction to cease after two alkynes have combined and lead to η^4-cyclobutadiene-Pd complexes. For smaller substituents (e.g. methyl) three or four acetylenes can be incorporated before rearrangement or decomposition reactions become fast with respect to further oligomerisation. Products obtained from the reaction of $PdCl_2(PhCN)_2$ and $C_2(CO_2Me)_2$ in MeOH included complexes **10** and **11** [24]. These reactions occur via alternative conformations of intermediate **G**, which either undergoes intramolecular ring closure to give **10** or adds to the fourth (coordinated) molecule of $C_2(CO_2Me)_2$ to form **11**. It is also interesting, in this regard, to recall the



(9) R = Bu^t, Ph



(12)

spontaneous tetramerisation of $C_2(CO_2Me)_2$ to the oxanorbornadiene **12** that occurs on standing [25].

The present work has demonstrated the formation of novel ligands from intramolecular oligomerisation of the activated alkyne $C_2(CO_2Me)_2$ on ruthenium. While trimerisation of alkynes to benzenes is well established, and that to other trimers or derived ligands has also been described, the formation of cyclohexadienyls is not common [18]. Even rarer is the tetramerisation of alkynes on mononuclear centres: the formation of cyclooctatetraenes on nickel catalysts was described by Reppe [26]; evidence for a stepwise or concerted cyclo-oligomerisation has been reported [27]. The only other examples to our knowledge are from the work of Maitlis, described above, and the formation of $Mn(CO)_3(\eta\text{-}C_5H_3CH{=}CHCH_2)$ from C_2H_2 and $Mn_2(CO)_{10}$ [28]. The formation of eight-carbon ligands at two metal centres, such as Cr [29], Mo [30] or Re [31], has been described by several groups.

The use of an odd-electron donor (C_5H_5) on an even-electron metal centre (Ru) has forced odd-electron ligands (or combinations thereof) to be formed. For **1** or **2** this is achieved by the (diene + X) combination, while in **4** and **5**, the 5e dienyl systems are found.

Experimental

General conditions

All reactions were carried out under dry high-purity nitrogen by standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Starting materials. Literature methods were used to prepare $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ [32], $RuI(PPh_3)_2(\eta\text{-}C_5H_5)$ [33], $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ [34] and $RuCl(\eta^4\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$ [35]. $C_2(CO_2Me)_2$ (Fluka) was routinely distilled before use and NH_4PF_6 (Aldrich) was used as received.

Instrumentation. IR: Perkin-Elmer 1700X FT IR; 683 double beam, NaCl optics; NMR: Bruker CXP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz). Spectra recorded in non-deuterated solvents used an external concentric tube containing D_2O for field lock. FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Synthesis

A. Reactions between $C_2(CO_2Me)_2$ and $RuX(PPh_3)_2(\eta\text{-}C_5H_5)$

(a) X = Cl. A suspension of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (206 mg, 0.284 mmol), NH_4PF_6 (46 mg, 0.284 mmol) and $C_2(CO_2Me)_2$ (0.05 ml, 0.41 mmol) in MeOH (25 ml) was heated at reflux point until a clear dark brown solution was obtained (ca. 1 h). Evaporation and separation of the residue by preparative TLC (acetone–light petroleum, 1/1) gave eleven bands. Band 1 (R_f 0.51, yellow) was crystallised (Et_2O/pentane) to give orange microcrystals of $RuCl\{\eta^4\text{-}CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ (**1**) (13 mg, 9%), m.p. 154–155 °C. Anal. Found: C, 41.86; H, 3.93; *M*(mass spectrometry), 488. $C_{17}H_{19}ClO_8Ru$ calc.: C, 41.80; H, 3.93%; *M*, 488. IR (Nujol): ν(C=O) 1760s, 1738m, 1710vs, 1697s; ν(C–O) 1283s, 1228vs, 1199s, 1163s cm^{-1}; other bands at 3107m, 1343m, 1180m, 1016w, 989m, 968m, 841m, 763w cm^{-1}. ^1H NMR: δ ($CDCl_3$) 2.02 (s, 2H, 2 × =C*H*); 3.73 (s, 6H, 2 × CO_2*Me*); 3.87 (s, 6H, 2 × CO_2*Me*); 5.58 (s, 5H, C_5H_5). FAB MS: 488, $[M]^+$, 26: 453, $[M-Cl]^+$, 75; 429, $[M-CO_2Me]^+$, 6; 391, $[M-CO_2Me-2OMe]^+$, 17; 284, $[C_4(CO_2Me)_4]^+$, 100.

The only product isolated from a similar reaction carried out in refluxing toluene was $C_6(CO_2Me)_6$ (32 mg, 5%). The remaining bands either contained trace amounts or were intractable (baseline), and were not identified.

(b) X = I. A deep orange-red solution was obtained after heating a mixture of $RuI(PPh_3)_2(\eta\text{-}C_5H_5)$ (694 mg, 0.85 mmol), NH_4PF_6 (144 mg, 0.88 mmol) and $C_2(CO_2Me)_2$ (1.05 ml, 8.54 mmol) in refluxing MeOH (200 ml) for 10.5 h. After cooling and removal of solvent, separation by preparative TLC (acetone–cyclohexane–CH_2Cl_2, 1/4/5) gave ten coloured bands. Replating (twice) the red fraction (R_f 0.69) further separated it into two components: the first afforded red crystals (from CH_2Cl/MeOH) of $RuI\{\eta^4\text{-}CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ (**2**) (72 mg, 15%), m.p. 161–163 °C. Anal. Found: C, 35.04; H, 3.26; *M* (mass spectrometry), 580. $C_{17}H_{19}IO_8Ru$ calc.: C, 35.24; H, 3.31%; *M*, 580. IR (Nujol): ν(C=O) 1762s, 1740m, 1712s, 1700s; ν(C–O) 1350m, 1285m, 1230s; other bands at 1200m, 1160m, 1020w, 990m, 970w, 930w, 848w, 835w, 801w, 775w, 761w, 720w cm^{-1}: (KBr): ν(C=C) 1449s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 2.07 (s, 2H, 2 × =C*H*); 3.66 (s, 6H, 2 × CO_2*Me*); 3.85 (s, 6H, 2 × CO_2*Me*); 5.57 (s, 5H, C_5H_5). ^{13}C NMR: δ ($CDCl_3$) 47.85 (s, CH); 51.74 (s, OMe); 53.44 (s, OMe); 91.09 (s, C_5H_5); 92.79 (s, C(2)); 165.43 (s, *C*O_2Me); 171.01 (s, *C*O_2Me). FAB MS: 580, $[M]^+$, 16; 549, $[M-OMe]^+$, 19; 521, $[M-CO_2Me]^+$, 2; 453, $[M-I]^+$, 39; 394, $[M-I-CO_2Me]^+$, 32; 286, $[C_4H_2(CO_2Me)_4]^+$, 3; 255, $[286-OMe]^+$, 27; 227, $[286-CO_2Me]^+$, 32.

The second band (R_f 0.77) gave white crystals (from MeOH) of tetramethyl (*Z*,*Z*)-buta-1,3-diene-1,2,3,4-tetracarboxylate (**3**) (59 mg, 2.4%), m.p. 89–90 °C (lit. [36] 90 °C), M^+ (EI MS), 286 ($C_{12}H_{14}O_4$ calc.: 286). ^1H NMR: δ 3.73 (s, 6H, 2 × CO_2*Me*); 3.87 (s, 6H, 2 × CO_2*Me*); 6.00 (s, 2H, 2 × =C*H*) (lit. [36]: δ 3.75, 3.88, 6.09).

A yellow fraction (R_f 0.54) was also resolved into two components after replating (acetone–cyclohexane–CH_2Cl_2, 1/4/5). The major fraction was crystallised (CH_2Cl_2/cyclohexane) to give yellow prisms of Ru(η-C_5H_5){η^5-$C_6H(CO_2Me)_6$} (4) (100 mg, 20%), m.p. 165–166 °C. Anal. Found: C, 46.47; H, 4.07, *M* (mass spectrometry), 594. $C_{23}H_{24}O_{12}Ru$ calc.: C, 46.55; H, 4.08%; *M*, 594. IR (KBr): ν(C=O) 1750vs, 1730vs(br), 1700s; ν(C–O) 1225vs(br); other bands at 2960m, 1438vs, 1420m, 1395w, 1375m, 1350s, 1330m, 1325m, 1115s, 1100w, 1080w, 1002s, 992s, 982s, 822s, 800m, 791m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 3.55 (s, 3H, CO_2*Me*); 3.76 (s, 6H, 2 × CO_2*Me*); 3.84 (s, 9H, 3 × CO_2*Me*); 4.54 (s, 1H, *CH*); 5.04 (s, 5H, C_5H_5). ^{13}C NMR: δ ($CDCl_3$) 42.38 (s, *C*H); 51.61 (s, OMe); 52.10 (s, 2 × OMe); 52.95 (s, 3 × OMe); 84.53 (s, C_5H_5); 87.81 (s C(6), C(10)); 94.86 (s, C(7), C(8), C(9)); 166.52 (s, 2 × *C*O_2Me); 167.13 (s, CO_2Me); 171.74 (s, 3 × CO_2Me). FAB MS: 594, $[M]^+$, 2.9; 563, $[M - OMe]^+$, 29; 535, $[M - CO_2Me]^+$, 100; 477, $[Ru(C_5H_5)\{C_6H_2(CO_2Me)_4\}]^+$, 65; 419, $[Ru(C_5H_5)\{C_6H_3(CO_2Me)_3\}]^+$, 41; 361, $[Ru(C_5H_5)\{C_6H_4(CO_2Me)_2\}]^+$, 47; 303, $[Ru(C_5H_5)\{C_6H_5(CO_2Me)\}]^+$, 5.3; 244, $[Ru(C_5H_5)(C_6H_6)]^+$, 7.1; 167, $[Ru(C_5H_5)]^+$, 7.7.

Further separation of a broad orange band (R_f 0.17) gave white crystals (from MeOH/EtOAc) of Ph_3PO (66 mg, 14%), identified by m.p., IR. The remaining bands contained only trace amounts, or was intractable (baseline), and were not identified.

(ii) A similar reaction between $RuI(PPh_3)_2$(η-C_5H_5) (1030 mg, 1.26 mmol), NH_4PF_6 (205 mg, 1.26 mmol) and $C_2(CO_2Me)_2$ (0.6 ml, 4.88 mmol) in MeOH (75 ml) was continued for 72 h. Filtration of the resulting orange suspension gave an orange powder of unreacted $RuI(PPh_3)_2$(η-C_5H_5) (460 mg, 37%). The orange

Table 3

Crystal data and refinement details for complexes **2**, **4** and **5**

Compound	**2**	**4**	**5**
Formula	$C_{17}H_{19}IO_8Ru$	$C_{23}H_{24}O_{12}Ru$	$C_{29}H_{30}O_{16}Ru$
Formula weight	579.3	593.5	735.6
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$	$P2_1/n$
a, Å	8.793(2)	7.572(4)	10.582(2)
b, Å	15.718(10)	16.152(5)	17.841(3)
c, Å	28.639(33)	20.142(7)	17.176(4)
β, deg.	98.56(5)	99.96(4)	108.07(2)
U, $Å^3$	3914.1	2426.3	3082.8
Z	8	4	4
D_c, g cm^{-3}	1.966	1.625	1.585
F (000)	2256	1208	1504
μ, cm^{-1}	23.56	6.61	5.37
Transmission factors (max/min)	0.691, 0.597	0.879, 0.749	n/a
θ limits, deg.	1.0–22.5	1.5–25.0	2.0–25.0
No. of data collected	5147	4795	5041
No. of unique data	2574	4263	5041
No. of reflections used	1405	3246	4154
Criterion of observability	$I \geqslant 3.0\sigma(I)$	$I \geqslant 2.5\sigma(I)$	$I > 2.0\sigma(I)$
R	0.087	0.027	0.030
g	0.017	0.004	0.003
R_w	0.089	0.030	0.034

filtrate was evaporated to dryness and the residue separated by preparative TLC (acetone–cyclohexane–CH_2Cl_2, 1/4/5) to give eleven bands. Band 1 (R_f 0.69, red) was crystallised to give red crystals of **2** (16 mg, 4%), identified by comparison (IR, FAB MS) with the sample prepared as above. Band 2 (R_f 0.60, yellow) was further separated by preparative TLC (acetone–cyclohexane–CH_2Cl_2, 1/10/9) into two bands: Band 1 (R_f 0.90 yellow) was crystallised (CH_2Cl_2–cyclohexane) to give yellow prisms of **4** (37 mg, 9%). Band 2 (R_f 0.88, yellow) was crystallised (CH_2Cl_2–cyclohexane) to give yellow prisms of $Ru(\eta\text{-}C_5H_5)\{\eta^5\text{-}C_8H(CO_2Me)_8\}$ (**5**) (32 mg, 6%), m.p. 240–241 °C. Anal. Found: C, 47.28; H, 4.13; $[M+H]$ (mass spectrometry), 737. $C_{29}H_{30}O_{16}Ru$ calc.: C, 47.35; H, 4.11%; M, 736. IR (KBr): ν(C=O) 1740vs (br); ν(C=C) 1640w, ν(C–O) 1270vs, 1255vs, 1230vs, 1210vs; other bands at 1365s, 1355m, 1340vs, 1320m, 1175s, 1142s, 1130s, 1110m, 1025m, 1010m, 1000s, 995s, 918w, 820s cm^{-1}. ^1H NMR: δ ($CDCl_3$) 3.52 (s, 3H, OMe); 3.59 (s, 9H, 3 × OMe); 3.76 (s, 6H, 2 × OMe); 3.80 (s, 3H, OMe); 3.81 (s, 3H, OMe); 5.15 (s, 5H, C_5H_5); 6.63 (s, 1H, =CH). FAB MS: 737, $[M+H]^+$, 3; 706, $[(M+H)-OMe]^+$, 50; 677, $[M-CO_2Me]^+$, 100; 619, $[(M+H)-2CO_2Me)]^+$, 3; 604, $[M-2CO_2Me-Me]^+$, 5; 594, $[M-C_2(CO_2Me)_2]^+$, 1; 559, $[M-3CO_2Me]^+$, 2; 167, $[Ru(C_5H_5)]^+$, 6.

Table 4

Fractional atomic coordinates ($\times 10^4$) for $RuI\{\eta^4\text{-}CH(CO_2Me)\text{=}C(CO_2Me)C(CO_2Me)\text{=}CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ (**2**)

Atom	x	y	z
I	2658(2)	4352(1)	2240(1)
Ru	1175(2)	4400(1)	1333(1)
O(1)	325(24)	2256(10)	1935(8)
O(2)	−258(22)	2256(11)	1153(8)
O(3)	−1864(24)	3770(12)	379(8)
O(4)	−3180(16)	3095(11)	885(5)
O(5)	−1143(22)	5787(12)	529(7)
O(6)	−3318(17)	5444(10)	782(6)
O(7)	−808(25)	6747(10)	1400(8)
O(8)	931(22)	6489(9)	1992(7)
C(1)	3635(41)	4492(27)	1191(13)
C(2)	2953(38)	3689(15)	1032(16)
C(3)	1804(40)	3845(24)	671(15)
C(4)	1677(42)	4689(31)	630(10)
C(5)	2714(57)	5054(25)	942(19)
C(6)	−458(25)	3547(13)	1614(10)
C(7)	−1172(26)	3977(14)	1217(8)
C(8)	−1105(23)	4921(11)	1225(10)
C(9)	−383(29)	5288(15)	1634(9)
C(10)	−193(34)	2614(15)	1511(13)
C(11)	−2014(30)	3598(14)	767(10)
C(12)	−1795(25)	5453(11)	826(10)
C(13)	−108(29)	6247(14)	1631(8)
C(14)	764(37)	1369(16)	1955(11)
C(15)	−4002(28)	2593(15)	514(9)
C(16)	−4077(30)	5939(17)	389(11)
C(17)	1454(55)	7372(16)	2061(13)

(iii) A mixture of RuI(PPh$_3$)$_2$(η-C$_5$H$_5$) (200 mg, 0.339 mmol) and C$_2$(CO$_2$Me)$_2$ (0.33 ml, 2.68 mmol) in MeOH was treated with HPF$_6$ · OEt$_2$ (1 drop) and refluxed for 16 h. The clear orange solution was evaporated to dryness and the residue separated by preparative TLC (acetone–light petroleum, 1/4) to give eleven bands. Band 1 (R_f 0.80, orange) gave solid RuI(PPh$_3$)$_2$(η-C$_5$H$_5$) (20 mg, 10%). Band 2 (R_f 0.40, red) was crystallised (CH$_2$Cl$_2$–MeOH) to give red crystals of **2** (11 mg, 11%), identified (IR, FAB MS) by comparison with an authentic sample. Band 3 (R_f 0.14, orange) was crystallised (MeOH) to give white prisms of C$_6$(CO$_2$Me)$_6$ (90 mg, 24%), identified (IR, NMR) by comparison with an authentic sample [37].

Table 5

Fractional atomic coordinates ($\times 10^5$ for Ru; $\times 10^4$ for remaining atoms) for Ru(η^5-C$_5$H$_5$){η^5-C$_6$H(CO$_2$Me)$_6$} (**4**)

Atom	*x*	*y*	*z*
Ru	57183(2)	29784(1)	38606(1)
O(1)	4703(3)	1617(1)	2208(1)
O(2)	4267(3)	2975(1)	2061(1)
O(3)	3409(3)	4480(1)	2760(1)
O(4)	981(3)	3692(1)	2429(1)
O(5)	2500(4)	4153(2)	4884(1)
O(6)	1441(3)	4493(1)	3824(1)
O(7)	2593(3)	2364(2)	5448(1)
O(8)	5151(3)	3088(1)	5551(1)
O(9)	6080(3)	1387(2)	5229(1)
O(10)	6174(3)	663(1)	4287(1)
O(11)	1278(3)	871(2)	3918(1)
O(12)	625(3)	1359(1)	2874(1)
C(1)	8190(4)	3076(2)	3429(2)
C(2)	8626(4)	2742(2)	4068(2)
C(3)	8185(4)	3314(2)	4542(2)
C(4)	7459(4)	4027(2)	4180(2)
C(5)	7452(4)	3881(2)	3487(2)
C(6)	3737(3)	2391(2)	3079(1)
C(7)	3083(3)	3157(2)	3297(1)
C(8)	2981(3)	3237(2)	4003(1)
C(9)	3780(3)	2592(2)	4460(1)
C(10)	4447(3)	1870(2)	4181(1)
C(11)	3559(3)	1614(2)	3479(1)
C(12)	4269(3)	2272(2)	2407(1)
C(13)	4790(6)	2935(3)	1406(2)
C(14)	2557(3)	3865(2)	2807(1)
C(15)	297(6)	4311(3)	1925(2)
C(16)	2317(3)	4009(2)	4293(1)
C(17)	929(5)	5292(2)	4037(2)
C(18)	3772(4)	2673(2)	5211(1)
C(19)	5076(6)	3222(3)	6261(2)
C(20)	5621(3)	1293(2)	4627(1)
C(21)	7485(5)	115(2)	4674(2)
C(22)	1701(3)	1237(2)	3459(1)
C(23)	−1081(4)	933(2)	2799(2)

Table 6

Fractional atomic coordinates ($\times 10^5$ for Ru; $\times 10^4$ for remaining atoms) for Ru(η^5-C_5H_5)\{η^5-C_6[C(CO_2Me)=CH(CO_2Me)](CO_2Me)$_6$\} (**5**)

Atom	*x*	*y*	*z*
Ru	62203(2)	19297(1)	93510(1)
O(1)	8506(3)	3013(1)	6380(2)
O(2)	8092(3)	1807(1)	6032(2)
O(3)	9549(2)	1818(1)	9493(1)
O(4)	10380(2)	1196(1)	8631(2)
O(5)	5832(2)	2347(1)	6643(1)
O(6)	6639(2)	3408(1)	7296(1)
O(7)	9221(2)	3401(1)	8943(1)
O(8)	8291(2)	3443(1)	9957(1)
O(9)	5037(3)	3792(1)	9614(2)
O(10)	6179(2)	4288(1)	8846(2)
O(11)	2551(2)	2369(1)	8398(2)
O(12)	3139(2)	3434(1)	7926(2)
O(13)	3099(2)	1450(1)	7093(2)
O(14)	3792(3)	676(1)	8164(2)
O(15)	7701(3)	511(1)	8392(2)
O(16)	5868(3)	560(1)	7328(2)
C(1)	7535(2)	1855(1)	10628(1)
C(2)	6235(2)	2027(1)	10649(1)
C(3)	5380(2)	1431(1)	10265(1)
C(4)	6152(2)	890(1)	10007(1)
C(5)	7483(2)	1152(1)	10232(1)
C(6)	6370(3)	1616(2)	8172(2)
C(7)	5032(3)	1793(2)	8111(2)
C(8)	4776(3)	2530(1)	8365(2)
C(9)	5884(3)	3002(1)	8755(2)
C(10)	7191(3)	2753(1)	8781(2)
C(11)	7232(3)	2281(1)	8046(2)
C(12)	8620(3)	2024(2)	8044(2)
C(13)	9080(3)	2060(2)	7406(2)
C(14)	8505(3)	2364(2)	6562(2)
C(15)	7526(5)	2018(3)	5179(2)
C(16)	9528(3)	1677(2)	8807(2)
C(17)	11333(4)	856(3)	9324(3)
C(18)	6492(3)	2677(2)	7233(2)
C(19)	5902(4)	3846(2)	6588(2)
C(20)	8351(3)	3225(2)	9220(2)
C(21)	9308(4)	3958(2)	10397(2)
C(22)	5644(3)	3731(2)	9132(2)
C(23)	6085(5)	5026(2)	9184(3)
C(24)	3353(3)	2762(2)	8247(2)
C(25)	1784(4)	3722(3)	7777(3)
C(26)	3917(3)	1238(2)	7811(2)
C(27)	1977(4)	966(3)	6750(3)
C(28)	6730(3)	837(2)	7991(2)
C(29)	6106(5)	−209(2)	7114(3)

B. Reaction between Z,Z-$CH(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)$ and $RuCl(\eta^4\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$

$RuCl(\eta^4\text{-}C_8H_{12})(\eta\text{-}C_5H_5)$ (54 mg, 0.175 mmol) was added to a solution of tetramethyl (*Z*,*Z*)-1,3-butadiene-1,2,3,4-tetracarboxylate in MeOH (17 ml) and the mixture was heated at 60 ° C for 3.5 h. The resulting yellow-orange solution was filtered through alumina, evaporated to dryness and the residue crystallised (Et_2O/light petroleum) to give orange crystals of **1** (51 mg, 60%), shown to be identical (IR, NMR) with the complex isolated from reaction A(a) above.

Crystallography

Intensity data for **2**, **4** and **5** were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted with Mo-K_α radiation, $\lambda = 0.7107$ Å. The data sets were corrected for Lorentz and polarisation effects and for absorption using an analytical procedure for **2** and **4** [38] and ϕ-scans for **5**. Table 3 summarises crystal data and refinement details.

The structures of **2** and **4** were solved from the interpretation of their respective Patterson maps and the structure of **5** was solved employing direct-methods [38]. Each structure was refined by a full-matrix least-squares procedure based on F [38]. Non-hydrogen atoms were refined with anisotropic thermal parameters and the cyclopentadienyl ring in **5** was refined as a pentagonal rigid group. Hydrogen atoms were included in the models at their calculated positions except for the H(13) atom in **5** which was located from a difference map. In each refinement a weighing scheme of the form $w = [\sigma^2(F) + g\,|F^2|]^{-1}$ was applied and the refinements continued until convergence. The relatively poor refinement of **2** reflects the poor quality of the crystals; however, the stereochemistry has been determined unambiguously. Final refinement details are given in Table 3, fractional atomic coordinates for the three structures are listed in Tables 4–6 and the crystallographic numbering schemes are shown in Figs. 1–3 drawn with the PLUTO programme [39]. Scattering factors for neutral Ru and I (corrected for f' and f'') were from ref. 40 and those for the remaining atoms were as given in the SHELX-76 programme [38].

Supplementary material available. Listings of thermal parameters, hydrogen atom parameters, bond lengths and angles, and of observed and calculated structure factors are available on request from the authors.

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