Cyclopentadienylruthenium Phosphine Complexes. Part 3.[1] Some Complexes Derived from 1-Alkynes: Molecular and Crystal Structure of the Cumulene Derivative $[Ru\{C(CF_3){:}C(H)C(CF_3){:}C{:}C{:}CH(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)]$

By **Michael I. Bruce,*** † **Richard C. F. Gardner, Judith A. K. Howard, F. Gordon A. Stone, Moira Welling,** and **Peter Woodward,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Reactions between $[RuX(PPh_3)_2(\eta\text{-}C_5H_5)]$ (X = H, Me, or CH_2Ph) and the alk-1-ynes RC_2H (R = CO_2Me, COMe, CF_3, or C_6F_5) have given products resulting from interaction of one, two, or three alkyne molecules per molecule of ruthenium complex. Methyl propiolate and the hydrido-compound afford the η^1-alkynyl complex $[Ru(C{:}CCO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)]$, the 1,3,4-$\eta^3$-buta-1,3-dienyl complex $[Ru\{C(CO_2Me){:}CHCH{:}CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)]$, and the 1,4,5-$\eta^3$-penta-1,3,4-trienyl complex $[Ru\{CH{:}C(CO_2Me)C(CO_2Me){:}C{:}CMe(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)]$. The methyl- and benzyl-ruthenium complexes give only the corresponding η^3-butadienyl complexes. Ethynyl methyl ketone and the methylruthenium complex afforded $[Ru\{C(COMe){:}CHC[C(O)Me]{:}CHMe\}(PPh_3)(\eta\text{-}C_5H_5)]$. The structure of the 1,3,4,5-tetraenyl complex $[Ru\{C(CF_3){:}C(H)C(CF_3){:}C{:}C{:}CHCF_3\}(PPh_3)(\eta\text{-}C_5H_5)]$, obtained from HC_2CF_3 and $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$, was determined by a single crystal *X*-ray study. This shows that the acetylenic fragments have joined head-tail, head-tail, tail-head, and that whereas the first carbon atom of the chain (head, carrying a CF_3 group) is directly bonded to the ruthenium atom, the other attachment is an η-interaction at the tail-tail juxtaposition. The whole unsaturated system, including the metal atom, is essentially planar.

The product $[Ru\{C(C_6F_5){:}CHCH{:}C(C_6F_5)CH{:}C(C_6F_5)C_6H_4PPh_2\}(\eta\text{-}C_5H_5)]$ from $HC_2C_6F_5$ and the hydride contains a 10-membered $RuPC_8$ heterocycle. Possible mechanisms for the formation of these complexes are discussed.

PREVIOUSLY [1,2] we have described the synthesis of the complexes $[RuX(PPh_3)_2(\eta\text{-}C_5H_5)]$ (X = H, Cl, Me, *etc.*), as well as reactions between the hydride and some disubstituted alkynes. A particular feature of the chemistry of these complexes is the ready loss of one of the tertiary phosphine ligands, and subsequent isolation of complexes containing alkenyl or butadienyl groups formed by insertion and oligomerisation of the alkyne. In this paper we give an account of the extension of these studies to reactions between the compounds $[RuX(PPh_3)_2(\eta\text{-}C_5H_5)]$ (X = H, Me, or CH_2Ph) and several monosubstituted alkynes.

RESULTS

Methyl propiolate.—Heating the hydride $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$ in 1,2-dimethoxyethane with excess of HC_2CO_2Me gave an orange solution from which three complexes were subsequently obtained in low yield. The first of these was readily identified as the σ-acetylide $[Ru(C_2CO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1), from analytical and spectroscopic evidence. Thus, the mass spectrum contains a parent ion cluster centred on *m/e* 774, which fragments by loss of OMe, CO_2Me, and PPh_3 groups. In the i.r. spectrum strong bands at 2 068 and 1 719 cm^{-1} can be assigned to $\nu(C\equiv C)$ and $\nu(CO)$, respectively, while the ^1H n.m.r. spectrum is relatively simple, containing three resonances at τ 2.85, 5.53, and 6.32, assigned to the PPh_3, C_5H_5, and CO_2Me protons, respectively.

A bis adduct, $[Ru\{C(CO_2Me){:}CHCH{:}CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)]$ was also isolated, for which structure (2) is favoured on the basis of the following evidence. Two strong i.r. bands at 1 703 and 1 671 cm^{-1} are assigned to $\nu(CO)$ vibrations, while in the ^1H n.m.r. spectrum, in addition to the anticipated aromatic, C_5H_5, and CO_2Me signals, three resonances at τ 5.28, 6.47, and 8.02 occur. These arise from the three vinylic protons, and comparison with the related products obtained from the methyl and benzyl complexes (see below) indicates that the two signals at τ 5.28 and 8.02 arise from H(a) and H(b), which are in a *cis* configuration [*J*(ab) 8.0 Hz]; H(b) is also coupled to phosphorus.

The third complex is a tris adduct, still retaining one tertiary phosphine ligand. The overall molecular formula $[RuH(ac)_3(PPh_3)(\eta\text{-}C_5H_5)]$ (ac = HC_2CO_2Me) is supported by the appearance of a parent-ion cluster centred on *m/e* 682. Around 1 700 cm^{-1} in the i.r., four strong bands occur, while the ^1H n.m.r. spectrum contains signals at τ 1.73, 2.75 (PPh_3), 5.02 (C_5H_5), 6.21, 6.31, 6.72 (all CO_2Me), and 9.12. The chemical shift of the lowest field signal is consistent with its assignment to an olefinic hydrogen attached to the α-carbon atom; it also exhibits a small coupling to phosphorus. The high-field signal, of relative intensity 3, also coupled to phosphorus, is assigned to a methyl group attached to a co-ordinated olefinic group. The formation of a methyl group from a terminal acetylene and metal hydride is unusual, and is discussed in more detail below. This feature severely restricts the possible structures of this complex, and in fact the spectroscopic data seem best accommodated by the η^2-allene structure (3). In a related complex, $[Fe\{COCH_2CH_2CH{:}C{:}CH_2\}(CO)(\eta\text{-}C_5H_5)]$

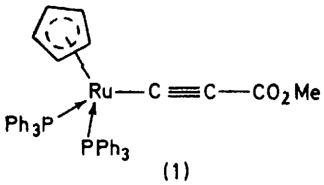
---

† *Present address*: Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001.

[1] Part 2, T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 106.

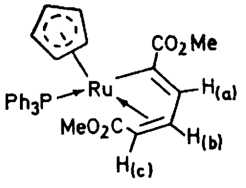
[2] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2376.

N.m.r. data [chemical shifts in τ (^1H) or p.p.m. upfield from $CFCl_3$(^{19}F); coupling constants in Hz]



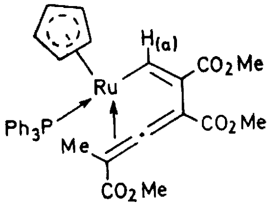
(1)

2.85m	Ph	
5.53s	C_5H_5	
6.32s	OMe	



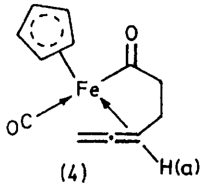
(2)

2.69m	Ph	J_{ab}	8.0
5.28m	H(a)	J_{bP}	12.7
5.66s	C_5H_5		
6.38s	OMe (both)		
6.47m	H(c)		
8.02m	H(b)		

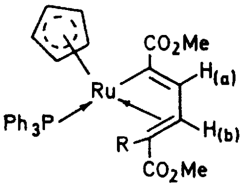


(3)

1.73d	H(a)	J_{aP}	3.3
2.75m	Ph	J_{MeP}	2.5
5.02s	C_5H_5		
6.21s	OMe		
6.31s	OMe		
6.72s	OMe		
9.12d	Me		



(4)



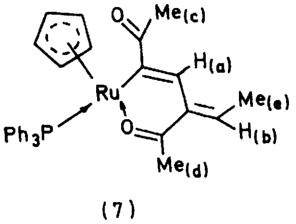
(5) R = Me
(6) R = CH_2Ph

R = Me

2.66m	Ph	J_{ab}	9.0
5.34s	C_5H_5	J_{aP}	1.0
5.45dd	H(a)	J_{bP}	11.0
7.57dd	H(b)		
6.37s	OMe		
6.51s	OMe		
7.83s	Me		

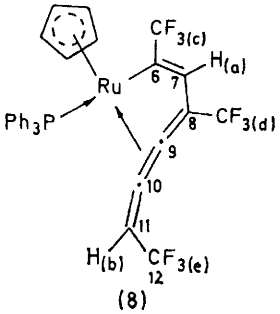
R = CH(c)H(d)Ph

2.62m	P*Ph*$_3$	J_{ab}	9.0
3.11m	CH_2*Ph*	J_{aP}	0
4.92d	H(c)	J_{bP}	11.0
5.46d	H(a)	J_{cd}	12.9
5.68s	C_5H_5		
6.35s	OMe		
6.48s	OMe		
6.96d	H(d)		
7.67dd	H(b)		



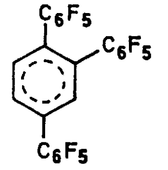
(7)

2.73m	Ph	J_{be}	7.0
3.38d	H(a)	J_{aP}	1.8
4.13q	H(b)	J_{dP}	2.5
5.69s	C_5H_5		
7.86s	Me(c)		
8.34d	Me(d)		
8.47d	Me(e)		

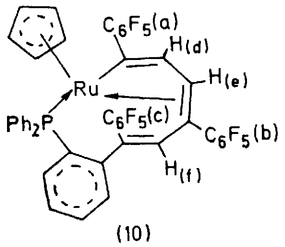


(8)

2.67m	Ph + H(a)	J_{aP}	4.0
4.72s	C_5H_5	J_{aF}	6.5
5.36dq	H(b)		
55.6s	CF_3(c)		
60.4t	CF_3(d)		
60.6m	CF_3(e)		



(9)



(10)

2.72m	Ph + H(f)	J_{ab}	8.6				
5.23dd	H(d)	J_{aP}	3.0				
5.36s	C_5H_5	J_{bP}	13.0				
7.36dd	H(e)						
137.9 155.8 163.3	C_6F_5(a)	140.5 159.1 164.2		C_6F_5 (b or c)	143.9 162.4 164.9	C_6F_5 (c or b)	

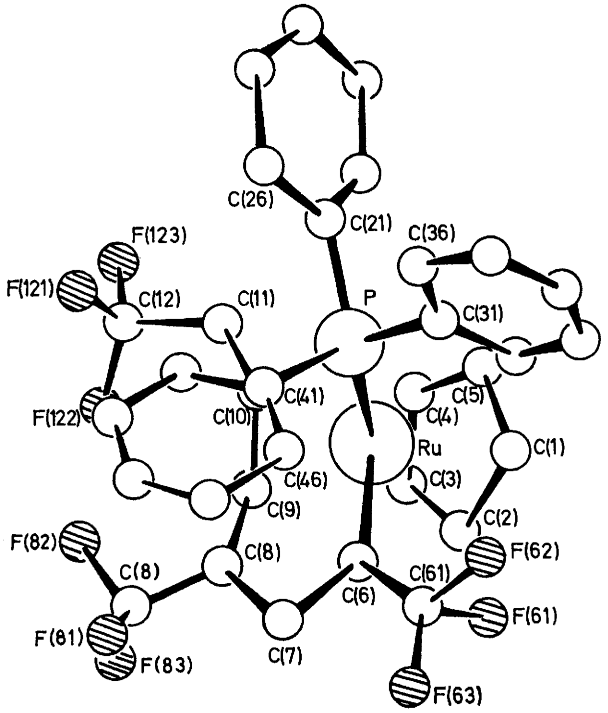
(4), an i.r. band at 1 750 cm^{-1} was assigned to the co-ordinated allene vibration.[3] In the ^{1}H n.m.r. spectrum of the iron complex, H(a) resonates at τ 5.9, while those of the terminal CH_2 group are found at τ 4.6 and 3.9. With the ruthenium complex, coupling of the methyl group to phosphorus suggests that the terminal allenic double bond is co-ordinated; while not conclusive, this feature also results in similar ring sizes for (3) and (4). The observation of this coupling also supports the idea that chelation occurs *via* the double bond rather than the ester carbonyl group.

In the reaction between $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ and HC_2CO_2Me, only the bis adduct (5) was isolated. The i.r. spectrum contained bands at 1 698 and 1 666 cm^{-1} [ν(CO)], and at 1 579 cm^{-1} [ν(C=C)]. In the ^{1}H n.m.r. spectrum signals at τ 2.66 (PPh_3), 5.34 (C_5H_5), 6.37 and 6.51 (CO_2Me) were accompanied by others at 5.45, 7.57, and 7.83. The latter, a singlet of intensity 3, was assigned to the methyl group originally attached to the ruthenium, which has now migrated to an olefinic carbon. The remaining two resonances arise from the two protons, H(a) and H(b), coupled together and also to phosphorus; the magnitude of the coupling constant J_{ab} (9.0 Hz) indicates that they are in a *cis* configuration, and that the olefinic bond is co-ordinated to the metal. It is not possible to determine whether the methyl group is *cis* or *trans* to H(b), although the latter seems more likely since in previous examples the two acetylene molecules have added in the *cis* configuration.

The analogous product (6) obtained from $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$ was also studied. The i.r. spectrum contains bands at 1 704 and 1 682 cm^{-1} [ν(CO)] and at 1 574 cm^{-1} [ν(C=C)], and in the mass spectrum the parent ion (cluster around *m/e* 688) fragments by loss of OMe, CO_2Me, C_7H_7, and PPh_3 groups. The ^{1}H n.m.r. spectrum is very similar to that of (5), containing the usual signals at τ 2.62 (PPh_3), 3.11 (CH_2Ph), 5.68 (C_5H_5), 6.35 and 6.48 (CO_2Me). Protons H(a) and H(b) resonate at τ 5.46 and 7.67, each showing a 9 Hz coupling to the other, with H(b) also coupled to phosphorus. Of some interest is the high degree of asymmetry about the benzylic methylene group, the two protons appearing at τ 4.92 and 6.96, with the separation of 204 Hz being larger than that found for $[Ru\{C(CO_2Me){:}C(CH_2Ph)C(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)]$.[4]

Ethynyl Methyl Ketone (*But-3-yn-2-one*).—The methyl complex $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ reacts with HC_2COMe to form the bis adduct $[RuMe(ac)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (7) (ac = HC_2COMe) as the only product isolated. The formula was established by analysis and the mass spectrum, which contains a parent ion at *m/e* 580, and other major ions formed by loss of COMe and PPh_3 groups.

The i.r. spectrum contains bands assigned to unco-ordinated and co-ordinated carbonyl groups at 1 668 and 1 606 cm^{-1}, respectively, and to ν(C=C) at 1 576 cm^{-1}. In the ^{1}H n.m.r. spectrum a single proton at τ 4.13 is coupled to the methyl group resonating at τ 8.47, and must be *gem* to it. Two other methyl groups give rise to signals at τ 7.86(s) and 8.34(d); the coupling of the latter to phosphorus suggests that it is attached to the co-ordinated acyl group. A signal at τ 3.38, with a 1.8 Hz coupling to phosphorus, can be assigned to a vinylic proton on a β-carbon (compare the cyclic adduct $[Ru\{C(CO_2Me){:}CHC(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)]$, in which the corresponding proton resonates at τ 3.89, and has J(HP) 2.5 Hz.[1]



Molecular structure of complex (8)

The data are consistent with structure (7), in which a *trans*-butadienyl moiety is chelated to ruthenium *via* a metal–carbon σ bond, and the acyl ketonic group. The methyl group originally bonded to the metal is now located on the exocyclic group. Again, the geometry about this group cannot be determined unequivocally, although mechanistic considerations suggest the isomer shown (see Scheme 2, below). Of interest is the small coupling of Me(d) to phosphorus, extending over five bonds, and not observed in OMe groups similarly situated.

3,3,3-*Trifluoropropyne*.—The reaction between $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ and HC_2CF_3 at 120 °C affords an orange crystalline complex characterised as the methyl-free tris adduct $[Ru\{(tfac)_3{-}H\}(PPh_3)(\eta\text{-}C_5H_5)]$ [(8), tfac = HC_2CF_3]. The spectroscopic data for this complex did not establish the molecular structure so a single crystal *X*-ray diffraction study was undertaken.

The *X*-ray analysis (Tables 1—3) establishes that the molecule has the overall configuration shown in the Figure. The ruthenium atom adopts a distorted

---

[3] J. L. Roustan and P. Cadiot, *Compt. rend.*, 1969, **268C**, 734; J. Benaim, J. Y. Mérour, and J. L. Roustan, *Tetrahedron Letters*, 1971, 983; J. L. Roustan, J. Benaim, C. Charrier, and J. Y. Mérour, *ibid.*, 1972, 1953.

[4] M. I. Bruce, R. C. F. Gardner, and F. G. A. Stone, *J. Organometallic Chem.*, 1972, **40**, C39.

TABLE 1

Atomic positional (fractional co-ordinates) and thermal parameters with estimated standard deviations in parentheses

Atom	x	y	z	10^2U/Å^2 *
Ru	0.210 83(9)	0.113 47(7)	0.327 16(6)	†
P	0.176 9(3)	0.222 1(2)	0.208 3(2)	†
Phenyl rings				
C(21)	0.222 0(11)	0.357 5(9)	0.235 0(7)	3.5(3)
C(22)	0.215 7(13)	0.408 3(11)	0.301 0(9)	5.6(4)
C(23)	0.245 5(14)	0.513 9(12)	0.323 2(10)	6.4(5)
C(24)	0.279 2(13)	0.569 6(12)	0.275 0(9)	5.9(4)
C(25)	0.287 8(14)	0.520 2(13)	0.209 4(10)	6.9(5)
C(26)	0.260 4(14)	0.416 5(12)	0.190 2(9)	6.2(4)
H(22)	0.186	0.370	0.335	5.0
H(23)	0.250	0.549	0.377	5.0
H(24)	0.297	0.647	0.288	5.0
H(25)	0.318	0.563	0.175	5.0
H(26)	0.277	0.380	0.143	5.0
C(31)	1.043 0(12)	0.247 1(9)	0.121 2(7)	3.8(3)
C(32)	0.959 1(14)	0.215 8(12)	0.131 3(10)	6.1(4)
C(33)	0.860 0(16)	0.232 5(14)	0.065 6(11)	7.8(5)
C(34)	0.845 2(15)	0.287 1(13)	−0.011 4(10)	6.7(5)
C(35)	0.922 3(15)	0.322 8(12)	−0.022 3(10)	6.4(4)
C(36)	1.029 9(14)	0.301 2(12)	0.048 4(10)	6.2(4)
H(32)	0.970	0.177	0.186	5.0
H(33)	0.801	0.210	0.070	5.0
H(34)	0.780	0.300	−0.058	5.0
H(35)	0.912	0.360	−0.073	5.0
H(36)	1.084	0.323	0.042	5.0
C(41)	0.241 6(11)	0.170 4(9)	0.147 5(7)	3.5(3)
C(42)	0.183 4(12)	0.105 1(11)	0.075 2(8)	4.8(4)
C(43)	0.236 8(13)	0.055 0(11)	0.036 8(9)	5.6(4)
C(44)	0.337 4(14)	0.069 9(12)	0.068 6(9)	5.9(4)
C(45)	0.395 9(13)	0.135 4(12)	0.137 6(9)	5.9(4)
C(46)	0.345 4(13)	0.187 5(10)	0.179 3(8)	4.7(4)
H(42)	0.107	0.094	0.050	5.0
H(43)	0.200	0.005	−0.015	5.0
H(44)	0.379	0.032	0.040	5.0
H(45)	0.475	0.149	0.162	5.0
H(46)	0.387	0.237	0.230	5.0
Cyclopentadienyl ring				
C(1)	0.072 2(14)	0.102 8(13)	0.351 1(9)	6.5(5)
C(2)	0.143 3(13)	0.021 5(12)	0.395 1(9)	5.7(4)
C(3)	0.234 5(13)	0.065 2(12)	0.458 2(9)	5.7(4)
C(4)	0.221 5(13)	0.173 7(11)	0.452 5(9)	5.5(4)
C(5)	0.124 4(14)	0.196 5(12)	0.387 5(10)	5.9(5)
H(1)	0.001	0.097	0.301	5.0
H(2)	0.127	−0.056	0.383	5.0
H(3)	0.303	0.026	0.500	5.0
H(4)	0.278	0.227	0.492	5.0
H(5)	0.096	0.270	0.371	5.0
Unsaturated ring				
C(6)	0.818 4(12)	0.481 7(10)	0.254 9(8)	4.2(4)
C(7)	0.735 6(13)	0.428 3(10)	0.247 8(8)	4.8(4)
C(8)	0.639 1(13)	0.476 7(10)	0.191 1(8)	4.6(4)
C(9)	0.647 7(12)	0.563 4(11)	0.152 8(8)	5.0(4)
C(10)	0.635 1(11)	0.661 8(10)	0.119 2(7)	3.8(3)
C(11)	0.574 6(13)	0.741 2(11)	0.077 4(9)	5.6(4)
H(7)	0.738	0.360	0.279	5.0
H(11)	0.610	0.801	0.066	5.0
Trifluoromethyl groups				
C(61)	0.915 6(15)	0.435 7(13)	0.312 1(10)	6.4(5)
F(61)	0.978 2(11)	0.413 4(14)	0.280 1(8)	†
F(62)	0.018 1(11)	0.490 6(11)	0.376 6(10)	†
F(63)	0.925 8(11)	0.353 1(11)	0.353 6(12)	†
C(81)	0.545 2(18)	0.428 7(16)	0.180 6(13)	8.9(7)
F(81)	0.542 4(10)	0.399 9(13)	0.249 5(7)	†
F(82)	0.465 0(11)	0.502 7(14)	0.152 4(11)	†
F(83)	0.492 9(13)	0.370 2(14)	0.115 9(10)	†
C(12)	0.461 7(17)	0.742 7(15)	0.043 2(12)	8.4(6)
F(121)	0.434 1(10)	0.772 1(18)	0.099 2(9)	†
F(122)	0.416 4(9)	0.653 2(12)	0.012 2(10)	†
F(123)	0.413 3(11)	0.805 7(15)	−0.022 2(11)	†

TABLE 1 (*Continued*)

Atom	U_{11}	U_{22}	U_{33}
Ru	3.35(10)	3.60(5)	3.21(5)
P	3.1(3)	3.5(2)	2.5(2)
F(61)	16(2)	34(2)	11(2)
F(62)	10(1)	13(1)	20(2)
F(63)	11(1)	14(1)	30(2)
F(81)	11(1)	27(2)	9(8)
F(82)	9(1)	20(2)	22(2)
F(83)	19(2)	27(2)	18(1)
F(121)	4(1)	42(3)	13(1)
F(122)	4(1)	17(1)	21(1)
F(123)	8(1)	24(2)	20(2)
Atom	U_{12}	U_{13}	U_{23}
Ru	−0.13(6)	1.59(4)	−0.14(4)
P	−0.0(2)	1.3(2)	−0.2(1)
F(61)	22(2)	9(2)	15(2)
F(62)	6(1)	−6(1)	−2(1)
F(63)	5(1)	8(1)	17(1)
F(81)	−10(1)	4(1)	2(1)
F(82)	−6(1)	9(1)	−0(1)
F(83)	−17(2)	13(1)	−15(1)
F(121)	4(1)	3(1)	−10(2)
F(122)	−1(1)	5(1)	−5(1)
F(123)	6(1)	1(1)	12(1)

* $B = 8\pi^2U$. † Anisotropic thermal parameters in the form: $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$, with parameters (× 10^2).

TABLE 2

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances	
Ru–P	2.335(3)
Ru–C (cyclopentadienyl) mean	2.24(1)
C–C (cyclopentadienyl) mean	1.39(1)
Ru–C(6)	2.11(1)
Ru–C(9)	2.05(2)
Ru–C(10)	2.09(1)
P–C(21)	1.83(1)
P–C(31)	1.84(1)
P–C(41)	1.86(2)
C–C (phenyl) mean	1.39(1)
C(6)–C(7)	1.35(2)
C(7)–C(8)	1.42(2)
C(8)–C(9)	1.33(2)
C(9)–C(10)	1.36(2)
C(10)–C(11)	1.31(2)
C(11)–C(12)	1.47(3)
C(6)–C(61)	1.42(2)
C(8)–C(81)	1.44(3)
C–F (trifluoromethyl) mean	1.30(1)
(*b*) Angles	
P–Ru–C(6)	89.2(4)
C(6)–Ru–C(9)	73.9(6)
C(9)–Ru–C(10)	38.3(5)
C(10)–Ru–P	86.6(4)
Ru–C(6)–C(61)	127.5(13)
Ru–C(6)–C(7)	117.4(9)
C(61)–C(6)–C(7)	114.8(13)
C(6)–C(7)–C(8)	113.8(13)
C(7)–C(8)–C(81)	118.8(14)
C(7)–C(8)–C(9)	113.6(16)
C(81)–C(8)–C(9)	127.5(14)
C(8)–C(9)–C(10)	163.3(20)
C(8)–C(9)–Ru	120.9(11)
C(9)–C(10)–C(11)	149.9(17)
C(9)–C(10)–Ru	69.1(9)
C(11)–C(10)–Ru	141.0(14)
C(10)–C(11)–C(12)	124.5(17)
C–C–F (trifluoromethyl) mean	117.0(2)
F–C–F (trifluoromethyl) mean	100.7(2)
Ru–P–C(21)	116.1(4)
Ru–P–C(31)	121.0(6)
Ru–P–C(41)	110.3(4)
C(21)–P–C(31)	99.2(5)
C(31)–P–C(41)	103.6(6)
C(41)–P–C(21)	104.8(7)

TABLE 3

Equations of some least-squares planes; distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Ru, C(6), C(7), C(8), C(9)

$$-3.372x + 8.384y + 12.862z = 4.417$$

[Ru 0.03; C(6) 0.14; C(7) −0.13; C(8) −0.13; C(9) 0.08]

Plane (2): Ru, C(6), C(61), C(7), C(8), C(81), C(9), C(10), C(11), C(12)

$$-2.890x + 7.217y + 13.848z = 4.517$$

[Ru 0.22; C(6) 0.12; C(61) 0.32; C(7) −0.13; C(8) −0.29; C(81) −0.48; C(9) −0.21; C(10) 0.09; C(11) 0.23; C(12) 0.12]

Plane (3): Ru, C(8), C(81), C(9), C(10), C(11), C(12)

$$-1.052x + 6.210y + 13.857z = 4.912$$

[Ru 0.10; C(8) 0.01; C(81) −0.31; C(9) 0.02; C(10) 0.20; C(11) 0.15; C(12) −0.17]

octahedral configuration, three co-ordination sites being occupied by the cyclopentadienyl ring and one by the triphenylphosphine group. Of the two remaining sites, one is occupied by the terminal carbon atom of a chain formed by oligomerisation of three acetylenic moieties, and this carbon atom carries a CF_3 group (which may be regarded as the ' head ' of the alkyne). The bonding sequence is then head-tail, head-tail, tail-head, and an η-bond from the two adjacent tail-carbon atoms to the ruthenium atom occupies the sixth co-ordination site. The acetylenic skeleton of the molecule is nearly planar (Table 3); indeed, the chelated ring portion Ru, C(6—9) gives a deviation from planarity ($= [(\Sigma\delta)^2/(n-1)]^{\frac{1}{2}}$) of only 0.12 Å. If the whole of the acetylenic chain, including the C atoms of the CF_3 groups, is incorporated, the deviation is still only 0.26 Å; whereas the deviation for the η^2-bonded portion [Ru, C(8), C(81), C(9), C(10), C(11), and C(12)] is 0.18 Å. There is in fact a slight twist at C(9) which brings the two planar sections of the molecule within less than 10° of one another. As would be expected from consideration of the bonding situation, the formalised description of the sequence C(8), C(9), C(10), C(11) as successive double bonds does not imply linearity; C(10)–C(11) and C(8)–C(9) both bend away from the metal to which C(9)–C(10) is bonded. The geometry of the CF_3 groups, the triphenylphosphine ligand, and the cyclopentadienyl ring show no unusual features, but, as is often observed in similar compounds, the F–C–F angles of the CF_3 groups are significantly less than the ideal tetrahedral value.

The structure determination enables most of the spectroscopic data to be satisfactorily rationalised. Thus, the i.r. spectrum contains a medium band at 1 590 cm^{-1}, assigned to ν(C⁚C), while strong bands in the 1 200—1 300 cm^{-1} region arise from the fluorocarbon groups. In the ^1H n.m.r. spectrum, signals at τ 4.72(s) and 5.36(dq) are readily assigned to the cyclopentadienyl protons and the cumulene proton H(b), while integration of the broad band at τ 2.67 suggests that the resonance of the vinylic proton attached to C(7) lies under those of the aromatic protons.

The ^{19}F n.m.r. spectrum contains three resonances at 55.6(s), 60.4(m), and 60.6(m) p.p.m. The singlet is assigned to CF_3(c) attached to C(6), and double irradiation experiments show that H(b) is coupled to the *gem*-CF_3(e) on C(11), allowing the third band to be assigned to CF_3(d). The mass spectrum of (8) contains a parent ion at *m/e* 710, which fragments by loss of F or CF_3.

Relatively few examples of mononuclear η-cumulene complexes are known, and structurally characterised. The reaction between $Fe_2(CO)_9$ and tetraphenylbutatriene affords $[Fe(CO)_4(Ph_2C{:}C{:}C{:}CPh_2)]$ and $[Fe_2(CO)_6(Ph_2C{:}C{:}C{:}CPh_2)]$,[5] and the crystal structure of the former complex has been determined.[6] The iron atom is co-ordinated to the central bond of the cumulene system, and the four carbon atoms of the triene are no longer collinear. A similar feature is present in (8), the two ' outer ' double bonds being bent away from the metal by 19 and 29°. In the iron complex, no differences are found in the C=C distances. The bending of substituents away from the metal is a common feature of complexes containing electron-deficient olefins or acetylenes η^2-bonded to electron-rich metal centres,[7] and the theoretical basis for this effect has also been extensively discussed.[7g,8] The closest parallels to the present case are the η^2-allene derivatives $[M(C_3H_4)(PPh_3)_2]$ (M = Pd [9a] or Pt [9b]), the dimethylallene complex $[Pt(H_2C_3Me_2)(PPh_3)_2]$ [10] and the carbon disulphide complexes $[M(SCS)(PPh_3)_2]$ (M = Pd [11] or Pt [12]). In all cases, the two double-bond systems are no longer collinear, and in the S⁚C⁚S complexes, the geometry has been likened to that of the first excited state of the neutral molecule.[8c]

The fact that the central double bond is η^2-bonded to the metal contrasts with the structures of $[Ru\overline{\{C(E){:}C(E)C(CF_3){:}C}(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)]$ (E = CF_3 [13] or CO_2Me [14]), and is in accord with our suggestion (above) that it is the terminal double bond in (3) that is attached to the metal. Of course, in the butadienyl complexes, there is no alternative site for attachment to

---

[5] K. K. Joshi, *J. Chem. Soc.* (*A*), 1966, 598.

[6] D. Bright and O. S. Mills, *J. Chem. Soc.* (*A*), 1971, 1979.

[7] See for example: (*a*) J. N. Francis, A. McAdam, and J. A. Ibers, *J. Organometallic Chem.*, 1971, **29**, 131; (*b*) A. McAdam, J. N. Francis, and J. A. Ibers, *J. Organometallic Chem.*, 1971, **29**, 149; (*c*) B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Canad. J. Chem.*, 1972, **50**, 2276; (*d*) L. J. Guggenberger, *Inorg. Chem.*, 1973, **12**, 499; (*e*) B. W. Davies and N. C. Payne, *Inorg. Chem.*, 1974, **13**, 1843; (*f*) B. W. Davies and N. C. Payne, *Inorg. Chem.*, 1974, **13**, 1848; (*g*) J. A. McGinnety, *J.C.S. Dalton*, 1974, 1038.

[8] (*a*) E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879; (*b*) A. C. Blizzard and D. P. Santry, *J. Amer. Chem. Soc.*, 1968, **90**, 5749; (*c*) R. McWeeny, R. Mason, and A. D. C. Towl, *Discuss. Faraday Soc.*, 1969, **47**, 20; (*d*) Lj. Manojlović-Muir, K. W. Muir, and J. A. Ibers, *Discuss. Faraday Soc.*, 1969, **47**, 84; (*e*) N. Rösch and R. Hoffmann, *Inorg. Chem.*, 1974, **13**, 2656.

[9] (*a*) K. Okamoto, Y. Kai, N. Yasuoka, and N. Kasai, *J. Organometallic Chem.*, 1974, **65**, 427; (*b*) M. Kadonaga, N. Yasuoka, and N. Kasai, *Chem. Comm.*, 1971, 1597.

[10] N. Yasuoka, M. Morita, Y. Kai, and N. Kasai, *J. Organometallic Chem.*, 1975, **90**, 111.

[11] T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, and M. Kakudo, *Bull. Chem. Soc. Japan*, 1967, **40**, 1998.

[12] R. Mason and A. I. M. Rae, *J. Chem. Soc.* (*A*), 1970, 1767.

[13] T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis, and A. Garza, *Chem. Comm.*, 1971, 852.

[14] L. E. Smart, *J.C.S. Dalton*, 1976, 390.

the metal, and the hydrocarbon chain is somewhat distorted. In the allene or cumulene systems, the π-electron systems of each double bond are orthogonal. Thus, if the skeleton of the $RuCH{\vdots}C(CO_2Me)C(CO_2Me)$ system in (3) is coplanar it will be the lobes of the π-orbitals of the terminal double bond of the allene system that will be pointing directly at the metal atom, and thus in the most favourable position for interaction with the metal. Similarly, in (8), it is the central double bond of the cumulene system that is so placed. However, the formation of the cyclic system still results in some distortion in the hydrocarbon chain.

Complex (8) is the first example of such a highly unsaturated system to be described, and represents a new type of acetylene-trimerisation reaction. A possible mechanism for its formation is discussed below.

Pentafluorophenylacetylene.—In refluxing 1,2-dimethoxyethane, the reaction between $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$ and $HC_2C_6F_5$ afforded two products. The first, a white solid, was readily identified as a trimer of the acetylene, *viz*. 1,2,4-$C_6H_3(C_6F_5)_3$ (9), from its mass spectrum (parent ion at *m/e* 576), and the ^{19}F n.m.r. spectrum, which was complex, containing three sets of characteristic 2 : 1 : 2 resonances, and indicating the asymmetric 1,2,4-isomer. The formation of this isomer is not unexpected, the usual trimerisation product obtained from non-fluorinated acetylenes, and from HC_2CF_3, having this geometry.

The mass spectrum of the second product, obtained in only 3% yield, contains a parent-ion cluster centred on *m/e* 1 004. We tentatively propose that this orange complex is the unusual tris adduct (10), containing an *ortho*-substituted $C_6H_4PPh_2$ group. In the i.r. spectrum, a band at 1 099 cm^{-1} is typical of this group, and bands at 1 649 [$\nu(C{\vdots}C)$] and 1 520 cm^{-1} (C_6F_5) are also present.

The ^1H n.m.r. spectrum contains a singlet at τ 5.36 (C_5H_5), and two double doublets at τ 5.23 and 7.36, assigned to H(d) and H(e). These protons are coupled to each other, and to phosphorus. The third proton H(f) probably lies below the extended multiplet arising from the aromatic protons around τ 2.72. Some evidence for this comes from double-irradiation experiments, which alters the profile of this signal, and from the integration which gives a total intensity of 15. Proton H(e) possesses the typical high-field shift of a hydrogen attached to a co-ordinated double bond, and also exhibits coupling to phosphorus. The ^{19}F n.m.r. spectrum contains nine signals arising from the *ortho*, *meta*, and *para* fluorines of three different C_6F_5 groups. Individual resonances were related by double-irradiation experiments, and we suggest that the group with the lowest chemical shift is attached to the carbon σ-bonded to the metal.

The above spectroscopic data are accommodated by structure (10), in which the central double bond of the trimerised acetylene is co-ordinated to ruthenium. The acyclic trimer is η-bonded to the metal, and to the *ortho*-position of one of the aryl groups of the remaining tertiary phosphine ligand, to form an unusual benzophospharutheniacyclodecatetraene system.

DISCUSSION

The nature of the complexes formed when alkynes interact with transition-metal complexes depends on both the alkyne and metal components.[15] The mechanisms of these reactions are now generally considered to involve initial formation of an η^2-alkyne–metal complex (alternatively considered to be a ' metallacyclopropene ' system), followed by ' insertion ' of the co-ordinated alkyne into a metal–hydrogen or metal–carbon σ bond if present, or by combination of the co-ordinated alkyne with a second molecule of alkyne, which may or may not be first co-ordinated. In some cases (alk-1-ynes), the metal–carbon σ bond may be formed by oxidative addition of the alkyne to the metal centre to form a metal acetylide.

An alternative proposal for alkynes with electron-withdrawing groups involves the initial formation of a dipolar intermediate, which may then react further, either intra- or inter-molecularly, to give the observed products.[1,16]

The formation of the η^1-acetylide (1) by the reaction

$$[L_nRu\text{-}H] + H\text{-}C{\vdots}C\text{-}CO_2Me \xrightarrow{-H_2} [L_nRu\text{-}C{\vdots}C\text{-}CO_2Me]$$

has a precedent in reactions between CF_3C_2H and some platinum(II) complexes,[17] and in the present work may proceed *via* initial oxidative-addition of the alk-1-yne to form an unstable dihydridoruthenium(IV) complex, followed by reductive-elimination of dihydrogen.

Discussion of the mode of oligomerisation of an unsymmetrical alkyne may be simplified by the ' head-tail ' notation in which for an alk-1-yne RC_2H the head (h) end bears the substituent R, and the tail (t) end, the proton. The bis adduct (2) can thus be described as containing the (h–t, t–h) dimer, and its formation is shown in Scheme 1, where the essential step is addition of the second alkyne to the intermediate (A). Similar reactions occur between HC_2CO_2Me and the methyl- and benzyl-ruthenium complexes to give (5) and (6) respectively, and between HC_2COMe and $[RuMe(PPh_3)_2(C_5H_5)]$ to give (7). It is noteworthy that the six-membered $RuOC_4$ ring in (7) is preferred to the usual 1,3,4-η^3-butadienyl group.

The formation of the tris adduct (3), containing the η^2-allenyl system [essentially a (t–h, h–t, t–h) trimer] is also shown in Scheme 1. Oxidative-addition of a second molecule of alkyne to the vinyl derivative (B) is followed by coupling of the vinyl and acetylide residues to give intermediate (C). Similar coupling of two phenylacetylene molecules on $[RhCl(PPh_3)_3]$ has been described

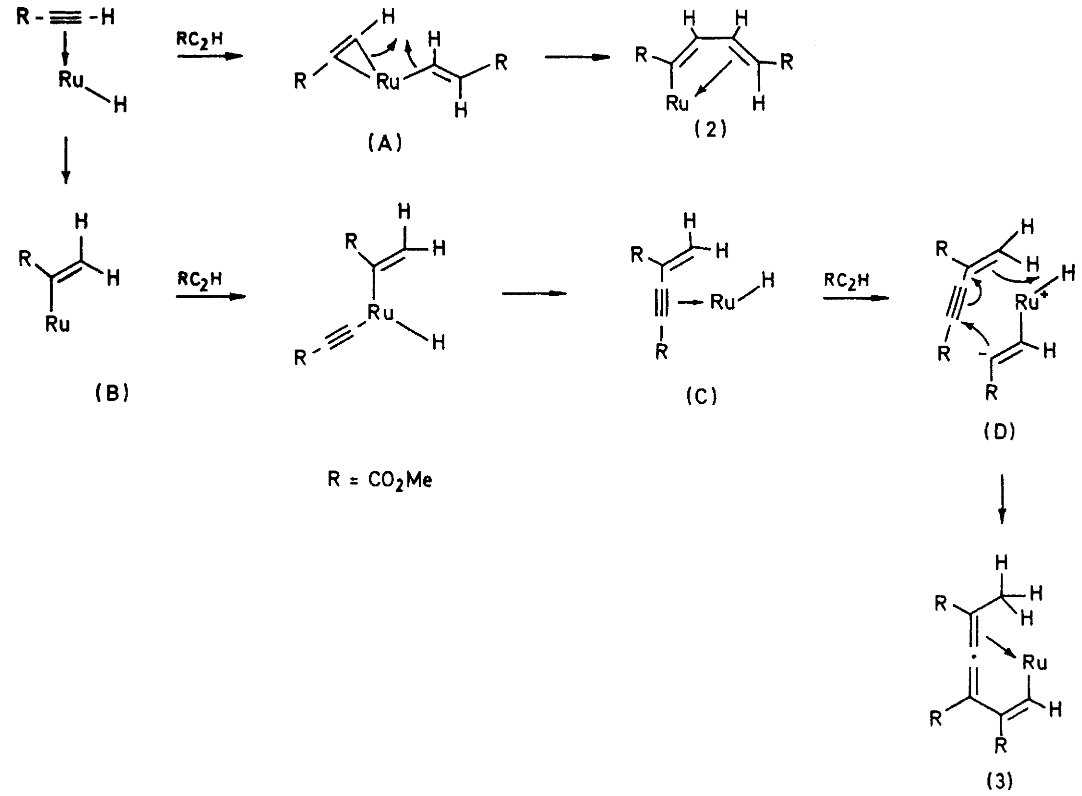
---

[15] (*a*) W. Hubel, in I. Wender and P. Pino, eds., ' Organic Synthesis *via* Metal Carbonyls,' Interscience, New York, 1968, p. 273; (*b*) F. L. Bowden and A. B. P. Lever, *Organometallic Chem. Rev.*, 1968, **3**, 227; (*c*) F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799; (*d*) P. M. Maitlis, *Pure Appl. Chem.*, 1972, **30**, 427; 1973, **33**, 489; (*e*) L. P. Yur'eva, *Usp. Khim.*, 1974, **43**, 95; *Russ. Chem. Rev.*, 1974, **43**, 48; (*f*) S. Otsuka and A. Nakamura, *Adv. Organometallic Chem.*, 1976, **14**, 245.

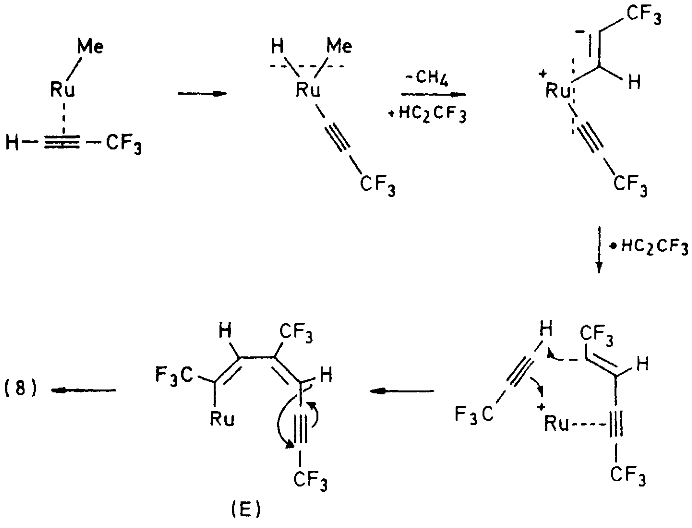
[16] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970 2981.

[17] T. G. Appleton, H. C. Clark, and R. J. Puddephatt, *Inorg. Chem.*, 1972, **11**, 2074.

previously.[18] In the present instance the vinylacetylene intermediate may remain co-ordinated to ruthenium, either *via* carbon–carbon unsaturation, or *via* the ester carbonyl group. The third molecule of alkyne reacts with the vinylalkyne as in (D) to give the observed product.



Scheme 1



Scheme 2

The formation of the cumulenyl complex (8), containing an (h–t, h–t, t–h) trimer of the alkyne, is shown in Scheme 2. Oxidative-addition of the alkyne to the ruthenium alkyl, with concomitant reductive-elimination of methane, affords the η^1-acetylide. Reaction with two further molecules of alkyne forms the diene-yne intermediate (E) as shown, which then undergoes a 1,3-hydrogen shift to give complex (8). The observed stereochemistry suggests that the hydrogen shift occurs *via* the metal atom, and it is possible that one reason for the formation of the cumulene system is that chelation by η-bonding to C(9)–C(10) [which is also found in the methyl propiolate derivative (3)], rather than to C(8)–C(9) or to C(10)–C(11), is sterically favoured.

We have reported previously the pronounced tendency of complexes containing the $Ru(PPh_3)(C_5H_5)$ group to enter into *ortho*-metallation reactions,[4,19,20] and a reaction between $[Ru(C_6H_4PPh_2)(PPh_3)(C_5H_5)]$ (11) and $C_2(CF_3)_2$ to give $[Ru\{[C(CF_3){:}C(CF_3)]_2C_6H_4PPh_2\}(PPh_3)(C_5H_5)]$.[19] Similar reactions can account for the formation of (10), and in this connection it is of interest to note the formation of the *ortho*-metallated complex $[Pt\{C(CO_2Me){:}CH(CO_2Me)\}(C_6H_4PPh_2)(PPh_3)]$ by pyrolysis of $[Pt\{\eta^2\text{-}C_2(CO_2Me)_2\}(PPh_3)_2]$.[21]

---

[18] R. J. Kern, *Chem. Comm.*, 1968, 706.

[19] M. I. Bruce, R. C. F. Gardner, and F. G. A. Stone, *J.C.S. Dalton*, 1976, 81.

[20] M. I. Bruce, R. C. F. Gardner, B. L. Goodall, F. G. A. Stone, R. J. Doedens, and J. A. Moreland, *J.C.S.'Chem.Comm.*, 1974, 185.

[21] H. C. Clark and K. E. Hine, *J. Organometallic Chem.*, 1976, **105**, C32.

EXPERIMENTAL

Spectra were obtained with Perkin-Elmer 257 or 457 (i.r.), Varian Associates HA100 (^{1}H n.m.r., at 100 MHz; ^{19}F n.m.r., at 94.1 MHz), or AEI–GEC MS902 (mass) instruments. The latter operated with 70 eV * ionising energy, 8 kV accelerating potential, 150 μA trap current, and a source temperature of *ca.* 150 °C. ^{19}F N.m.r. chemical shfts are relative to CCl_3F (0.0 p.p.m.), positive values indicating a shift to high field.

Solvents were dried and distilled before use, and all reactions were carried out under nitrogen. Light petroleum was a fraction b.p. 40—60 °C. Chromatography was carried out on columns of Florisil (column F) or alumina (BDH chromatography grade, used as received) (column A), initially packed in light petroleum. Carius tubes were evacuated and cooled to −196 °C, before sealing. Analytical data for the new compounds are given in Table 4.

TABLE 4

M.p. and analytical data

Complex [a]	M.p.(θ_c/°C)	Found (calc.)/% C	H	Molecular weight [b]
$[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$	127—132	72.9	5.5	690
	decomp.	(73.5)	(5.4)	(690)
$[Ru(C_2CO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1)		69.5	4.7	774
		(69.7)	(4.9)	(774)
$[RuH(HC_2CO_2Me)_3(PPh_3)(\eta\text{-}C_5H_5)]$ [c] (3)	188—191	61.6	4.9	682
		(61.7)	(4.9)	(682)
$[RuMe(HC_2CO_2Me)_2(PPh_3)(\eta\text{-}C_5H_5)]$ [d] (5)	168—170	62.9	5.3	
		(62.9)	(5.1)	
$[Ru(CH_2Ph)(HC_2CO_2Me)_2(PPh_3)(\eta\text{-}C_5H_5)]$ [e] (6)	177—180	66.4	5.3	688
		(66.5)	(5.2)	(688)
$[RuMe(HC_2COMe)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (7)	135—138	66.5	5.5	580
		(66.5)	(5.4)	(580)
$[Ru(HC_2CF_3)_3(PPh_3)(\eta\text{-}C_5H_5)]$ [f] (8)	208—210	53.9	3.3	710
		(54.1)	(3.3)	(710)
$C_6H_3(C_6F_5)_3$ (9)	115—117	50.0	0.8	516
		(49.5)	(0.5)	(516)
$[Ru(HC_2C_6F_5)_3(PPh_3)(\eta\text{-}C_5H_5)]$ [g] (10)	181—183	56.7	2.3	1 004
		(56.2)	(2.2)	(1 004)

[a] Composition indicated only. [b] Mass spectrometry, based on ^{102}Ru. [c] Found: P, 4.3. Calc. 4.6%. [d] Found: P, 4.8. Calcd. 5.0%. [e] Found: P, 4.5. Calcd. 4.5%. [f] Found: F, 23.2. Calcd. 24.0%. [g] Found: F, 28.5; P, 3.3. Calcd. F, 28.4; P, 3.1%.

Improved preparations of $[RuR(PPh_3)_2(\eta\text{-}C_5H_5)]$ (R = H or Me),[2] and of the benzyl complex, which is new, are described below.

(*a*) $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$.—A typical preparation involved treating a diethyl ether suspension of $[RuCl(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1.0 g, 1.35 mmol) with an excess of a filtered ethereal solution of $LiAlH_4$. The mixture was stirred at room temperature until the orange suspension (total volume *ca.* 100 cm^3) turned pale yellow (16—24 h). Excess of $LiAlH_4$ was destroyed by cautious dropwise addition of ethanol until no more effervescence occurred, and the resulting pale yellow solution was evaporated to dryness. The mixed solids were extracted with benzene until colourless, and the extracts were evaporated to dryness. Recrystallisation of the solid so obtained from a small volume of diethyl ether afforded pale yellow microcrystalline $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$ (760 mg, 80%), characterised as described previously.[2]

(*b*) $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$.—The chloride (1.0 g, 1.35 mmol) in benzene (150 cm^3) was treated with methyl-lithium (3 cm^3 of a 2.3 mol dm^{-3} solution in ether). After being stirred for 18 h at room temperature, the mixture was hydrolysed with water. The organic layer was separated, dried ($MgSO_4$), filtered, and evaporated to dryness. Recrystallisation from dichloromethane–light petroleum afforded $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ (760 mg, 78%).[2] Extreme care was taken during this preparation to ensure that all solvents were oxygen-free.

(*c*) $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$.—The chloride (1.0 g, 1.35 mmol) in benzene (110 cm^3) was treated with a freshly prepared solution of benzylmagnesium chloride [from benzyl chloride (1.9 g, 1.5 mmol) and magnesium (0.36 g, 0.015 g-atom) in diethyl ether (10 cm^3)]. The mixture was stirred for 2 h at 70 °C, and water (30 cm^3) was added. The benzene layer was separated, dried ($MgSO_4$), filtered, and evaporated to dryness. The crystalline solid which formed on trituration of the resulting oil with ether was filtered off and washed with small volumes of ether and light petroleum. Recrystallisation from larger amounts of ether afforded pure yellow *crystals* of $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (810 mg, 75%).

Reactions of $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$.—(*a*) *With methyl propiolate.* The hydride (500 mg, 0.72 mmol) and HC_2CO_2Me (160 mg, 1.91 mmol) were heated in refluxing 1,2-dimethoxyethane (50 cm^3) for 22 h. Work-up of the resulting orange solution, including chromatography (column A), gave a yellow fraction (eluted with 19 : 1 ether–light petroleum), which was further purified to give two pale yellow complexes, $[Ru(C_2CO_2Me)(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1) and $[Ru\{C(CO_2Me){:}CHCH{:}CH(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)]$ (2) (total yield *ca.* 5%). Ether slowly eluted an orange fraction, which after evaporation and recrystallisation (ether–light petroleum) afforded orange *crystals* of $[Ru\{CH{:}C(CO_2Me)C(CO_2Me){:}C{:}C(Me)\}(PPh_3)(\eta\text{-}C_5H_5)]$ (3) (28 mg, 6%).

Another experiment using equimolar proportions of the two reactants gave only (3) (6% yield), together with recovered hydride (22%).

(*b*) *With pentafluorophenylacetylene.* The hydride (700 mg, 1.0 mmol) and $HC_2C_6F_5$ (500 mg, 2.6 mmol) were heated in refluxing 1,2-dimethoxyethane (65 cm^3) for 18 h.

---

* 1 eV ≃ 1.60 × 10^{-19} J.

Filtration, evaporation, and chromatography of the residue (transferred in the minimum amount of benzene to column A) gave white 1,2,4-$C_6H_3(C_6F_5)_3$ (9) (eluted with 1 : 9 ether–light petroleum), and a yellow fraction (with 3 : 1 ether–light petroleum). Crystallisation afforded orange *crystals* of $[Ru\{C(C_6F_5){:}CHCH{:}C(C_6F_5)CH{:}C(C_6F_5)C_6H_4PPh_2\}(\eta\text{-}C_5H_5)]$ (10) (26 mg, 2.6%).

Reactions of $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$.—(*a*) *With methyl propiolate.* The methyl complex (600 mg, 0.85 mmol) and HC_2CO_2Me (200 mg, 2.4 mmol) were heated in refluxing 1,2-dimethoxyethane (60 cm^3) for 4.5 h to give a dark orange solution which was filtered and evaporated to dryness. A benzene extract of the residue was chromatographed (column A), elution with 1 : 4 ether–light petroleum giving the methyl complex (101 mg, 17% recovery). A yellow fraction was eluted with diethyl ether, and concentration of this, followed by addition of light petroleum, afforded pale yellow *crystals* of $[Ru\{C(CO_2Me){:}CHCH{:}CMe(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)]$ (5) (48 mg, 11%).

(*b*) *With but-3-yn-2-one.* A solution of the methyl complex (500 mg, 0.71 mmol) and HC_2COMe (140 mg, 2.06 mmol) in 1,2-dimethoxyethane (50 cm^3) was heated at reflux for 20 h. Chromatography (column A) gave unchanged methyl complex (48 mg, 9.6% recovery) (with 1 : 9 ether–light petroleum), followed by a red solution (with 1 : 2 ether–light petroleum) which afforded red *crystals* of $[Ru\{C(COMe){:}CHC[C(O)Me]{:}CHMe\}(PPh_3)(\eta\text{-}C_5H_5)]$ (7) (19 mg, 5.1%).

(*c*) *With* 3,3,3-*trifluoropropyne.* A mixture of the methyl complex (600 mg, 0.85 mmol), HC_2CF_3 (3.5 mmol), and 1,2-dimethoxyethane (20 cm^3) was sealed in a Carius tube and heated at 60 °C (96 h) and 120 °C (24 h). The resulting dark orange solution was filtered, evaporated, and the residue transferred to column F in the minimum volume of benzene. The orange fraction eluted with 1 : 6 ether–light petroleum was crystallised to give orange crystals of the cumulene complex $[Ru\{C(CF_3){:}CHC(CF_3){:}C{:}C{:}CH(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)]$ (8) (26 mg, 4.3%).

Reaction between $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$ *and* HC_2CO_2Me.—The benzyl complex (450 mg, 0.58 mmol) and methyl propiolate (170 mg, 2.02 mmol) were refluxed in 1,2-dimethoxyethane (50 cm^3) for 2¼ h, after which time considerable darkening had occurred. Work-up followed by chromatography (column A) gave a pale yellow solution (eluted with 3 : 1 ether–light petroleum) which on concentration afforded pale yellow *microcrystals* of $[Ru\{C(CO_2Me){:}CHCH{:}C(CH_2Ph)(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)]$ (6) (35 mg, 9%).

Crystal Structure Study.—Intensities were collected from a crystal mounted on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[22] Of the total (3 277) reflections for $3.7 < 2\theta < 50°$, 2 712 were deemed ' observed ' according to the criterion $I > 4.0\sigma(I)$ and only these were used in the solution and refinement of the structure.

Crystal Data.—$C_{32}F_9H_{22}PRu$, $M = 678.2$. Monoclinic, $a = 14.778(9)$, $b = 12.749(5)$, $c = 17.417(6)$ Å, $\beta = 119.04(4)°$, $U = 2\,869$ Å^3, $D_m = 1.5$ g cm^{-3}, $Z = 4$, $D_c = 1.61$ g cm^{-3}, $F(000) = 1\,492$. Space group $P2_1/c$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) $= 6.37$ cm^{-1}.

The structure was solved by conventional heavy-atom methods, and refined by full-matrix least squares with anisotropic thermal parameters for the Ru, P, and F atoms only. Weights were applied according to the scheme $w = 1$ for $F_o \leqslant 40$, $w = (40/F_o)^2$ for $F_o > 40$. Hydrogen atoms were incorporated at calculated positions ($10^2U = 5.0$), but neither their positional nor thermal parameters were refined. The refinement converged to R 0.079 (R' 0.088).

Positional and thermal parameters are in Table 1, interatomic distances and bond angles in Table 2, and some least-squares planes in Table 3. No absorption correction was applied, and the atomic scattering factors were those of ref. 23 for Ru, P, and F, and those of ref. 24 for H. All computational work was carried out at the University of London Computing Centre wih the ' X-Ray System ' of programmes.[25] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21861 (12 pp., 1 microfiche).†

We thank the U.S.A.F. Office of Scientific Research for support and the S.R.C. for a Science ASSIST award (to R. C. F. G.).

[6/515 *Received*, 16*th March*, 1976]

---

† For details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

[22] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[23] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[24] R. F. Stewart, E. R. Davidson, and W. Simpson, *J. Chem. Phys.*, 1968, **42**, 3175.

[25] Technical Report TR 192 of the Computer Science Centre, University of Maryland, June 1972.