Crystal and Molecular Structure of η-Cyclopentadienyl[1,3,4-η-(1,2-dimethoxycarbonyl-5,5,5-trifluoro-3-trifluoromethylpent-1,3-dienyl)]triphenylphosphineruthenium. An Unexpected Reaction Product from Hexafluorobut-2-yne and a Vinylruthenium Complex

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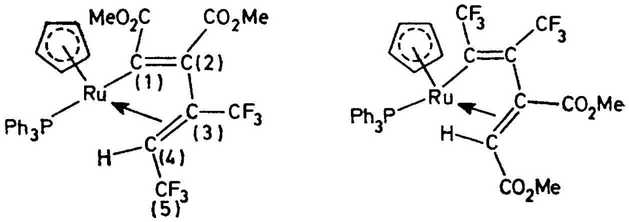
Crystals of $[\overline{\mathrm{Ru{\cdot}C(CO_2Me){:}C(CO_2Me){\cdot}C(CF_3){:}C}}(CF_3)H(PPh_3)(\eta\text{-}C_5H_5)]$ are triclinic, space group, $P\bar{1}$, with Z = 2 in a unit cell of dimensions a = 9.353(4), b = 16.346(16), c = 10.875(6) Å, α = 93.82(7), β = 113.07(4), γ = 94.26(6)°. The structure has been solved by conventional heavy-atom methods from 4 184 diffracted intensities measured on a diffractometer and refined by block-matrix least-squares to R 0.039. The skeleton of the vinylruthenium complex remains intact, but the chain is extended by σ-addition of one molecule of hexafluorobut-2-yne with subsequent π-bonding of this acetylene to the ruthenium atom to form a cyclic system, $\overline{\mathrm{Ru{\cdot}C(CO_2Me){:}C(CO_2Me){\cdot}C(CF_3){:}C}}(CF_3)H$. The co-ordination around the ruthenium atom is approximately octahedral, three sites being occupied by the η^5-cyclopentadienyl ring and one by the triphenylphosphine ligand.

TRANSITION-METAL complexes in which the metal atoms are in relatively low oxidation states undergo a variety of reactions with acetylenes.[1,2] Often oligomerisation of the acetylene is observed, together with formation of organometallic compounds having many different kinds of molecular structure. Cyclic tri- and tetra-merizations occur *via* intermediates with metallacarbon rings, many of which have been isolated.[1,3] Acetylenes having electron-withdrawing substituents, notably $C_2(CF_3)_2$ (refs. 4 and 5) and $C_2(CO_2Me)_2$,[6] have been extensively used as models in studies on reactions of this type.

Insertion reactions of acetylenes with transition-metal hydrides and alkyls have been described for several years but relatively little is known of the mechanisms of these reactions. In this context the very reactive hydrido-complex $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$ [7] was recently shown [4] to form addition products with the two acetylenes RC:CR [R = CF_3 or CO_2Me]. During the course of this work a novel reaction was observed between the vinylic complex $[Ru\{C(CO_2Me){:}CH(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ and hexafluorobut-2-yne. The product (I) was formulated as a butadienyl complex. Moreoever, on the basis of n.m.r. coupling constant data it appeared as if the compound had a molecular structure in which the $C(CF_3){:}C(CF_3)$ unit was not η^1 bonded to the metal but formed an η^2-C_2 bond as shown. This result [4] was unexpected since it would have been reasonable to assume that the reaction product would have had the alternative structure (II), and that the complex would have formed by insertion of $CF_3{\cdot}C{:}C{\cdot}CF_3$ into the ruthenium–carbon bond of the vinyl compound.



(I) (II)

Showing the systematic numbering

To account for the product having structure (I) rather than (II), Blackmore *et al.*[4] suggested that the vinyl

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[1] R. F. Heck, ' Organotransition-Metal Chemistry,' Academic Press, New York, 1974, ch. VII.

[2] F. L. Bowden and A. P. B. Lever, *Organometallic Chem. Rev.*, 1968, **3**, 227.

[3] S. Otsuka and A. Nakamura, *Adv. Organometallic Chem.*, in the press.

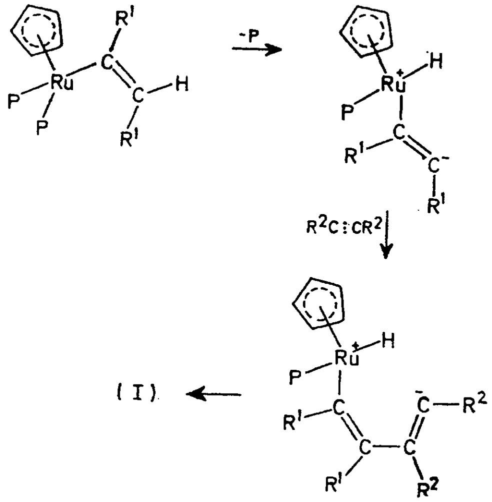
[4] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 106.

[5] M. I. Bruce and W. R. Cullen, *Fluorine Chem. Rev.*, 1969, **4**, 79.

[6] D. M. Roe, C. Calvo, N. Krischnamachari, and P. M. Maitlis. *J.C.S. Dalton*, 1975, 125; and refs. therein.

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

complex formed from $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$ and $C_2(CO_2Me)_2$ underwent a hydride migration to give a dipolar intermediate, which subsequently reacted with a molecule of hexafluorobut-2-yne, as shown in the Scheme. Otsuka and Nakamura[3] have recently discussed other metalla-cyclisations of acetylenes involving possible Zwitterionic intermediates.



SCHEME $P = PPh_3$, $R^1 = CO_2Me$, $R^2 = CF_3$

A single-crystal X-ray diffraction study of the butadienyl complex was clearly required in order to establish whether structure (I) was correct, and the results are herein described.

EXPERIMENTAL

Crystals of (I) grow as elongated yellow prisms from toluene. Diffracted intensities were collected from a crystal of dimensions 0.1 × 0.1 × 0.4 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[8] Of the total 5 292 independent reflections (complete for $2.9° < 2\theta < 50.0°$), 4 184 were observed according to the criterion $I > 2.5\sigma(I)$, and were used in the solution and refinement of the structure.

During data collection the crystal moved accidentally and had to be recentred. Data collected before, and after, centring were given separate scale factors in the refinement cycles.

Crystal Data.—$C_{33}H_{27}F_6O_4PRu$, $M = 733.6$, Triclinic, $a = 9.353(4)$, $b = 16.346(16)$, $c = 10.875(6)$ Å, $\alpha = 93.82(7)$, $\beta = 113.07(4)$, $\gamma = 94.26(6)°$, $D_c = 1.61$, $Z = 2$, $D_m = 1.59$, g cm^{-3}, $F(000) = 740$. Space group $P\bar{1}$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.71069$ Å; μ(Mo-K_α) = 6.4 cm^{-1}.

The structure was solved by conventional heavy-atom methods, and refined by block-matrix least-squares. In the final stages of refinement all non-hydrogen atoms were

TABLE 1

Atomic positional and thermal parameters,* with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	10^2U/Å^2
(*a*) Butadienyl ligand				
Ru	0.08143(4)	0.17173(2)	0.24372(4)	
C(6)	−0.0209(5)	0.1899(3)	0.0411(4)	
C(7)	−0.1718(5)	0.1671(3)	0.0169(5)	
C(8)	−0.1738(5)	0.1533(3)	0.1520(5)	
C(9)	−0.1230(5)	0.2224(3)	0.2521(5)	
C(61)	0.0373(6)	0.2119(3)	−0.0638(5)	
C(62)	0.1680(11)	0.1653(5)	−0.1972(8)	
O(61)	0.0225(6)	0.2757(2)	−0.1117(4)	
O(62)	0.1116(4)	0.1513(2)	−0.0933(3)	
C(71)	−0.3062(6)	0.1503(3)	−0.1148(5)	
C(72)	−0.3756(10)	0.1188(7)	−0.3479(7)	
O(71)	−0.4420(5)	0.1477(3)	−0.1318(4)	
O(72)	−0.2576(4)	0.1361(3)	−0.2144(4)	
C(81)	−0.2729(6)	0.0769(3)	0.1550(5)	
F(81)	−0.2740(4)	0.0143(2)	0.0691(4)	
F(82)	−0.4238(4)	0.0915(2)	0.1193(4)	
F(83)	−0.2317(4)	0.0483(2)	0.2759(3)	
C(91)	−0.1540(6)	0.2263(4)	0.3775(5)	
F(91)	−0.3069(4)	0.2094(3)	0.3545(3)	
F(92)	−0.1107(5)	0.3022(2)	0.4423(4)	
F(93)	−0.0807(4)	0.1755(3)	0.4688(3)	
H(9)	−0.127(5)	0.274(3)	0.221(4)	0.2.7(11)
H(621)	0.087(11)	0.160(5)	−0.278(9)	10.3(31)
H(622)	0.213(10)	0.219(6)	−0.181(8)	9.4(26)
H(623)	0.219(10)	0.124(5)	−0.217(8)	10.0(27)
H(721)	−0.442(10)	0.074(5)	−0.353(8)	9.3(31)
H(722)	−0.307(10)	0.114(5)	−0.408(9)	10.7(28)
H(723)	−0.441(10)	0.159(5)	−0.370(8)	8.6(24)
(*b*) Triphenylphosphine ligand				
P	0.20965(14)	0.30759(7)	0.29408(12)	
C(11)	0.3522(6)	0.3260(3)	0.4699(5)	
C(12)	0.3001(8)	0.3204(4)	0.5742(6)	
C(13)	0.4074(9)	0.3299(4)	0.7067(6)	
C(14)	0.5641(9)	0.3422(4)	0.7385(7)	
C(15)	0.6157(9)	0.3475(5)	0.6383(7)	
C(16)	0.5118(6)	0.3405(4)	0.5042(5)	
C(21)	0.3332(5)	0.3359(3)	0.2041(4)	
C(22)	0.3838(6)	0.2760(3)	0.1381(5)	
C(23)	0.4876(7)	0.2981(4)	0.0800(6)	
C(24)	0.5411(7)	0.3793(4)	0.0861(6)	
C(25)	0.4923(8)	0.4390(4)	0.1509(7)	
C(26)	0.3887(7)	0.4188(4)	0.2091(6)	
C(31)	0.0935(6)	0.3954(3)	0.2675(5)	
C(32)	0.1025(9)	0.4545(4)	0.3676(7)	
C(33)	0.0173(11)	0.5224(4)	0.3366(12)	
C(34)	−0.0770(10)	0.5313(4)	0.2056(10)	
C(35)	−0.0868(8)	0.4738(4)	0.1062(8)	
C(36)	−0.0052(7)	0.4053(4)	0.1346(6)	
H(12)	0.193(7)	0.315(3)	0.558(5)	5.1(16)
H(13)	0.366(6)	0.325(3)	0.766(5)	3.5(13)
H(14)	0.639(8)	0.344(4)	0.826(7)	6.3(18)
H(15)	0.705(9)	0.355(5)	0.648(7)	7.7(24)
H(16)	0.542(7)	0.346(4)	0.430(6)	6.0(17)
H(22)	0.348(6)	0.223(3)	0.132(5)	3.7(13)
H(23)	0.517(6)	0.262(3)	0.044(5)	4.2(15)
H(24)	0.609(8)	0.389(4)	0.044(6)	6.4(18)
H(25)	0.526(8)	0.489(4)	0.147(6)	6.7(19)
H(26)	0.366(8)	0.458(4)	0.265(6)	6.7(19)
H(32)	0.166(6)	0.450(3)	0.448(5)	2.5(13)
H(33)	0.033(10)	0.553(5)	0.400(9)	9.5(29)
H(34)	−0.125(8)	0.577(5)	0.193(7)	7.6(21)
H(35)	−0.151(8)	0.482(4)	0.010(7)	7.6(21)
H(36)	−0.009(7)	0.366(4)	0.066(6)	5.3(16)
(*c*) Cyclopentadienyl ligand				
C(1)	0.1024(7)	0.0357(3)	0.2359(7)	
C(2)	0.1124(7)	0.0640(4)	0.3669(6)	
C(3)	0.2448(6)	0.1211(4)	0.4283(6)	
C(4)	0.3178(6)	0.1289(3)	0.3363(5)	
C(5)	0.2315(7)	0.0757(3)	0.2202(6)	
H(1)	0.026(8)	−0.001(4)	0.176(7)	7.1(20)
H(2)	0.043(7)	0.048(4)	0.401(6)	5.5(17)
H(3)	0.277(7)	0.148(4)	0.517(6)	5.7(17)
H(4)	0.402(6)	0.161(3)	0.351(5)	3.1(13)
H(5)	0.254(8)	0.069(4)	0.158(7)	6.0(20)

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

TABLE 1 (*Continued*)

(*d*) Anisotropic thermal parameters

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	2.58(3)	2.95(3)	3.06(3)	−0.002(13)	0.672(15)	0.120(13)
C(6)	3.4(3)	2.9(2)	3.3(2)	0.6(2)	0.9(2)	0.1(2)
C(7)	3.2(3)	3.4(2)	3.5(3)	0.6(2)	0.6(2)	−0.1(2)
C(8)	2.7(3)	3.6(2)	4.1(3)	0.2(2)	1.0(2)	0.1(2)
C(9)	2.9(2)	3.4(3)	4.2(3)	0.1(2)	1.3(2)	0.2(2)
C(61)	3.6(3)	4.0(3)	3.3(2)	0.1(2)	1.0(2)	0.0(2)
C(62)	8.1(5)	6.7(5)	5.6(4)	−0.1(4)	4.5(4)	−0.2(3)
O(61)	9.0(3)	4.3(2)	5.6(2)	1.5(2)	3.4(2)	1.8(2)
O(62)	4.3(2)	4.2(2)	4.0(2)	0.2(2)	2.1(2)	0.3(2)
C(71)	3.2(3)	4.5(3)	4.3(3)	1.2(2)	0.0(2)	−0.1(2)
C(72)	6.4(5)	10.1(6)	3.5(3)	2.4(5)	−1.1(3)	−0.6(4)
O(71)	3.1(2)	10.9(4)	5.3(3)	1.1(2)	0.27(2)	−0.4(2)
O(72)	4.1(2)	8.8(3)	3.3(2)	1.7(2)	0.2(2)	−0.9(2)
C(81)	3.3(3)	4.9(3)	4.9(3)	−0.6(2)	0.8(3)	−0.2(3)
F(81)	5.8(2)	4.4(2)	8.0(2)	−1.3(2)	2.2(2)	−1.5(2)
F(82)	3.5(2)	7.4(2)	8.9(3)	−0.8(2)	1.8(2)	0.4(2)
F(83)	6.0(2)	6.7(2)	6.6(2)	−1.3(2)	2.2(2)	1.6(2)
C(91)	3.7(3)	5.7(3)	4.8(3)	−0.1(3)	1.8(3)	−0.6(3)
F(91)	4.4(2)	10.6(3)	6.7(2)	0.1(2)	3.1(2)	0.1(2)
F(92)	10.1(3)	7.4(3)	8.5(3)	−1.8(2)	6.0(3)	−3.0(2)
F(93)	6.8(2)	10.6(3)	4.7(2)	1.8(2)	2.2(2)	1.6(2)
P	3.24(7)	3.16(6)	3.36(6)	−0.22(5)	1.41(5)	−0.26(5)
C(11)	4.2(3)	3.7(3)	3.7(3)	−0.7(2)	1.5(2)	−0.5(2)
C(12)	5.4(4)	6.1(4)	4.5(3)	−1.5(3)	2.2(3)	−0.4(3)
C(13)	8.0(5)	6.3(4)	3.7(3)	−1.7(4)	2.6(3)	−0.1(3)
C(14)	7.2(5)	6.3(4)	4.0(4)	−1.1(4)	0.5(4)	−0.3(3)
C(15)	4.7(4)	7.6(5)	5.7(4)	−0.8(4)	0.9(3)	0.0(3)
C(16)	4.3(3)	5.6(3)	3.7(3)	−0.6(3)	1.1(3)	−0.2(3)
C(21)	3.3(3)	3.6(3)	3.2(3)	−0.2(2)	1.1(2)	0.2(2)
C(22)	3.5(3)	4.2(3)	4.1(3)	−0.0(3)	1.3(2)	0.0(2)
C(23)	4.4(3)	6.3(4)	4.7(3)	1.0(3)	2.3(3)	−0.3(3)
C(24)	5.0(4)	7.0(4)	5.8(4)	−0.1(3)	3.4(3)	0.9(3)
C(25)	6.4(4)	4.9(4)	8.0(4)	−0.4(3)	4.3(4)	1.3(3)
C(26)	5.3(3)	4.5(3)	6.1(4)	0.3(3)	3.4(3)	0.5(3)
C(31)	4.0(3)	3.1(3)	5.7(3)	0.1(2)	2.8(3)	−0.1(3)
C(32)	7.1(4)	4.6(4)	6.4(4)	0.0(3)	3.6(4)	−0.5(3)
C(33)	10.7(7)	4.1(4)	12.2(8)	1.1(4)	8.0(7)	−0.6(4)
C(34)	8.0(5)	4.3(4)	13.4(8)	2.5(4)	7.0(6)	2.9(4)
C(35)	5.6(4)	5.2(4)	9.5(5)	1.7(3)	4.1(4)	2.5(4)
C(36)	4.6(3)	4.3(3)	6.2(4)	0.5(3)	2.3(3)	0.4(3)
C(1)	4.6(3)	2.8(3)	6.9(4)	0.4(3)	0.8(3)	0.6(3)
C(2)	4.9(3)	4.9(3)	6.3(4)	0.8(3)	2.0(3)	2.8(3)
C(3)	3.9(3)	5.4(3)	4.1(3)	1.3(3)	0.3(3)	1.2(3)
C(4)	2.7(3)	4.3(3)	5.1(3)	0.7(2)	0.9(2)	0.7(3)
C(5)	4.9(3)	4.4(3)	5.0(3)	2.1(3)	1.8(3)	1.0(3)

* $B = 8\pi^2 U$. 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 ($\times 10^2$).

given anisotropic thermal parameters. Hydrogen atoms were incorporated in the structure-factor calculations at positions estimated from the electron-density maps, and both positional and thermal parameters were refined. Weights were applied according to the scheme $w = P.Q$, where $P = 1$ when $\sin\theta > b$, and $P = \sin\theta/b$ when $\sin\theta < b$; and $Q = 1$ when $c > F_o$, and $Q = c/F_o$ when $c < F_o$. The values of b and c used here were 0.22 and 50.0 respectively, chosen from an analysis of the variaton of $w\Delta^2$ with F_o and with $\sin\theta$. A final electron-density difference map showed no peaks > 0.6 or < 0.7 eÅ^{-3}. Refinement converged at R 0.039 (R' 0.047) for 4 184 independent reflections. Positional and thermal parameters are given in Table 1, and bond lengths and angles with their respective standard deviations in Table 2. No absorption correction was applied, and the atomic scattering factors used were those of ref. 9 for the non-hydrogen atoms, and ref. 10 for the hydrogen atoms. Those for ruthenium and phosphorus were corrected ($\Delta f'$, $\Delta f''$) for anomalous dispersion.[11] All computational work was carried out at the University of London Computing Centre, with the 'X-Ray' system of programs.[12] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21 527 (17 pp., 1 microfiche).*

DISCUSSION

The overall configuration of the molecule, projected on to the plane of the C_5 ring, and the atom numbering system, are shown in Figure 1. Hydrogen atoms are numbered according to the carbon atoms to which they are attached, methyl group hydrogen atoms being differentiated by a third number 1—3.

The results establish that the title compound has the structure (I), thereby confirming the original deduction.[4]

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[9] D. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[10] R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[11] 'International Tables for X-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

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

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances

(i) Butadienyl ligand			
Ru–C(6)	2.082(5)	C(71)–O(72)	1.344(8)
C(6)–C(7)	1.348(7)	O(72)–C(72)	1.431(7)
C(7)–C(8)	1.509(8)	C(8)–C(81)	1.508(8)
C(8)–C(9)	1.428(7)	C(81)–F(81)	1.336(7)
C(8)–Ru	2.185(5)	C(81)–F(82)	1.354(7)
C(9)–Ru	2.171(6)	C(81)–F(83)	1.345(7)
C(6)–C(61)	1.497(8)	C(9)–C(91)	1.501(9)
C(61)–O(61)	1.190(7)	C(91)–F(91)	1.355(7)
C(61)–O(62)	1.342(7)	C(91)–F(92)	1.336(7)
O(62)–C(62)	1.446(11)	C(91)–F(93)	1.344(7)
C(7)–C(71)	1.480(6)	Ru–C(8,9) *	2.057(10)
C(71)–O(71)	1.206(7)		
(ii) Triphenylphosphine ligand			
Ru–P	2.366(3)	C(23)–C(24)	1.370(9)
P–C(11)	1.841(5)	C(24)–C(25)	1.373(11)
C(11)–C(12)	1.404(10)	C(25)–C(26)	1.381(11)
C(12)–C(13)	1.386(8)	C(26)–C(21)	1.404(8)
C(13)–C(14)	1.363(11)	P–C(31)	1.834(6)
C(14)–C(15)	1.359(12)	C(31)–C(32)	1.379(9)
C(15)–C(16)	1.390(8)	C(32)–C(33)	1.398(11)
C(16)–C(11)	1.387(8)	C(33)–C(34)	1.375(14)
P–C(21)	1.837(6)	C(34)–C(35)	1.354(13)
C(21)–C(22)	1.393(8)	C(35)–C(36)	1.385(9)
C(22)–C(23)	1.391(10)	C(36)–C(31)	1.406(8)
(iii) Cyclopentadienyl ligand			
C(1)–C(2)	1.433(10)	Ru–C(1)	2.245(6)
C(2)–C(3)	1.396(8)	Ru–C(2)	2.251(7)
C(3)–C(4)	1.421(10)	Ru–C(3)	2.247(6)
C(4)–C(5)	1.397(7)	Ru–C(4)	2.230(6)
C(5)–C(1)	1.405(10)	Ru–C(5)	2.247(7)

(*b*) Angles

(i) Butadienyl ligand			
Ru–C(6)–C(7)	99.4(4)	C(8)–C(81)–F(81)	112.5(5)
C(6)–C(7)–C(8)	105.5(4)	C(8)–C(81)–F(82)	110.9(4)
C(7)–C(8)–C(9)	117.2(4)	C(8)–C(81)–F(83)	115.0(4)
Ru–Cu(6)–C(61)	135.7(3)	C(81)–C(8)–C(9)	124.4(5)
C(6)–C(61)–O(61)	124.1(5)	C(8)–C(9)–C(91)	124.2(5)
C(6)–C(61)–O(62)	111.0(4)	C(9)–C(91)–F(91)	113.7(4)
C(61)–O(62)–C(62)	115.4(5)	C(9)–C(91)–F(92)	110.3(5)
O(61)–C(61)–O(62)	124.9(6)	C(9)–C(91)–F(93)	116.5(5)
C(61)–C(6)–C(7)	124.6(4)	C(7)–C(8)–Ru	90.2(3)
C(6)–C(7)–C(71)	128.0(5)	Ru–C(8)–C(9)	70.3(3)
C(7)–C(71)–O(71)	125.3(6)	C(8)–C(9)–Ru	71.4(3)
C(7)–C(71)–O(72)	110.9(5)	Ru–C(9)–C(91)	121.8(3)
O(71)–C(71)–O(72)	123.7(4)	C(71)–C(7)–C(8)	126.2(5)
C(71)–O(72)–C(72)	117.1(5)	C(7)–C(8)–C(81)	115.7(4)
(ii) Triphenylphosphine ligand			
Ru–P–C(11)	111.4(2)	C(21)–C(22)–C(23)	120.4(5)
Ru–P–C(21)	117.2(2)	C(22)–C(23)–C(24)	120.5(6)
Ru–P–C(31)	119.5(2)	C(23)–C(24)–C(25)	119.6(7)
C(11)–P–C(21)	101.2(2)	C(24)–C(25)–C(26)	121.1(6)
C(21)–P–C(31)	99.9(3)	C(25)–C(26)–C(21)	120.0(6)
C(31)–P–C(11)	105.5(2)	C(26)–C(21)–P	120.3(5)
C(16)–C(11)–C(12)	118.1(5)	C(22)–C(21)–P	121.2(4)
C(11)–C(12)–C(13)	119.8(6)	C(36)–C(31)–C(32)	117.9(5)
C(12)–C(13)–C(14)	121.3(7)	C(31)–C(32)–C(33)	120.6(7)
C(13)–C(14)–C(15)	119.2(6)	C(32)–C(33)–C(34)	120.4(9)
C(14)–C(15)–C(16)	121.3(7)	C(33)–C(34)–C(35)	119.6(7)
C(15)–C(16)–C(11)	120.2(7)	C(34)–C(35)–C(36)	121.1(7)
C(12)–C(11)–P	119.5(4)	C(35)–C(36)–C(31)	120.4(6)
C(16)–C(11)–P	122.3(5)	C(36)–C(31)–P	117.4(4)
C(26)–C(21)–C(22)	118.3(6)	C(32)–C(31)–P	124.6(4)
(iii) Cyclopentadienyl ligand			
C(5)–C(1)–C(2)	107.3(5)	C(3)–C(4)–C(5)	108.4(5)
C(1)–C(2)–C(3)	108.2(6)	C(4)–C(5)–C(1)	108.5(6)
C(2)–C(3)–C(4)	107.6(5)		
(iv) Geometry around Ru			
P–Ru–C(6)	90.1(1)	P–Ru–C(8,9)	104.0(3)
C(6)–Ru–C(8,9)	73.4(3)		

* C(8,9) is the midpoint between atoms C(8) and C(9).

The skeleton of the vinylruthenium complex remains intact, but the chain is extended by σ-addition of one molecule of hexafluorobut-2-yne with subsequent η^2-bonding of this group to the Ru atom to form a five-membered $\overline{Ru\cdot C(CO_2Me)\vdots C(CO_2Me)\cdot C(CF_3)\vdots C}(CF_3)H$ ring. The other two ligands on the ruthenium atom, PPh_3, and η-C_5H_5, give an overall approximately octahedral configuration if the η^5-C_5H_5 group is assumed to occupy three co-ordination sites.

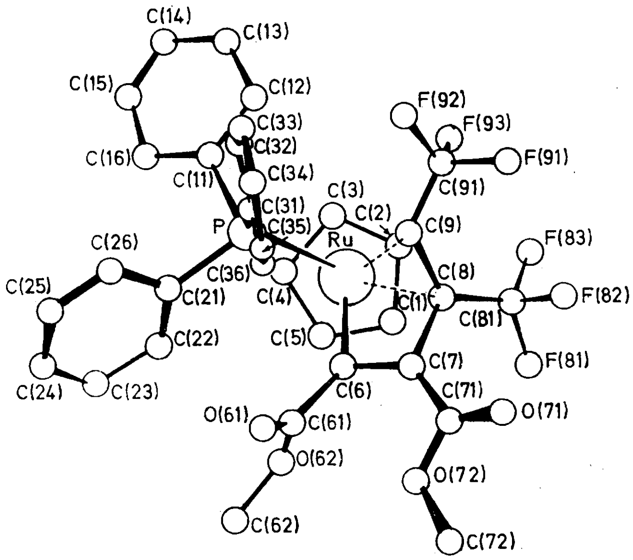
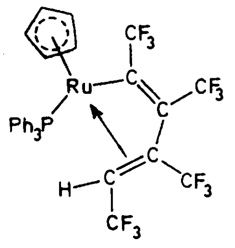


FIGURE 1 Projection of the molecule on the cyclopentadienyl ring, showing the atom numbering system used in the analysis

The Ru–C(6) σ bond distance [2.082(5) Å] is typical for a carbon–metal single bond and is hardly significantly different from the value (2.05 Å) found [13] for the closely related molecule (III).



(III)

In (I) the Ru atom is π-bonded to atoms C(8) and C(9) at distances of 2.185(5) and 2.171(6) Å, respectively, and

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

the Ru···C(7) non-bonded distance is 2.659(4) Å. These compare with 2.16 and 2.19 Å for the π bonds, and 2.65 Å for the equivalent non-bonded distance in (III).[13] The linkage C(6)–C(7) is a normal double-bond [1.348(7) Å], and the C(7)–C(8) (single) bond distance is 1.509(8) Å, while the C(8)–C(9) distance [1.428(7) Å] is indicative of a bond order of <2. The mean C–F distance in the perfluoromethyl groups is 1.345(7) Å.

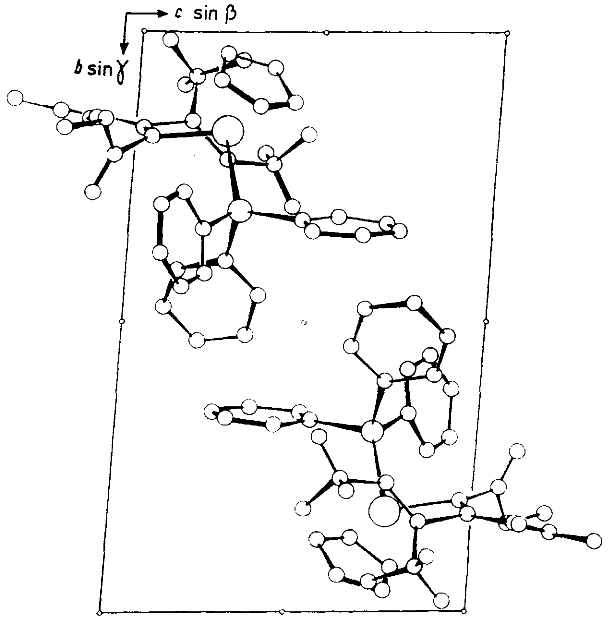

FIGURE 2 Arrangement of the molecules in the unit cell, viewed down *a*

The atom sequences C(6), O(61), C(61), O(62), C(62) and C(7), O(71), C(71), O(72), C(72) are approximately coplanar (to within ±0.025 Å), the dihedral angle between these planes being 75.5°. The orientation adopted by the methoxycarbonyl group on C(6) is necessitated by the proximity of phenyl group C(21)—(26) and the methoxycarbonyl group on C(7) (Figure 1).

In the cyclopentadienyl ligand the mean C–C [1.411(9) Å]and C–Ru distances [2.245(7) Å] are unexceptional. In the triphenylphosphine ligand mean distances are C–C 1.383(10) and P–C 1.837(5) Å.

The overall packing of the molecules in the crystal is illustrated in Figure 2. There are no significantly short intermolecular contacts.

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