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Cyclopentadienyl-ruthenium and -osmium chemistry

XXVIII *. Reactions and isomerisation of 1,2-bis(methoxycarbonyl)ethenyl complexes: X-ray structures of $Ru\{(Z)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)\cdot 0.5EtOH$, $Ru\{(E)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(dppe)(\eta\text{-}C_5H_5)$ and $Ru\{C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$

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Abstract

A reinvestigation of the reaction between $C_2(CO_2Me)_2$ and $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ and some related complexes is reported. Initial *cis* addition is followed by conversion into the *trans* isomer. In the case of the bis-(PPh_3) complex, isomerisation is followed by chelation of the ester CO group with concomitant displacement of one PPh_3 ligand. The resulting chelate complex reacts with CO or $CNBu^t$ to give the (Z)-$RuC(CO_2Me){=}CH(CO_2Me)$ complexes; the (E)-isomer of the carbonyl complex is obtained by addition of $C_2(CO_2Me)_2$ to $RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)$. The ^1H and ^{13}C NMR spectra are not a reliable guide to assignment of the stereochemistry of the vinyl group. Other products isolated from the initial reaction are the bis-insertion product $Ru\{C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$ and the 1/2 $PPh_3/C_2(CO_2Me)_2$ adduct. The molecular structures of $Ru\{(Z)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)\cdot 0.5EtOH$, $Ru\{(E)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(dppe)(\eta\text{-}C_5H_5)$ and $Ru\{C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$ have been determined. The *cis* isomer is monoclinic, space group $P2_1$, with a 9.328(8), b 17.385(10), c 10.356(7) Å, β 101.78(3)°

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* For Part XXVII, see ref. 17.

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and $Z = 2$; 2107 data with $I \geqslant 2.5\sigma(I)$ were refined to $R = 0.076$, $R_w = 0.085$. The *trans* isomer is triclinic, space group $P\bar{1}$, with a 10.404(7), b 11.221(6), c 13.230(9) Å, α 92.67(5), β 110.56(5), γ 106.21(5)° and $Z = 2$; 2520 data with $I \geqslant 2.5\sigma(I)$ were refined to $R = 0.055$, $R_w = 0.068$. The butadienyl complex is monoclinic, space group $P2_1/a$, with a 19.655(8), b 8.674(4), c 21.060(5) Å, β 116.22(3)° and $Z = 4$; 2724 data with $I \geqslant 2.5\sigma(I)$ were refined to $R = 0.042$, $R_w = 0.047$.

Introduction

Reactions between $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ and alkynes have given a number of interesting products, including vinyl, butadienyl, and cumulenyl complexes [1]. The reaction with hexafluorobut-2-yne, for example, afforded the adduct (E)-$Ru\{C(CF_3)=CH(CF_3)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (**1**) and the butadienyl derivative $Ru\{C(CF_3)=C(CF_3)C(CF_3)=CH(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)$ (**2**). The geometry of **1** was readily assigned on the basis of ^1H and ^{19}F NMR studies. Two complexes were also obtained from dimethyl acetylenedicarboxylate: the 1/1 adduct $Ru\{(E)\text{-}C(CO_2Me)=CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (**3**) and the chelate complex $Ru\{C(CO_2Me)=CHC(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)$ (**4**). For **3** the assignment of geometry was not as clear-cut as for **1**, but on the basis of a small value for $J(HP)$ (ca. 0.7 Hz) found for the vinyl proton, and the ready conversion to **4**, the *trans* configuration was preferred *. However, it was recognised that the isolated complex was not necessarily the initial product, since a facile isomerisation might have occurred. In this regard it is relevant to recall that the first-formed *cis* adduct of $C_2(CO_2Me)_2$ with $ReH(\eta\text{-}C_5H_5)_2$ isomerises on heating in benzene (Pt catalyst) [2]. This paper reports a more detailed investigation of the reactions between $C_2(CO_2Me)_2$ and selected ruthenium hydrido complexes, including ^{13}C NMR and X-ray crystallographic studies which allow confident determinations of configuration. In addition, we have now isolated and characterised the butadienyl complex $Ru\{C(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$ (**5**), analogous to complex **2** mentioned above, and also to the major product **6** isolated from reactions between $RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$ and $C_2(CO_2Me)_2$ [3].

Results and discussion

The original preparation of $Ru\{C(CO_2Me)=CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (**3**) was carried out in diethyl ether for 5 h and gave over 90% isolated yields [1]; in contrast, reaction in refluxing benzene for 40 min afforded four products: complex **3** (51%), the cyclic vinyl complex **4** (6%), yellow $Ru\{C(CO_2Me)=C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$ (**5**) (20%), and the $PPh_3/C_2(CO_2Me)_2$ adduct (**7**) (12%). Complex **5** was identified by elemental microanalysis and from its characteristic ^1H NMR spectrum, which contains three sharp singlet resonances between δ 3.13–3.80 ppm with relative intensities 3/6/3, assigned to the O*Me* groups, together with a vinyl proton resonance at δ 2.22 ppm, which is coupled to a single ^{31}P nucleus. The FAB mass spectrum contains a parent molecular ion at *m/z* 714. Full stereochemical characterisation was achieved by a single-crystal X-ray

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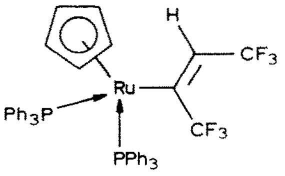
* In this paper, *cis* and *trans* refer to the configuration of the two CO_2Me groups.



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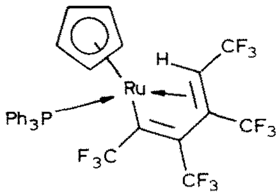
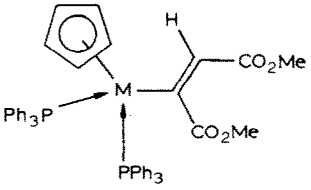
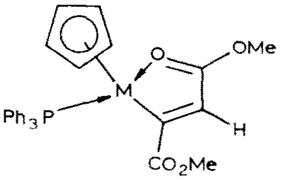


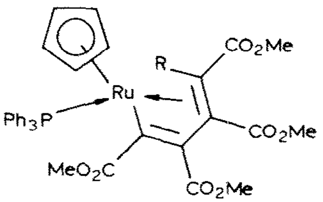
(2)



(3) M = Ru
(8) M = Os



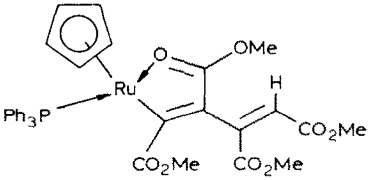
(4) M = Ru
(9) M = Os



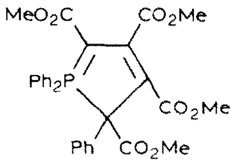
(5) R = H
(6) R = Me

structure determination (see below). Compound **7** was identified as the yellow 1/2 adduct of PPh_3 with $C_2(CO_2Me)_2$ by comparison with an authentic sample prepared as described by Johnson and Tebby [4]; presumably it is formed by combination of PPh_3 displaced in the formation of **4** or **5** with unreacted $C_2(CO_2Me)_2$.

The osmium analogues of complexes **3** and **4** have also been obtained during this



(5a)



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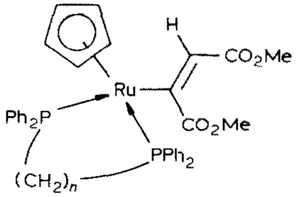
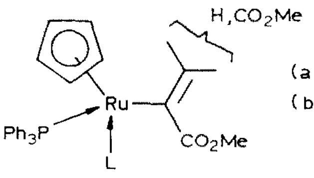


(10) $n = 1$
(11) $n = 2$



(a) *trans*—$(CO_2Me)_2$
(b) *cis*—$(CO_2Me)_2$

(12) L = CO
(13) L = $CNBu^t$

work; yellow $\mathrm{Os\{C(CO_2Me){=}CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)}$ (**8**) was obtained in 71% yield from $\mathrm{OsH(PPh_3)_2(\eta\text{-}C_5H_5)}$ and an excess of $\mathrm{C_2(CO_2Me)_2}$ in 1,2-dimethoxyethane (dme) at 120 °C for 16 h. It was accompanied by a small amount of deep red $\mathrm{Os\{C(CO_2Me){=}CHC(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)}$ (**9**), the proportion of which could be increased by carrying out the reaction at 150 °C for 16 h. Conversion of **8** into **9** was achieved by heating in toluene at 150 °C for 7 h. Identification of these complexes was from elemental microanalyses and the general similarity of their IR, NMR and mass spectra with those of complexes **3** and **4**. However, in contrast with **3**, the mass spectrum of **8** showed a parent ion centred on *m/z* 922, which fragmented by loss of OMe, CO and $\mathrm{PPh_3}$ groups. The two ruthenium complexes give identical mass spectra, presumably as a result of the thermal conversion of **3** to **4** occurring in the ion source.

Similar reactions between $\mathrm{RuH(L{-}L)(\eta\text{-}C_5H_5)}$ (L–L = dppm ($\mathrm{CH_2(PPh_2)_2}$), dppe ($\mathrm{Ph_2PCH_2CH_2PPh_2}$)) afforded yellow $\mathrm{Ru\{C(CO_2Me){=}CH(CO_2Me)\}(L{-}L)(\eta\text{-}C_5H_5)}$ (L–L = dppm (**10**), dppe (**11**)), the former as a hemi-ethanol solvate. Complex **10** decomposes during some hours in air, although complex **11**, like **3**, is quite stable in air. Both complexes are very soluble in benzene, less soluble in chlorinated solvents, and only sparingly soluble in diethyl ether, ethanol or acetone; they are both insoluble in light petroleum. The new complexes were characterised on the basis of elemental microanalyses and their IR, NMR and mass spectra. Infrared absorptions were found for ν(C=O) (1705 and 1725 $\mathrm{cm^{-1}}$ in **10**, 1695 $\mathrm{cm^{-1}}$ in **11**), ν(C=C) (1529 and 1531 $\mathrm{cm^{-1}}$, respectively) and ν(C–O) (1192 and 1142 $\mathrm{cm^{-1}}$ (**10**), 1146 $\mathrm{cm^{-1}}$ (**11**)). The salient features of the NMR spectra are discussed below. In their mass spectra, molecular ions centred on *m/z* 694 (**10**) or 708 (**11**) decompose by loss of the vinyl and $\mathrm{C_5H_5}$ groups.

Conversion of **3** into the chelate complex **4** occurs on heating, with concomitant loss of $\mathrm{PPh_3}$. An attempt to improve the yield by addition of sulphur gave the expected $\mathrm{SPPh_3}$, but only as one component of a complex, intractable black product. However, addition of iodomethane to a solution of **3** in refluxing toluene rapidly gave a white precipitate of $\mathrm{[PMePh_3]I}$; the red solution gave **4** in 80% yield after chromatography.

Reactions between **4** and small ligands, such as CO or $\mathrm{CNBu^t}$, result in opening of the chelate ring to give complexes $\mathrm{Ru\{C(CO_2Me){=}CH(CO_2Me)\}(L)(PPh_3)(\eta\text{-}C_5H_5)}$ (L = CO (**12**), $\mathrm{CNBu^t}$ (**13**)). Thus, carbonylation of **4** under mild conditions in tetrahydrofuran (thf) solution afforded a yellow product **12a**, which proved to be different from the complex **12b** obtained by addition of $\mathrm{C_2(CO_2Me)_2}$ to $\mathrm{RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)}$. Elemental microanalyses showed the two complexes to be isomers; the most marked difference in their IR spectra was in the position of ν(CO) for the metal-bonded CO group (1954 $\mathrm{cm^{-1}}$ in **12a**, 1940 $\mathrm{cm^{-1}}$ in **12b**). The NMR spectra are discussed below. Carbonylation of **3** in a methanol/dichloromethane mixture gave complex **12b** (65%).

The reaction between **4** and $\mathrm{Bu^tNC}$ in refluxing 1,2-dimethoxyethane gave pale yellow **13** in high yield. In the IR spectrum, ν(CN) bands were found at 2095 and 2065 $\mathrm{cm^{-1}}$, and the ester ν(CO) was at 1703 $\mathrm{cm^{-1}}$. In the mass spectrum, the parent ion (*m/z* 654) fragments by loss of CNBu, $\mathrm{PPh_3}$, OMe and CO groups.

Stereochemistry of the $\mathrm{MC(CO_2Me){=}CH(CO_2Me)}$ group

The ^{1}H and ^{13}C NMR spectra of the several complexes described above are summarised in Tables 1 and 2. These can be interpreted readily in conjunction with the X-ray structural determinations which we have carried out on complexes **11** and **12a**.

Molecular structure of $Ru\{(E)\text{-}C(CO_2Me)=CH(CO_2Me)\}(dppe)(\eta\text{-}C_5H_5)$ *(11)*

A molecule of **11** is shown in Fig. 1, from which it is clear that the vinyl ligand carries the two CO_2Me groups in a mutually *cis* configuration. The ruthenium atom coordination is distorted octahedral (angles P(1)–Ru–P(2) 85.1(1), P(1)–Ru–C(32) 93.3(4), P(2)–Ru–C(32) 92.2(5)°). The Ru–C(sp^2) distance (Ru–C 2.07(1) Å) is within experimental error the same as that found in the *trans* complex **12a** (see below). The ruthenium is also bonded to the two phosphorus atoms of the chelating dppe ligand (Ru–P 2.271(4), 2.249(4) Å) and the η-C_5H_5 group (Ru–C(cp) 2.21–2.28(1), av. 2.25 Å). The two longest Ru–C(cp) vectors are approximately *trans* to the shorter of the two Ru–P vectors.

Molecular structure of $Ru\{(Z)\text{-}C(CO_2Me)=CH(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ *(12a)*

A molecule of **12a** is shown in Fig. 2. In this case, the vinyl group has mutually *trans* CO_2Me groups, as expected from the mode of preparation. Coordination of the ruthenium atom to the vinyl group (Ru–C 2.080(8) Å), a CO ligand (Ru–C 1.847(7) Å), the PPh_3 ligand (Ru–P 2.310(2) Å) and the η-C_5H_5 group (Ru–C(cp) 2.250–2.264(7), av. 2.258 Å) is unexceptional; as found in similar complexes, the ruthenium coordination is distorted octahedral (P(1)–Ru–C(24) 85.0(2), P(1)–Ru–C(25) 94.7(2), C(24)–Ru–C(25) 93.1(3)°). Compared with **11** above, the C_5 ring is more symmetrically bonded to the metal atom.

In both complexes, the $C(CO_2Me)=CH(CO_2Me)$ groups show no significant

(Continued on p. 66)

Table 1

^1H NMR spectra ($CDCl_3$) of some $MLL'\{C(CO_2Me)=CH(CO_2Me)\}(\eta\text{-}C_5H_5)$ complexes

MLL′	Configuration	Chemical shifts (ppm) [a]				
		CO_2Me	CH=	C_5H_5	PPh	Other
$Ru(PPh_3)_2$ (**3**)	*cis*	3.27s,3.96s	4.55s	4.15s	7.22m	
$Os(PPh_3)_2$ (**8**)	*cis*	3.25s,3.95s	4.75t (1.0)	4.30s	7.20m	
Ru(dppm) (**10**)	*cis*	3.15s,3.25s	5.00s (–)	4.80s	7.35m	PCH_2 3.80m
Ru(dppe) (**11**)	*cis*	3.19s,3.52s	4.29s (–)	4.44s	7.29m	PCH_2 2.73m EtOH 1.18t,3.64q
$Ru(CO)(PPh_3)$ (**12a**)	*trans*	2.88s,3.66s	6.60d (2.0)	4.98s	7.25m	
$Ru(CO)(PPh_3)$ (**12b**)	*cis*	3.55s,3.57s	5.33d (1.0)	4.98s	7.37m	
$Ru(CNBu^t)(PPh_3)$ (**13**)	*cis*	3.55s,3.58s	5.60d (2.0)	4.80s	7.43m	
$Ru(PPh_3)$ (**4**)	*trans* (chelate)	3.21s,3.49s	6.20d (2.5)	4.41s	7.36m	
$Os(PPh_3)$ (**9**)	*trans* (chelate)	3.30s,3.45s	5.90d (1.0)	4.65s	7.35m	

[a] *J*(HP) (Hz) in parentheses.

Table 2

^{13}C NMR spectra ($CDCl_3$) of some RuLL′{C(CO_2Me)=CH(CO_2Me)}(η-C_5H_5) complexes

LL′	Config-uration	Chemical shifts (ppm)						
		CO_2Me	C_5H_5	PPh	CH=	RuC [a]	CO_2Me	Other [a]
(PPh_3)$_2$ (**3**)	*cis*	49.51s, 50.31s	86.25s	126–140m	163.0s	182.2t (16)	182.5s	
dppm (**10**) [b]	*cis*	50.05s	85.6s	128–134m	162.45s	191.9t (0.5)	181.45s	PCH_2 29.05m
(CO)(PPh_3) (**12a**)	*trans*	49.9s, 50.25s	87.45s	127.7–136.6m	168.65s	172.7d (11)	178.25s, 178.4s	RuCO 205.0d (21)
(CO)(PPh_3) (**12b**)	*cis*	50.5s	87.95s	128–136m	162.3s	176.6d (13)	179.65s	RuCO 204.7d (21)
(CNBu^t)(PPh_3) (**13**)	*cis*	50.0s, 50.3s	84.95s	127.5–134.0m	162.45s	137.05d (44)	180.4s, 186.7s	C*Me*$_3$ 31.0s *C*Me$_3$ 56.3s CN 124.1s
PPh_3 (**4**)	*trans* (chelate)	50.55s, 50.6s	77.25s	127–136m	116.25s	179.1d (17)	176.4s	

[a] *J*(CP) (Hz) in parentheses. [b] EtOH: Me 27.35, CH_2 55.95.

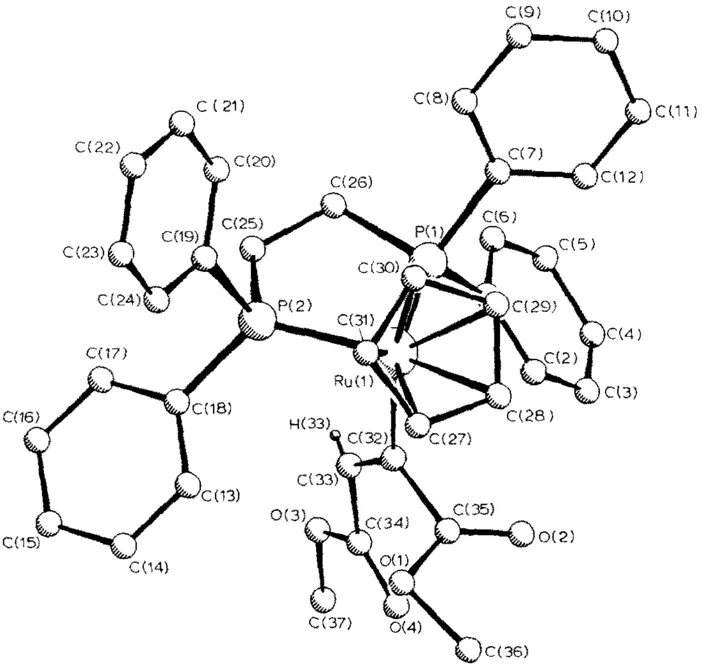
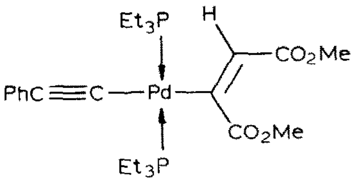


Fig. 1. A molecule of Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(dppe)(η-C_5H_5) (**11**), showing atom numbering scheme.



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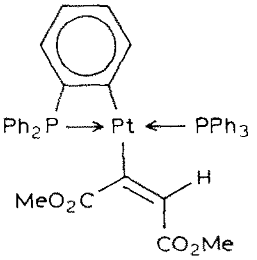

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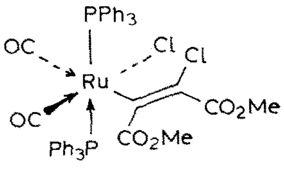

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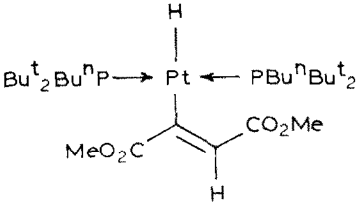

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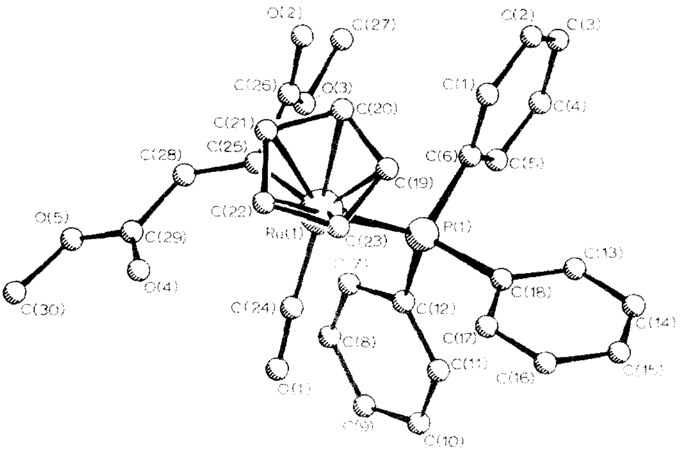
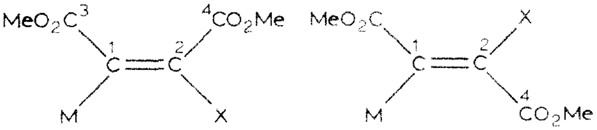


Fig. 2. A molecule of Ru{(*Z*)-C(CO_2Me)=CH(CO_2Me)}(CO)(PPh_3)(η-C_5H_5) (**12a**), showing atom numbering scheme.

differences from those found in related molecules such as Pd{(*E*)-C(CO_2Me)=CH(CO_2Me)}(C_2Ph)(PEt_3)$_2$ (**14**) [5], $\overline{\mathrm{Pt(C_6H_4PPh_2)}}${(*E*)-C($CO_2$Me)=CH($CO_2$Me)}($PPh_3$) (**15**) [6], RuCl{(*Z*)-C(CO_2Me)=CCl(CO_2Me)}$(CO)_2(PPh_3)_2$ (**16**) [7], *trans*-

Table 3

Stereochemistry of some M{C(CO_2Me)=CX(CO_2Me)} groups



(**A**) *cis* (**B**) *trans*

Complex	**11**	**14** [a]	**15**	**16**	**12a**	**17**	**18**
M	Ru	Pd	Pt	Ru	Ru	Pt	Pt
X	H	H	H	Cl	H	H	Cl
Configuration	**A**	**A**	**A**	**A**	**B**	**B**	**B**
Bond lengths (Å)							
M–C(1)	2.07(1)	2.05(2)	2.026(8)	2.16(2)	2.080(8)	2.086(12)	1.97(2)
C(1)–C(2)	1.43(2)	1.38(2)	1.337(12)	1.41(3)	1.373(10)	1.37(2)	1.31(2)
C(1)–C(3)	1.47(2)	1.48(2)	1.508(13)	1.49(3)	1.494(9)	1.50(2)	1.56(3)
C(2)–C(4)	1.53(2)	1.48(3)	1.480(13)	1.49(3)	1.462(10)	1.49(2)	1.51(3)
Bond angles (deg)							
M–C(1)–C(2)	126.1(10)	94.5(5)	126.7(7)	129.9(14)	133.2(5)	129.9(5)	129.9(11)
M–C(1)–C(3)	113.7(10)	91.7(4)	122.8(6)	114.7(15)	114.7(6)	117.9(5)	112.6(9)
C(3)–C(1)–C(2)	120.1(11)	123 (2)	120.5(8)	114.5(18)	111.5(7)	111.8(8)	117.4(9)
C(1)–C(2)–C(4)	124.3(13)	121 (2)	126.4(9)	122.1(14)	124.6(7)	124.8(8)	124.4(8)
C(1)–C(2)–X	–	–	–	122.4(16)	–	–	125.8(10)
C(4)–C(2)–X	–	–	–	115.4(17)	–	–	109.8(8)
Reference	This work	[5]	[6]	[7]	This work	[8]	[9]

[a] Average of two values.

$PtH\{(Z)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(PBu^nBu^t_2)_2$ (**17**) [8] or $[N(PPh_3)_2][Pt\{(E)\text{-}C(CO_2Et){=}CCl(CO_2Pr^i)\}Cl_2(CO)]$ (**18**) [9] (Table 3).

The structure determinations unequivocally establish the configurations of the vinyl ligands in complexes **11**, **12a** and **12b**. Furthermore, since both carbonylation of **3** and the reaction between $RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)$ and $C_2(CO_2Me)_2$ afforded **12b**, it is likely that *cis* addition of the metal hydride to the alkyne occurs, as has been found previously. The ^1H NMR spectra are entirely consistent with these structures. In the *cis* isomer, the vinyl C*H* resonance would be expected at higher field than in the *trans* isomer because of the shielding effect of metal electron density: the observed values are 5.33 and 6.60, respectively. The magnitude of the *J*(HP) coupling is also helpful, having values of 2 and 1 Hz in **12a** and **12b**, respectively; the *trans* coupling in other compounds containing the PC=CH moiety is usually twice the *cis* coupling [10].

We find that chemical shifts of the O*Me* resonances differ by only ca. 0.02 ppm in the *cis* isomer, compared with ca. 0.8 ppm in the *trans* isomer; this is consistent with the CO_2Me groups being in more similar environments in the former. There is also observed a separation of the OMe resonances of ca. 0.3 ppm in the chelate complex **4**.

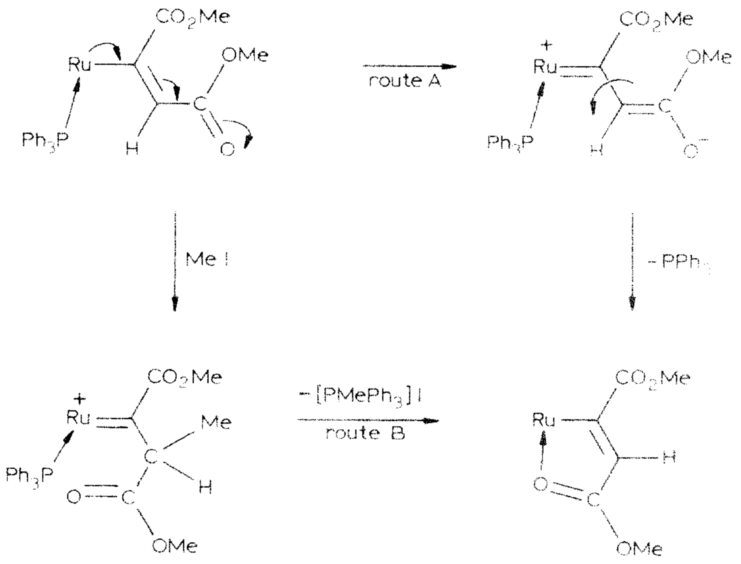
The ^{13}C NMR spectra of the isomeric complexes also show differences in the CO_2Me resonances which can be related to the observed geometrical isomerism. In the *cis* isomer **12b**, both groups are accidentally equivalent, with the OMe and CO resonances at 50.5 and 179.6 ppm, respectively, whereas in the *trans* isomer **12a**, two sets of resonances are found, at 49.9 and 50.2, and 178.25 and 178.4 ppm, respectively. Other resonances are readily assigned to C_5H_5 (88.0 and 87.5 ppm, respectively), CH (162.3 and 168.7), Ru–C (176.6 and 172.7) and Ru–CO carbons (204.7 and 205.0). The metal-bonded carbons show 11–13 (Ru–C) or 21 Hz (Ru–CO) coupling to phosphorus.

It is evident that the effects of differing geometry of the vinyl ligand on the NMR spectra are subtle, and of limited use in assigning the stereochemistry unless both isomers are available for study. However, on the basis of the above results we have been able to assign the structures of the various complexes encountered in this work with some confidence.

The isomerisation reaction

We have previously suggested that the initial *cis* adduct might transform into the *trans* isomer by virtue of a partial withdrawal of electron density from the C=C double bond on to the β-ester carbonyl group (Scheme 1, route A) [1]. The reduction in C=C bond order would allow rotation of the $CH(CO_2Me)$ group about this bond, a possible driving force being the extra stability derived from chelation of the ester carbonyl group.

The isomerisation proceeds slowly on heating, but the reaction is accelerated by addition of iodomethane to the solution of complex **3**. In this way, the displaced PPh_3 ligand is removed as $[PMePh_3]I$, which separates from the solution. The primary role of the iodomethane, however, is to alkylate the β-carbon, generating a carbene intermediate (Scheme 1, route B). Carbenes containing electron-withdrawing substituents are relatively unstable, and we would expect that rotation and displacement of the PPh_3 would be accompanied by rapid transfer of the methyl group from the β-carbon to the PPh_3 ligand.



Scheme 1. One PPh_3 and C_5H_5 ligands omitted for clarity.

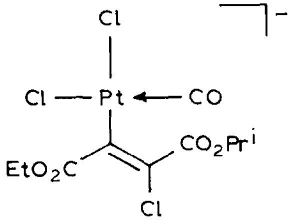
Formation and molecular structure of the butadienyl complex 5

First observed in the reaction between $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ and $C_2(CF_3)_2$ [1], and subsequently in the addition of $C_2(CO_2Me)_2$ to $RuMe(PPh_3)_2(\eta\text{-}C_5H_5)$ [3], was the formal insertion of two alkyne molecules into the Ru–H or Ru–C bonds of the precursor complexes, generating the butadienyl complexes **2** or **6**. Complex **5** was not observed in initial studies of the reaction between the hydride and $C_2(CO_2Me)_2$, although, as we have now shown, it can be isolated as a stable yellow crystalline solid if the reaction conditions are modified. We have shown previously [1] that vinyl complex **3** reacts with $C_2(CF_3)_2$ to give the mixed insertion product **19**, where the entering alkyne has apparently inserted into the vinylic C–H bond of **3**, a result which has been rationalised on the basis of a dipolar intermediate similar to route A in Scheme 1.

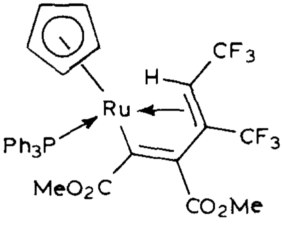
The spectroscopic evidence did not distinguish between the butadienyl formulation and an ester-CO chelate structure such as **5a**, so a single crystal X-ray study was carried out. As mentioned above, this confirmed the 1,3,4-η^3-butadienyl structure, a diagram of which is given in Fig. 3. The ruthenium atom is coordinated by the C_5H_5 group (Ru–C(cp) 2.207(6)–2.247(7) Å, av. 2.228 Å), the PPh_3 ligand (Ru–P 2.346(2) Å), and the butadienyl group, which is attached by the σ-bonded carbon (Ru–C(6) 2.060(6) Å) and the outer C=C double bond of the butadiene (Ru–C(8) 2.189(6), Ru–C(9) 2.194(6) Å). These distances may be compared with those found in $Ru\{C(CF_3)=C(CF_3)C(CF_3)=CH(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)$ (**2**) [11] and $Ru\{C(CO_2Me)=C(CO_2Me)C(CF_3)=CH(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)$ (**19**) [12] (Table 4); no significant differences are found.

Other reactions of $Ru\{C(CO_2Me)=CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)$

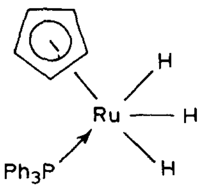
The Ru–C bond in complex **3** was easily cleaved by reagents such as HCl or H_2. Thus, when a suspension of **3** in aqueous methanolic hydrochloric acid was heated, an orange precipitate of $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ formed.



(18)



(19)



(20)

Hydrogenation of **3** in tetrahydrofuran solution under mild conditions afforded a moderate yield of a white complex identified as $RuH_3(PPh_3)(\eta\text{-}C_5H_5)$ **(20)** by comparison of its IR and ^1H NMR spectra with those previously reported [13].

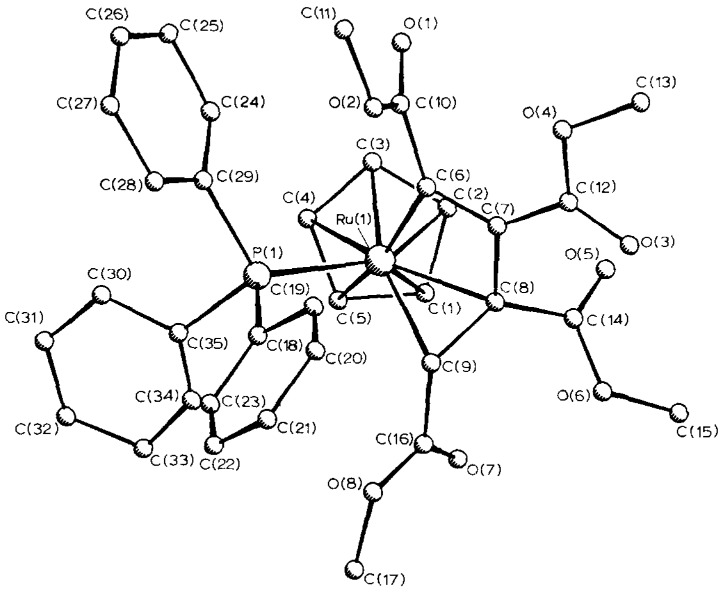
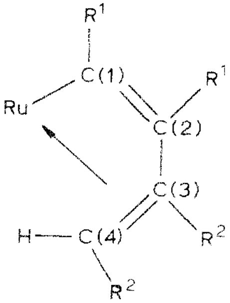


Fig. 3. A molecule of $\overline{Ru\{C(CO_2Me)=C(CO_2Me)C(CO_2Me)}=CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$ (5), showing atom numbering scheme.

Table 4

Some structural parameters for η^3-butadienylruthenium complexes



Complex	**5**	**2**	**19**
R^1	CO_2Me	CF_3	CO_2Me
R^1	CO_2Me	CF_3	CF_3
Bond distances (Å)			
Ru–C(1)	2.060(6)	2.05	2.082(1)
Ru–C(3)	2.189(6)	2.16	2.185(5)
Ru–C(4)	2.194(6)	2.19	2.171(6)
C(1)–C(2)	1.355(9)	1.33	1.348(7)
C(2)–C(3)	1.515(8)	1.51	1.509(8)
C(3)–C(4)	1.421(9)	1.42	1.428(7)
Bond angles (deg)			
Ru–C(1)–C(2)	100.4(4)	[a]	99.4(4)
C(1)–C(2)–C(3)	104.7(5)	[a]	105.5(4)
C(2)–C(3)–C(4)	117.7(6)	[a]	117.2(4)
Reference	This work	[11]	[12]

[a] Not available.

Interestingly, this trihydride was not obtained by similar hydrogenation of the chelate complex **4**, suggesting that replacement of PPh_3 by 2H occurs before cleavage of the Ru–C bond. We have previously noted that ligand exchange in $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ is slow [14]. The trihydride was obtained previously from the reaction between $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ and $LiAlH_4$ in tetrahydrofuran [13].

Conclusions

The results described allow the following conclusions to be drawn:

(i) Initial *cis* addition occurs in the reaction between $RuH(L)_2(\eta\text{-}C_5H_5)$ ($L = PPh_3$, $L_2 = (CO)(PPh_3)$, dppm, dppe) and $C_2(CO_2Me)_2$.

(ii) On heating of **3**, isomerisation to the *trans* complex occurs, followed by chelation of the ester carbonyl group with displacement of a PPh_3 ligand.

(iii) Subsequent addition of ligands to the chelate complex **4** affords the *trans* vinyl complex.

(iv) The bis-insertion product, butadienyl complex **5**, is also formed in the reaction between $C_2(CO_2Me)_2$ and $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$, presumably by attack of a dipolar intermediate, such as in route A (Scheme 1), on a second molecule of the alkyne.

Experimental

General conditions. All reactions were carried out under nitrogen except those involving CO or H_2; no special precautions were taken to exclude air during work-up, since most complexes proved to be stable in air as solids, and for short times in solution. Pressure reactions were carried out in a small stainless steel laboratory autoclave (Carl Röth, Karlsruhe) of internal volume 100 ml, equipped with an internal glass liner.

Instruments. Perkin–Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^{1}H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz); GEC-Kratos MS3074 mass spectrometer (mass spectra at 70 eV ionising energy, 4 kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 *M* solutions in acetone or dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip.

Starting materials. The literature method was used to prepare $RuH(L)_2(\eta\text{-}C_5H_5)$ ($L = PPh_3$, $L_2 = (CO)(PPh_3)$, dppm, dppe) and $OsH(PPh_3)_2(\eta\text{-}C_5H_5)$ [14]. Solvents were extensively dried and distilled (dme and thf from sodium/benzophenone) before use.

Chromatography. For column chromatography, the packing was Florisil or silica. Preparative TLC was on 20 × 20 cm plates coated with Kieselgel 60 GF_{254} (Merck, Darmstadt).

Reaction between $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ and $C_2(CO_2Me)_2$

A solution of $RuH(PPh_3)_2(\eta\text{-}C_5H_5)$ (502 mg, 0.73 mmol) and $C_2(CO_2Me)_2$ (0.25 ml, 2.03 mmol) in benzene (50 ml) was heated (oil bath at 82–86 °C) for 45 min. Evaporation of the cooled solution gave a red oil, which was chromatographed (Florisil). After washing out of the excess of alkyne with light petroleum, elution with 1/10 acetone/light petroleum gave an orange band containing $Ru\{C(CO_2Me){=}CHC(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)$ (**4**) (26 mg, 6%) (from diethyl ether/light petroleum; identified by melting point and IR spectrum). Further elution with 1/4 acetone/light petroleum gave a yellow fraction containing $Ru\{C(CO_2Me){=}CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (**3**) (308 mg, 51%) (from diethyl ether/light petroleum; identified by melting point and IR spectrum). A second yellow band was eluted with 1/3 acetone/light petroleum, and crystallisation from diethyl ether/pentane gave $Ru\{C(CO_2Me){=}C(CO_2Me)C(CO_2Me){=}CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (**5**) (106 mg, 20%), m.p. 180–181 °C (Found: C, 58.81; H, 4.64; *M* (mass spectrometry) 714; $C_{35}H_{33}O_8PRu$ calcd.: C, 58.90; H, 4.66%, *M* 714). IR (Nujol): ν(CO) 1716vs, 1699s; ν(C=C) 1585w; other bands at 1310m, 1250(sh), 1212s, 1192m, 1150m, 1140m, 1093m, 1012w, 895w, 785w, 758w, 745w, 697m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 2.22 (d, *J*(HP) 16 Hz, 1H, =CH), 3.13 (s, 3H, OMe), 3.60 (s, 6H, 2 × OMe), 3.80 (s, 3H, OMe); 4.89 (s, 5H, C_5H_5); 7.2–7.4 (m, 15H, Ph). FAB mass spectrum: 714, $[M]^+$, 29; 682, $[M - MeOH]^+$, 12; 655, $[M - CO_2Me]^+$, 15; 429, $[Ru(PPh_3)(C_5H_5)]^+$, 100; 262, $[PPh_3]^+$, 31; 167, $[Ru(C_5H_5)]^+$, 18. Continued elution with the same solvent afforded a yellow fraction, further purified by TLC (silica gel; 1/1 acetone/light petroleum) to give **7** (60 mg, 12%) (R_f 0.36; from CH$_2$Cl$_2$/light petroleum), m.p. 248–249 °C (lit. [4] 248–250 °C) (Found: M (mass spectrometry) 546; C$_{30}$H$_{27}$O$_8$P calcd. M 546).

Preparation of 1,2-bis(carbomethoxy)ethenyl complexes

(i) $\overline{\mathit{Ru\{C(CO_2Me)=CHC(O)}}\mathit{OMe\}(PPh_3)(\eta\text{-}C_5H_5)}$ *(**4**).* Refluxing a mixture of Ru{C(CO$_2$Me)=CH(CO$_2$Me)}(PPh$_3$)$_2$(η-C$_5$H$_5$) (400 mg, 0.48 mmol) and MeI (2280 mg, 16.1 mmol) in toluene (25 ml) for 45 min resulted in the precipitation of a white powder, identified (m.p. and NMR) as [PMePh$_3$]I (198 mg, 88%), and a red solution. This was evaporated and the resulting red oil chromatographed on a column of silica. Elution with ether produced a red-orange band which was collected and evaporated to dryness. Extraction of the residue with ether, addition of light petroleum, concentration and refrigeration at −30 °C resulted in the formation of orange microcrystals. Concentration of the mother liquor and refrigeration gave a further crop of $\overline{\mathrm{Ru\{C(CO_2Me)=CHC(O)}}\mathrm{OMe\}(PPh_3)(\eta\text{-}C_5H_5)}$ (**4**) (total yield 219 mg, 80%) m.p. 125–126 °C (Lit. [1] 126–127 °C). Infrared (Nujol): ν(CO free) 1710s, ν(CO coord) 1570s, ν(CC) 1579 cm^{-1} (Lit. [1] ν(CO free) 1699m, ν(CO coord) 1586 cm^{-1}).

*(ii) Os{(E)-C(CO$_2$Me)=CH(CO$_2$Me)}(PPh$_3$)$_2$(η-C$_5$H$_5$) (**8**).* A mixture of OsH(PPh$_3$)$_2$(η-C$_5$H$_5$) (500 mg, 0.64 mmol) and C$_2$(CO$_2$Me)$_2$ (200 mg, 1.41 mmol) in dme (50 ml) was heated under nitrogen in a small autoclave (120 °C, 16 h; working pressure 35 atm). After cooling, evaporation gave a red oil which was chromatographed on Florisil. A red fraction, eluted with benzene, was recrystallised (Et$_2$O) to give deep red crystals of $\overline{\mathrm{Os\{C(CO_2Me)=CHC(O)}}\mathrm{OMe\}(PPh_3)(\eta\text{-}C_5H_5)}$ (**6**) (40 mg, 7%). Elution with benzene/diethyl ether (20/1) gave bright yellow crystals (from dme) of Os{(*E*)-C(CO$_2$Me)=CH(CO$_2$Me)}(PPh$_3$)$_2$(η-C$_5$H$_5$) (**8**) (290 mg, 71%), m.p. 205 °C. Found: C, 60.63; H, 4.63; M (mass spectrometry) 922; C$_{47}$H$_{42}$O$_4$OsP$_2$ calcd.: C, 61.16; H, 4.24%; M 922. IR (Nujol): ν(C=O) 1703s, 1685(sh); ν(C=C) 1516m; ν(C–O) 1196s, 1138s; other bands at 1312m, 1178(sh), 1090m, 1009m, 869m, 836w, 813w, 754(sh), 746w, 705w, 697m cm^{-1}.

(iii) $\overline{\mathit{Os\{C(CO_2Me)=CHC(O)}}\mathit{OMe\}(PPh_3)(\eta\text{-}C_5H_5)}$ *(**9**).* A mixture of OsH(PPh$_3$)$_2$(η-C$_5$H$_5$) (1410 mg, 1.81 mmol) and C$_2$(CO$_2$Me)$_2$ (520 mg, 3.64 mmol) in dme (50 ml) was heated under nitrogen in a small autoclave (150 °C, 16 h). Separation of the products by preparative TLC (Et$_2$O) afforded PPh$_3$ (R_f 0.91), deep red $\overline{\mathrm{Os\{C(CO_2Me)=CHC(O)}}\mathrm{OMe\}(PPh_3)(\eta\text{-}C_5H_5)}$ (**9**) (R_f 0.57) (640 mg, 54%) and yellow Os{C(CO$_2$Me)=CH(CO$_2$Me)}(PPh$_3$)$_2$(η-C$_5$H$_5$) (**8**) (R_f 0.32) (210 mg, 12%). Complex **9** was recrystallised (Et$_2$O) to give deep red crystals, m.p. 171–173 °C. Found: C, 52.86; H, 4.24; M (mass spectrometry) 660; C$_{29}$H$_{27}$O$_4$OsP calcd.: C, 52.73; H, 4.09%; M 660. IR (Nujol): ν(C=O) 1710s, 1694s, 1574w; ν(C=C) 1675s; ν(C–O) 1292s, 1242s; other bands at 1198m, 1177m, 1156w, 1111m, 1078m, 1019w, 793w, 759w, 721w, 718w, 671m, 667m cm^{-1}. The baseline was extracted with dme to give white needles of C$_6$(CO$_2$Me)$_6$ (from Et$_2$O) (340 mg, 65%, m.p. 186–187 °C, identified by comparison with an authentic sample (IR, MS).

The chelate complex **9** was also obtained by heating a solution of Os{C(CO$_2$Me)=CH(CO$_2$Me)}(PPh$_3$)$_2$(η-C$_5$H$_5$) (**8**) (500 mg, 0.54 mmol) in toluene (50 ml) (150 °C, 7 h; autoclave). After cooling, evaporation and chromatography (Florisil) afforded complex **9** (from benzene) (320 mg, 89%), eluted with toluene/diethyl ether (1/1).

(iv) Ru{(E)-C(CO_2Me)=CH(CO_2Me)}(dppm)(η-C_5H_5) **(10)**. A mixture of RuH(dppm)(η-C_5H_5) (240 mg, 0.35 mmol) and excess $C_2(CO_2Me)_2$ (120 mg, 0.84 mmol) was heated in refluxing diethyl ether (60 ml) for 48 h. Cooling afforded yellow crystals of Ru{C(CO_2Me)=CH(CO_2Me)}(dppm)(η-C_5H_5) (**10**) (113 mg, 32%), m.p. 86–90 ° C (dec.) (Found: C, 59.79; H, 4.86; *M* (mass spectrometry) 694; $C_{36}H_{34}O_4P_2Ru$ calcd.: C, 62.25; H, 4.90%, *M* 694). IR (Nujol): ν(C=O) 1725m, 1705s; ν(C=C) 1529m; ν(C–O) 1146s; other bands at 1318w, 1244w, 1201m, 1120(sh), 1100m, 1071(sh), 1027w, 999w, 832w, 786w, 737w, 723s, 699s cm^{-1}.

(v) Ru{(E)-C(CO_2Me)=CH(CO_2Me)}(dppe)(η-C_5H_5) **(11)**. This complex was prepared from RuH(dppe)(η-C_5H_5) (300 mg, 0.53 mmol) and $C_2(CO_2Me)_2$ (150 mg, 1.06 mmol) in refluxing diethyl ether (60 ml) for 15 h. The yellow crystals which separated on cooling were recrystallised ($CHCl_3$/EtOH) to give the hemi-ethanol solvate (223 mg, 69%), m.p. 170–174° C (dec.) (Found: C, 61.73; H, 5.36, *M* (mass spectrometry) 708; $C_{37}H_{36}O_4P_2Ru \cdot 0.5C_2H_6O$ calcd.: C, 62.38; H, 5.34%, *M* 708). IR (Nujol): ν(C=O) 1695s(br), ν(C=C) 1531s, ν(C–O) 1192s, 1142s; other bands at 3060m, 1585w, 1573w, 1482m, 1432s, 1321s, 1160(sh), 1107(sh), 1095m, 1072w, 1029m, 1000m, 958w, 935w, 915w, 868w, 857m, 831m, 802m, 782m, 744s, 709(sh), 697s, 665s, 658(sh), 641m, 628m, 617m cm^{-1}.

(vi) Ru{(Z)-C(CO_2Me)=CH(CO_2Me)}(CO)(PPh_3)(η-C_5H_5) **(12a)**. A red solution of Ru{C(CO_2Me)=CHC(O)OMe}(PPh_3)(η-C_5H_5) (**4**) (254 mg, 0.44 mmol) in thf (20 ml) was carbonylated in a small autoclave (12.5 atm, 100 ° C, 2 h). The resulting yellow solution was evaporated to dryness and separation on preparative TLC plates (silica, 1/1 light petroleum/ether) revealed a mixture of six bands. The major yellow band (R_f 0.52) was isolated and crystallisation from ether/light petroleum afforded light yellow crystals of Ru{(*Z*)-C(CO_2Me)=CH(CO_2Me)}-(CO)(PPh_3)(η-C_5H_5) (**12a**) (173 mg, 66%), m.p. 128–130 ° C. (Found: C, 60.17; H, 4.65; $C_{30}H_{27}O_5PRu$ calcd.: C, 60.00; H, 4.50%). IR (Nujol): ν(RuCO) 1954vs(br), ν(CO) 1718s, 1700s, ν(CC) 1556s cm^{-1}; other bands at 1540w, 1482w, 1440w, 1396(sh), 1355w, 1322m, 1208s, 1188s, 1162vs, 1096s, 1092s, 1020m, 1014s, 1000m, 995(sh), 862w, 845m, 835w, 825w, 814m, 798w, 762m, 752m, 724w, 703m, 694m, 668w cm^{-1}.

(vii) Ru{(E)-C(CO_2Me)=CH(CO_2Me)}(CO)(PPh_3)(η-C_5H_5) **(12b)**. (a) A solution of Ru{C(CO_2Me)=CH(CO_2Me)}$(PPh_3)_2$(η-C_5H_5) (**3**) (300 mg, 0.36 mmol) in a mixture of MeOH and CH_2Cl_2 (1/5, 60 ml) was carbonylated in an autoclave (40 atm, 110 ° C, 21 h) giving a pale yellow solution which was evaporated to dryness. Separation by preparative TLC (silica, 1/1 light petroleum/acetone) revealed a complex mixture of seven bands of which only the major yellow band (R_f 0.6) was isolated. Crystallisation (ether/light petroleum) gave yellow microcrystals of Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(CO)(PPh_3)(η-C_5H_5) (**12b**) (140 mg, 65%), m.p. 165–168°C. IR (Nujol): ν(RuCO) 1940vs(br), ν(CO) 1708s, 1690s; ν(CC) 1557s cm^{-1}; other bands at 1482(sh), 1441(sh), 1438s, 1325s, 1212s, 1191m, 1167(sh), 1154vs, 1100(sh), 1095m, 1074w, 1023m, 1009m, 1000(sh), 960w, 870w, 855(sh), 849m, 841m, 832w, 810w, 750m, 725w, 710(sh), 700w, 661w cm^{-1}.

(b) Dropwise addition of $C_2(CO_2Me)_2$ (330 mg, 2.3 mmol) to a stirred solution of RuH(CO)(PPh_3)(η-C_5H_5) (450 mg, 0.75 mmol) in dme (30 ml) caused an instant colour change from bright yellow to red. After heating a reflux point for 3 h, evaporation, purification of the resultant oil by preparative TLC (diethyl ether/light petroleum 9/1) and crystallisation of the yellow product (diethyl ether/n-hexane) afforded bright yellow crystals of Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)](CO)(PPh_3)(η-C_5H_5) (110 mg, 30%). This complex was identified by comparison with a sample made previously [1].

(viii) Ru{(E)-C(CO_2Me)=CH(CO_2Me)}(CNBu^t)(PPh_3)(η-C_5H_5) ***(13)***. A mixture of Ru{C(CO_2Me)=CHC(O)OMe}(PPh_3)(η-C_5H_5) (**4**) (200 mg, 0.31 mmol) and Bu^{t}NC (120 mg, 0.72 mmol) was heated in refluxing dme (20 ml) for 2 h, during which time the colour of the solution changed from red to yellow. Evaporation, purification by preparative TLC (diethyl ether/light petroleum 9/1) and crystallisation of the yellow band (R_f 0.77) afforded yellow crystals of Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}(CNBu^t)(PPh_3)(η-C_5H_5) (**10**) (160 mg, 71%), m.p. 165–166 °C. Found: C, 61.57; H, 5.64; N, 2.19. $C_{35}H_{36}NO_4PRu$ calcd.: C, 62.97; H, 5.40; N, 2.10%. IR (Nujol): ν(CN) 2095s, 2065(sh); ν(C=O) 1703s, ν(C=C) 1560s, ν(C–O) 1200s, 1142s; other bands at 1312m, 1158w, 1095(sh), 1090m, 1008w, 839w, 801m, 756m, 719w, 697m, 656w cm^{-1}.

Other reactions of Ru{(E)-C(CO_2Me)=CH(CO_2Me)}(PPh_3)$_2$(η-C_5H_5) (3)

(i) With HCl. Refluxing of a mixture of Ru{(*E*)-C(CO_2Me)=CH(CO_2Me)}-(PPh_3)$_2$(η-C_5H_5) (500 mg, 0.60 mmol) and HCl (4 ml of 1 *M* solution) in MeOH (25 ml) for 23 h afforded an orange precipitate which was collected, washed

Table 5

Crystal data and refinement details for **11**, **12a** and **5**

	11	**12a**	**5**
Formula	$C_{37}H_{38}O_4P_2Ru$	$C_{30}H_{27}O_5PRu$	$C_{35}H_{33}O_8PRu$
Mol.wt.	709.7	599.6	713.7
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1$ (C_2^2, No 4)	$P\bar{1}$ (C_i^1, No 2)	$P2_1/a$ (C_{2h}^5, No 14)
a, Å	9.328(8)	10.407(7)	19.655(8)
b, Å	17.385(10)	11.221(6)	8.674(4)
c, Å	10.356(7)	13.230(9)	21.060(5)
α, deg	90	92.67(5)	90
β, deg	101.78(3)	110.56(5)	116.22(3)
γ, deg	90	106.21(5)	90
Vol, Å^3	1643	1371	3221
Z	2	2	4
D_c, g cm^{-3}	1.435	1.452	1.472
F(000)	732	600	1464
μ, cm^{-1}	5.70	6.20	5.41
θ limits, deg	1.3–21	1.5–23	1.5–22.5
No. of data collected	3750	2013	5639
No. of unique data	2194	2634	4216
No. of unique data used with $I \geqslant 2.5\sigma(I)$	2107	2520	2724
R	0.076	0.055	0.042
k	6.86	7.95	1.0
g	0.0012	0.0003	0.0032
R_w	0.085	0.068	0.047
ρ_{max}, e Å^{-3}	1.7	1.2	0.62

(methanol), dried and identified (IR, NMR) as $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ (330 mg, 76%).

(ii) With dihydrogen. A solution of $Ru\{(E)\text{-}C(CO_2Me)\text{=}CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)$ (300 mg, 0.36 mmol) in thf (20 ml) was hydrogenated in an

Table 6

Non-hydrogen atom coordinates for $Ru\{C(CO_2Me)\text{=}CH(CO_2Me)\}(dppe)(\eta\text{-}C_5H_5)\cdot 0.5EtOH$ (**11**) (Ru $\times 10^5$, others $\times 10^4$)

Atom	*x*	*y*	*z*
Ru(1)	10824(10)	25000(-)	8502(9)
P(1)	3119(4)	3115(3)	506(4)
P(2)	2225(4)	1421(2)	414(3)
C(2)	3822(8)	3936(5)	2894(8)
C(3)	4681(8)	4442(5)	3774(8)
C(4)	6034(8)	4684(5)	3550(8)
C(5)	6530(8)	4421(5)	2445(8)
C(6)	5671(8)	3916(5)	1565(8)
C(1)	4318(8)	3673(5)	1789(8)
C(8)	2527(9)	3650(5)	−2117(8)
C(9)	2227(9)	4214(5)	−3094(8)
C(10)	2206(9)	4988(5)	−2744(8)
C(11)	2484(9)	5198(5)	−1416(8)
C(12)	2784(9)	4635(5)	−439(8)
C(7)	2805(9)	3861(5)	−789(8)
C(14)	1691(9)	−171(5)	3196(8)
C(15)	2727(9)	−736(5)	3075(8)
C(16)	3618(9)	−645(5)	2163(8)
C(17)	3492(9)	12(5)	1373(8)
C(18)	2465(9)	576(5)	1495(8)
C(13)	1565(9)	485(5)	2406(8)
C(20)	1606(9)	1246(5)	−2337(8)
C(21)	852(9)	942(5)	−3531(8)
C(22)	−190(9)	366(5)	−3536(8)
C(23)	−477(9)	94(5)	−2348(8)
C(24)	277(9)	397(5)	−1154(8)
C(19)	1319(9)	973(5)	−1149(8)
C(25)	4124(15)	1620(10)	184(14)
C(26)	4320(12)	2430(11)	−124(12)
C(27)	−1285(9)	2440(5)	955(8)
C(28)	−919(9)	3233(5)	938(8)
C(29)	−493(9)	3390(5)	−275(8)
C(30)	−595(9)	2695(5)	−1008(8)
C(31)	−1084(9)	2108(5)	−248(8)
C(32)	1885(14)	2393(12)	2859(11)
C(33)	3289(17)	2091(11)	3474(14)
C(34)	3898(18)	2097(12)	4957(16)
C(35)	889(17)	2694(10)	3673(14)
C(36)	−981(21)	2551(18)	4735(19)
C(37)	5861(21)	1801(17)	6642(21)
O(1)	−44(13)	2133(11)	3919(11)
O(2)	886(15)	3357(9)	3977(11)
O(3)	5162(12)	1837(10)	5226(11)
O(4)	3171(15)	2279(11)	5751(13)

autoclave (14 atm, 100 ° C, 3 h). Addition of methanol and concentration afforded a white precipitate of $RuH_3(PPh_3)(\eta\text{-}C_5H_5)$ (62 mg, 40%) (**19**). IR (Nujol): ν(Ru–H) 2040 and 2000 cm^{-1} (Lit. [13] 2040 and 1995 cm^{-1}). ^1H NMR: δ (C_6D_6) −10.0, d, J(HP) 19 Hz, 3H, RuH; 4.89, s, 5H, C_5H_5; 7.0–7.7, m, 15H, Ph. (Lit. [13] −9.8, d, J(HP) 18 Hz; 4.8, s; 7.0–7.8, m, respectively).

Crystallography

Intensity data for **5**, **11** (as its ethanol solvate) and **12a** were measured at room temperature on an Enraf–Nonius CAD4F diffractometer fitted with Mo-K_α (graphite monochromatized) radiation, λ 0.71073 Å, with the use of the $\omega:2\theta$ scan

Table 7

Non-hydrogen atom coordinates for $Ru\{C(CO_2Me)=CH(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**12a**) (Ru $\times 10^5$, others $\times 10^4$)

Atom	x	y	z
Ru(1)	30683(5)	9862(4)	23059(4)
P(1)	4059(1)	2583(1)	1499(2)
C(1)	6814(5)	2439(3)	2122(5)
C(2)	8297(5)	2885(3)	2357(5)
C(3)	8984(5)	4168(3)	2449(5)
C(4)	8188(5)	5005(3)	2307(5)
C(5)	6705(5)	4560(3)	2072(5)
C(6)	6017(5)	3277(3)	1980(5)
C(7)	3645(4)	3613(3)	2508(3)
C(8)	3059(4)	5587(3)	2531(3)
C(9)	2229(4)	5886(3)	1554(3)
C(10)	1985(4)	5212(3)	556(3)
C(11)	2570(4)	4239(3)	533(3)
C(12)	3401(4)	3940(3)	1509(3)
C(13)	4525(3)	2699(3)	−474(4)
C(14)	4127(3)	2357(3)	−1595(4)
C(15)	2813(3)	1434(3)	−2201(4)
C(16)	1898(3)	853(3)	−1686(4)
C(17)	2297(3)	1195(3)	−565(4)
C(18)	3610(3)	2118(3)	41(4)
C(19)	3499(12)	−574(6)	1471(8)
C(20)	4323(12)	−390(6)	2611(8)
C(21)	3344(12)	−673(6)	3157(8)
C(22)	1916(12)	−1032(6)	2354(8)
C(23)	2011(12)	−971(6)	1312(8)
C(24)	1483(7)	1554(5)	1870(6)
C(25)	3957(7)	2060(5)	3856(7)
C(26)	5572(7)	2547(7)	4334(7)
C(27)	7668(8)	4347(9)	4922(8)
C(28)	3384(7)	2289(6)	4606(7)
C(29)	1848(8)	1817(7)	4425(8)
C(30)	129(8)	1957(9)	5199(8)
O(1)	458(5)	1849(5)	1518(5)
O(2)	6373(6)	1903(5)	4557(5)
O(3)	6092(4)	3813(4)	4503(4)
O(4)	865(6)	1001(6)	3726(5)
O(5)	1625(5)	2371(5)	5234(5)

technique. No significant decomposition of any of the crystals occurred during their respective data collections. Routine corrections were made for Lorentz and polarization effects [15] and for absorption. Relevant crystal data are summarized in Table 5.

Table 8

Non-hydrogen atom coordinates for $\overline{\mathrm{Ru\{C(CO_2Me)=C(CO_2Me)C(CO_2Me)=C}}\mathrm{H(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)}$ (**5**) (Ru × 10^5, others × 10^4)

Atom	x	y	z
Ru	47059(3)	8679(5)	20579(2)
P	5993(1)	188(2)	2638(1)
O(1)	4560(3)	234(6)	3774(2)
O(2)	5622(2)	1669(5)	4201(2)
O(3)	4076(4)	5752(6)	2786(3)
O(4)	4414(3)	4245(6)	3733(3)
O(5)	3056(3)	3491(7)	1423(3)
O(6)	3741(2)	5120(5)	1122(2)
O(7)	4440(3)	3127(6)	568(3)
O(8)	5709(3)	3392(6)	1177(3)
C(1)	3733(4)	408(9)	1025(4)
C(2)	3497(4)	155(8)	1568(4)
C(3)	3928(4)	−1092(8)	1987(4)
C(4)	4420(4)	−1570(8)	1714(4)
C(5)	4308(4)	−672(9)	1106(4)
C(6)	4805(3)	1843(7)	2987(3)
C(7)	4551(3)	3288(7)	2761(3)
C(8)	4419(4)	3319(7)	1996(3)
C(9)	5059(3)	3142(7)	1858(3)
C(10)	4959(4)	1171(8)	3685(3)
C(11)	5832(5)	1027(10)	4899(3)
C(12)	4342(4)	4526(9)	3090(4)
C(13)	4121(7)	5454(13)	4016(6)
C(14)	3659(4)	3945(7)	1488(3)
C(15)	3046(4)	5779(9)	598(4)
C(16)	5001(4)	3220(7)	1122(4)
C(17)	5770(5)	3332(11)	519(5)
C(18)	6711(2)	1716(4)	2921(2)
C(19)	6679(2)	2842(4)	3380(2)
C(20)	7210(2)	4033(4)	3608(2)
C(21)	7774(2)	4097(4)	3376(2)
C(22)	7807(2)	2971(4)	2918(2)
C(23)	7275(2)	1780(4)	2690(2)
C(24)	5783(2)	−1967(5)	3528(2)
C(25)	6015(2)	−2885(5)	4132(2)
C(26)	6761(2)	−2804(5)	4657(2)
C(27)	7275(2)	−1805(5)	4579(2)
C(28)	7043(2)	−887(5)	3975(2)
C(29)	6297(2)	−968(5)	3450(2)
C(30)	6578(3)	−2515(5)	2290(2)
C(31)	6757(3)	−3410(5)	1835(2)
C(32)	6623(3)	−2841(5)	1170(2)
C(33)	6309(3)	−1377(5)	961(2)
C(34)	6131(3)	−482(5)	1417(2)
C(35)	6265(3)	−1051(5)	2082(2)

Table 9

Selected bond distances and angles

Bond distances (Å)		Bond angles (deg)	
(a) $Ru\{(E)\text{-}C(CO_2Me)=CH(CO_2Me)\}(dppe)(\eta\text{-}C_5H_5)$ (**11**)			
Ru(1)–C(27)	2.24(1)	P(1)–Ru(1)–P(2)	85.1(1)
Ru(1)–C(28)	2.28(1)	P(1)–Ru(1)–C(32)	93.3(4)
Ru(1)–C(29)	2.28(1)	P(2)–Ru(1)–C(32)	92.2(5)
Ru(1)–C(30)	2.24(1)		
Ru(1)–C(31)	2.21(1)	Ru(1)–P(1)–C(1)	122.8(3)
Ru(1)–C(cp) (av.)	2.25	Ru(1)–P(1)–C(7)	115.5(3)
		Ru(1)–P(1)–C(26)	109.8(6)
Ru(1)–P(1)	2.271(4)	Ru(1)–P(2)–C(18)	123.4(3)
Ru(1)–P(2)	2.249(4)	Ru(1)–P(2)–C(19)	112.2(3)
		Ru(1)–P(2)–C(25)	111.8(6)
Ru(1)–C(32)	2.07(1)		
		Ru(1)–C(32)–C(33)	126(1)
P(1)–C(1)	1.83(1)	Ru(1)–C(32)–C(35)	114(1)
P(1)–C(7)	1.85(1)		
P(1)–C(26)	1.84(1)	C(33)–C(32)–C(35)	120(1)
P(2)–C(18)	1.83(1)	C(32)–C(33)–C(34)	124(1)
P(2)–C(19)	1.84(1)		
P(2)–C(25)	1.87(1)		
C(32)–C(33)	1.43(2)		
C(32)–C(35)	1.47(2)		
C(33)–C(34)	1.53(2)		
(b) $Ru\{(Z)\text{-}C(CO_2Me)=CH(CO_2Me)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)$ (**12a**)			
Ru(1)–C(19)	2.256(5)	P(1)–Ru(1)–C(24)	85.0(2)
Ru(1)–C(20)	2.250(7)	P(1)–Ru(1)–C(25)	94.7(2)
Ru(1)–C(21)	2.255(6)	C(24)–Ru(1)–C(25)	93.1(3)
Ru(1)–C(22)	2.263(7)		
Ru(1)–C(23)	2.264(8)	Ru(1)–P(1)–C(6)	119.8(2)
Ru(1)–C(cp) (av.)	2.258	Ru(1)–P(1)–C(12)	113.9(2)
		Ru(1)–P(1)–C(18)	113.5(1)
Ru(1)–C(24)	1.847(7)		
Ru(1)–P(1)	2.310(2)	Ru(1)–C(24)–O(1)	174.6(7)
Ru(1)–C(25)	2.080(8)	Ru(1)–C(25)–C(26)	114.7(6)
		Ru(1)–C(25)–C(28)	133.2(5)
P(1)–C(6)	1.822(4)		
P(1)–C(12)	1.837(4)	C(26)–C(25)–C(28)	111.5(7)
P(1)–C(18)	1.829(5)	C(25)–C(28)–C(29)	124.6(7)
O(1)–C(24)	1.151(8)		
C(25)–C(26)	1.49(1)		
C(25)–C(28)	1.37(1)		
C(28)–C(29)	1.46(1)		
(c) $Ru\{\overline{C(CO_2Me)=C(CO_2Me)C(CO_2Me)=}CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)$ (**5**)			
Ru(1)–C(1)	2.207(6)	P(1)–Ru(1)–C(6)	88.9(2)
Ru(1)–C(2)	2.219(6)	P(1)–Ru(1)–C(8)	117.7(2)
Ru(1)–C(3)	2.247(7)	P(1)–Ru(1)–C(9)	88.1(2)
Ru(1)–C(4)	2.225(7)	C(6)–Ru(1)–C(8)	64.6(2)
Ru(1)–C(5)	2.243(7)	C(6)–Ru(1)–C(9)	84.7(2)
Ru(1)–C(cp) (av.)	2.228		
		Ru(1)–P(1)–C(18)	119.0(1)
Ru(1)–P(1)	2.346(2)	Ru(1)–P(1)–C(29)	117.0(1)
		Ru(1)–P(1)–C(35)	111.5(2)

Table 9 (continued)

Bond distances (Å)		Bond angles (deg)	
Ru(1)–C(6)	2.060(6)		
Ru(1)–C(7)	2.663(6)	Ru(1)–C(6)–C(7)	100.4(4)
Ru(1)–C(8)	2.189(6)	Ru(1)–C(6)–C(10)	132.2(5)
Ru(1)–C(9)	2.194(6)	C(6)–C(7)–C(8)	104.7(5)
		C(6)–C(7)–C(12)	131.6(6)
P(1)–C(18)	1.833(4)	C(7)–C(8)–C(9)	117.7(6)
P(1)–C(29)	1.839(4)	C(7)–C(8)–C(14)	114.4(6)
P(1)–C(35)	1.835(4)	C(8)–C(9)–C(16)	122.3(6)
C(6)–C(7)	1.36(1)		
C(6)–C(10)	1.48(1)		
C(7)–C(8)	1.52(1)		
C(7)–C(12)	1.43(1)		
C(8)–C(9)	1.42(1)		
C(8)–C(14)	1.50(1)		
C(9)–C(16)	1.50(1)		

The structures were solved by normal heavy-atom methods and each refined by a full-matrix least-squares procedure based on F [15]. Phenyl atoms were refined as hexagonal rigid groups with individual isotropic thermal parameters in all three structures, in **11** and **12a** the cp rings were refined as pentagonal rigid groups, and the remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the models at their calculated positions. A weighting scheme, $w = k/[\sigma^2(F) + gF^2]$, was included for each model and the refinements continued until convergence. Final refinement details are listed in Table 5.

The absolute configuration of **11** could not be determined as there were no significant differences in the Friedel pairs included in the data set.

Scattering factors for neutral Ru (corrected for f' and f'') were from ref. 16 and values for the remaining atoms were those incorporated in SHELX [15].

Fractional atomic coordinates for non-hydrogen atoms are listed in Tables 6–8 and the numbering schemes used are shown in Fig. 1–3. Selected interatomic bond distances and angles are given in Table 9. Full lists of thermal parameters, hydrogen atom parameters, bond lengths and angles, and of the observed and calculated structure factors are available on request from the authors.

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