Cyclopentadienylruthenium Phosphine Complexes. Part II.[1] Reactions between Hydridobis(triphenylphosphine)(π-cyclopentadienyl)ruthenium and Acetylenes

By **Timothy Blackmore, Michael I. Bruce,†** and **F. Gordon A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

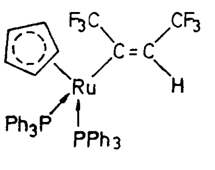
Reaction between $RuH(PPh_3)_2(\pi\text{-}C_5H_5)$ and $C_2(CF_3)_2$ affords $Ru[cis\text{-}CF_3C{:}C(H)(CF_3)](PPh_3)_2(\pi\text{-}C_5H_5)$ (I) and the butadienyl complex $\overline{RuC(CF_3){:}C(CF_3)C(CF_3){:}CH(CF_3)}(PPh_3)(\pi\text{-}C_5H_5)$ (II). With $C_2(CO_2Me)_2$ the hydride affords the *trans*-adduct $RuC(CO_2Me){:}CH(CO_2Me)(PPh_3)_2(\pi\text{-}C_5H_5)$ (IV), together with the cyclic ester complex $\overline{RuC(CO_2Me){:}CHC(OMe)O}(PPh_3)(\pi\text{-}C_5H_5)$ (V). Reaction of (IV) or (V) with $C_2(CF_3)_2$ affords a butadienyl complex $\overline{RuC(CO_2Me){:}C(CO_2Me)C(CF_3){:}CH(CF_3)}(PPh_3)(\pi\text{-}C_5H_5)$ (VI). Hexafluoroacetone and (IV) react to give a complex (VII) containing a co-ordinated ester group and an intramolecular hydrogen bond, formal insertion of the ketone into a C–H bond of the cyclopentadienyl ligand having occurred.

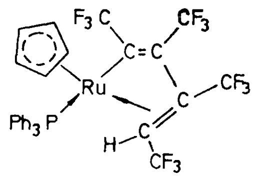
It has been known for many years that olefins or acetylenes bearing electron-withdrawing substituents, for example, fluorine or perfluoromethyl, and more recently cyano or carboxyalkyl groups, react readily with metal hydrides to form complexes containing metal-carbon σ-bonds. The fluoro-compounds have been reviewed.[2] Recent examples of the second group of reactions are those between $IrH(CO)(PPh_3)_3$ and tetracyanoethylene,[3] and between manganese,[4] rhodium,[5] or iridium [6] hydride complexes and dimethyl acetylenedicarboxylate and related olefinic esters.

This paper describes the reactions of $Ru(H)(PPh_3)_2(\pi\text{-}C_5H_5)$ with C_2R_2 ($R = CF_3$ or CO_2Me), and with $(CF_3)_2C{:}C(CN)_2$, and the characterisation of a butadienylruthenium complex containing the group $\overline{Ru\cdot C(CO_2Me){:}C(CO_2Me)C(CF_3){:}CH(CF_3)}$. As with the earlier studies,[1,7] an important factor in determining the nature of the products is the lability of a phosphine ligand in $Ru(H)(PPh_3)_2(\pi\text{-}C_5H_5)$.

Reaction with Hexafluorobut-2-yne.—The hydride reacts with excess of $C_2(CF_3)_2$ in diethyl ether to give three products (I), (II), and $Ph_3PC_8F_{12}$ (III). The latter was readily identified as the cyclic phosphorane, previously isolated as a by-product in reactions between the alkyne and Ph_3PAuMe,[8] and will not be discussed further.

Compound (I) has been characterised as the *cis*-vinyl complex by analysis, i.r., n.m.r., and mass spectrometry. The i.r. spectrum contains a ν(C=C) band at 1573 cm^{-1}. The ^{1}H n.m.r. spectrum contains signals at τ 2·84 (m) (30H, C_6H_5), 5·22 (q) (1H, =C*H*), and 5·87 (s) (5H, C_5H_5).


(I)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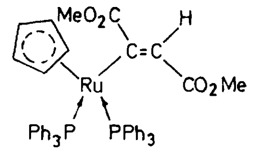
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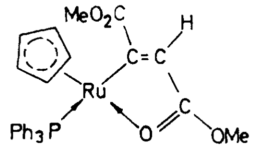
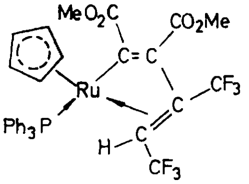
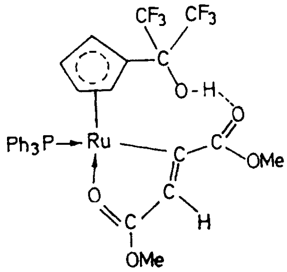
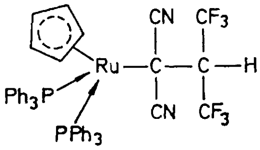

(V)


(VI)


(VII)


(VIII)

The *cis*-proton exhibits coupling to the *gem*-CF_3 group, but no measurable interaction with the second CF_3 group, nor with phosphorus. The ^{19}F n.m.r. spectrum contains two signals at 51·57 (q) and 57·35 (m) p.p.m.

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

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

[2] M. I. Bruce and F. G. A. Stone, *Preparative Inorg. React.*, 1968, **4**, 177; M. I. Bruce and W. R. Cullen, *Fluorine Chem. Rev.*, 1969, **4**, 79.

[3] M. S. Fraser, G. F. Everitt, and W. H. Baddley, *J. Organometallic Chem.*, 1972, **35**, 403.

[4] B. L. Booth and R. G. Hargreaves, *J. Chem. Soc.* (*A*), 1969, 2766.

[5] B. L. Booth and A. D. Lloyd, *J. Organometallic Chem.*, 1972, **35**, 195.

[6] W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, 1969, **91**, 3661.

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

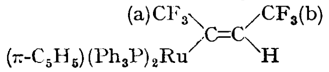
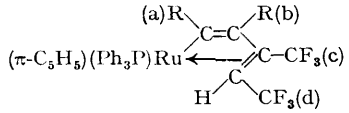
[8] C. M. Mitchell and F. G. A. Stone, *J.C.S. Dalton*, 1972, 102.

(upfield from $CFCl_3$), from which the various coupling constants obtained (Table 1) were in agreement with those observed with many other metal derivatives containing the *cis*-$(CF_3)C{=}C(CF_3)H$ group.[9] The mass spectrum of complex (I) shows no parent ion, ready loss of triphenylphosphine occurring to give the ion $[C_5H_5Ru(PPh_3)C_4F_6H]^+$. Loss of HF gives an ion at *m/e* 571 ($[C_5H_5Ru(PPh_3)C_4F_5]^+$).

The bis-insertion product (II) shows a single sharp ν(C=C) band in the i.r. at 1640 cm^{-1}. The structure of this complex has been established by a single crystal *X*-ray diffraction study.[7] Four resonances in the ^{19}F n.m.r. spectrum can be assigned as shown (Table 1) as a result of decoupling experiments. The proton resonance at τ 7·98 (m) (1H, =C*H*) is coupled to the geminal CF_3 and to the phosphorus atom. The mass spectrum contains a parent ion cluster centred on *m/e* 754, major fragmentation routes involving loss of F and HF, and of PPh_3. The fluorinated C_8 unit is preserved in many ions, and no elimination of a C_4F_n ($n \leqslant 6$) group was observed.

TABLE 1

Fluorine-19 n.m.r. data

Complex		Chemical shifts/p.p.m.	Coupling constants/Hz
	(I)[a]	CF_3 (a) 51·57(q)	*J*(ab) 14·4; *J*(aH) 0
		CF_3 (b) 57·3(m)	*J*(ab) 14·4; *J*(bH) 11·0; *J*(bP) 3·0
	(II)R = CF_3[b]	CF_3 (a) CF_3 (b) } 57·36(m), 64·85(m)	
		CF_3 (c) 55·12(dq)	*J*(cd) 10·0; *J*(cP) 2·0
		CF_3 (d) 50·12(m)	*J*(cd) 10·0; *J*(dH) 8·8
	(VI)R = CO_2Me[c]	CF_3 (c) 54·35(dq)	*J*(cd) 10·0; *J*(cP) 3·3
		CF_3 (d) 50·37(qu)	*J*(cd) 10·0; *J*(dH) 10·0
$[\pi\text{-}C_5H_4C(CF_3)_2OH]Ru(PPh_3)C_2(CO_2Me)_2H$	(VII)	CF_3 75·6(qd) 77·96(q)	*J*(FF), 10·2; *J*(HF) 1·5
$(\pi\text{-}C_5H_5)Ru(PPh_3)_2C(CN)_2C(CF_3)_2H$	(VIII)[d]	CF_3 68·31(d)	*J*(HF) 8·2

[a] Vinylic H at τ 5·22q; *J*(bH) 11·0 Hz. [b] Vinylic H at τ 7·98m; *J*(dH) 8·8; *J*(HP) 14·5 Hz. [c] Vinylic H at τ 7·82m; *J*(dH) 10·0; *J*(HP) 14·5 Hz. [d] Protons resonate at τ 2·86 (PPh_3), 5·85s (C_5H_5), 7·26 sep [$C(CF_3)_2H$; *J*(HF) 8·2 Hz].

Abbreviations: dq, doublet of quartets; qu, quintet; sep, septet; m, multiplet.

Reactions with Dimethyl Acetylenedicarboxylate.—Reaction between $RuH(PPh_3)_2(\pi\text{-}C_5H_5)$ and $C_2(CO_2Me)_2$ affords complex (IV) in high yield. From the mother liquor, a small amount of the red mono-phosphine complex (V) was obtained although a better preparation of (V) (40% yield) involves heating (IV) in benzene at 80° (24 h).

Two bands in the i.r. spectrum of (IV) at 1688 and 1699 cm^{-1} are assigned to ν(ester CO), while ν(C=C) occurs at 1528 cm^{-1}. The ^1H n.m.r. spectrum (Table 2) contains signals at τ 2·96 (m) (30H, C_6H_5), 5·76 (t) (1H, =C*H*), 6·10 (5H, C_5H_5), 6·34 (3H, O*Me*), and 6·98 (3H, O*Me*). This relatively simple spectrum indicates that only one isomer is present. The vinyl proton shows a 0·7 Hz coupling to phosphorus, and this tentatively suggests that complex (IV) is the *trans*-isomer, since with complex (I), *J*(HP) = 0, whereas the CF_3 group *trans* to ruthenium showed a small coupling to phosphorus. In only one case do both *cis* or ***trans*** isomers appear to have been obtained from reactions of this type. The reaction between $ReH(\pi\text{-}C_5H_5)_2$ and the acetylenic diester[10] affords the *cis* (maleate) adduct initially which was subsequently isomerised to the ***trans*** (fumarate) complex by heating with platinum in benzene at 70°.

The reactions between other metal hydride complexes and either dimethyl acetylenedicarboxylate or methyl propiolate have given products which have been assigned *cis* or *trans* stereochemistries on the basis of their chemical reactions.[4-6] The chemical shifts of the various methoxy groups are predictably of little value in determining stereochemistry. More importantly, however, the same appears to be true of the chemical shift of the methine proton in the adduct, which is much more strongly affected by the metal atom and associated ligands (Table 2). In contrast to hexafluorobut-2-yne, the adducts of the diester rearrange readily (*cf.* the rhenium complex above, and results reported below), and we believe that assignment of the stereochemistry of these adducts is by no means as certain as indicated in the literature.

The red complex (V), formed from (IV) by loss of a triphenylphosphine molecule, shows a band at 1586 cm^{-1} assigned to ν(CO) of a co-ordinated carbonyl group, together with a broad band at 1699 (m) [ν(CO) (free CO_2Me) and ν(C=C)]. The ^1H n.m.r. spectrum contains five signals at τ 2·77 (m) (15H, P*Ph*$_3$), 3·89 (d) (1H, =C*H*), 5·67 (s) (5H, C_5H_5), 6·56 (s) and 6·84 (s) (3H each, O*Me*). The methine proton shows a 2·5 Hz coupling to phosphorus. These data are consistent with the cyclic structure shown, in which the carbonyl oxygen of one of the ester groups co-ordinates to the ruthenium atom.

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[9] P. K. Maples, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 2069; and refs. 18, 23—26 cited therein.

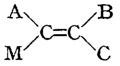
[10] M. Dubeck and R. A. Schell, *Inorg. Chem.*, 1964, **3**, 1757.

Similar complexes have previously been described containing manganese [11,12] or rhenium.[13]

The mass spectra of complexes (IV) and (V) are very similar. The former shows no parent ion, the highest ion corresponding to $[(C_5H_5)Ru(PPh_3)C_2(CO_2Me)_2H]^+$, demonstrating again the lability of the phosphine ligand in these complexes. In the present case, thermal decomposition to (V) probably occurs in the spectrometer. Ions are formed by the expected loss of MeO and CO groups, and ions characteristic of the phosphine ligand are also present.

TABLE 2

N.m.r. data for $C_2(CO_2Me)_2$ derivatives



	M	A	B	C	Stereochemistry	Chemical shift (τ)			Ref.
						O*Me*		=C*H*	
(IV)	$(\pi\text{-}C_5H_5)Ru(PPh_3)_2$ [a]	CO_2Me	H	CO_2Me	*trans*	6·34(s) 6·98(s)		5·76(t) *J*(HP) 0·7	*b*
(V)	$(\pi\text{-}C_5H_5)Ru(PPh_3)$ [c]	CO_2Me	H	CO_2Me	cyclic	6·56(s) 6·84(s)		3·89(d) *J*(HP) 2·5	*b*
(VII)	$[\pi\text{-}C_5H_4C(CF_3)_2OH]Ru(PPh_3)$ [d]	CO_2Me	H	CO_2Me	cyclic	6·63(s) 6·83(s)		3·92(d) *J*(HP) 3·0	*b*
(VI)	$(\pi\text{-}C_5H_5)Ru(PPh_3)$ [e]	CO_2Me	CO_2Me	$C_2H(CF_3)_2$	*cis*	6·45(s) 6·98(s)			*b*
	$(\pi\text{-}C_5H_5)_2Re$	CO_2Me	CO_2Me	H	*cis*	6·28(s)	(both)	3·52(s)	10
	$(\pi\text{-}C_5H_5)_2Re$	CO_2Me	H	CO_2Me	*trans*	6·08(s) 6·34(s)		3·06(s)	10
	$(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_7)Re$	CO_2Me	H	CO_2Me	cyclic	5·37(s) 6·70(s)		3·43(s)	10
	$(\pi\text{-}C_5H_5)_2MoH$	CO_2Me	CO_2Me	H	*cis*	6·46(s) 6·51(s)		3·83(s)	20
	$(\pi\text{-}C_5H_5)_2WH$	CO_2Me	CO_2Me	H	*cis*	6·50(s) 6·60(s)		4·00(s)	20
	$Mn(CO)_5$	CO_2Me	H	CO_2Me	*trans*	6·27(s)	(both)	2·93(s)	4
	$Mn(CO)_4$	CO_2Me	H	CO_2Me	cyclic	6·11(s) 6·19(s)		3·45(s)	4
	$Mn(CO)_4(PPh_3)$	CO_2Me	CO_2Me	H	*cis*	6·31(s) 6·84(s)		4·68(d) *J*(HP) 1·5	4
	$Mn(CO)_3(PPh_3)$	CO_2Me	H	CO_2Me	cyclic	6·41(s) 6·58(s)		3·81(d) *J*(HP) 4	4
	$Rh(CO)(PPh_3)_2$	CO_2Me	H	CO_2Me	*trans*	6·74(s) 6·98(s)		5·49(s)	5

[a] Other signals at τ 2·96(m) (P*Ph*$_3$), 6·10(s) (C_5H_5). [b] This work. [c] Other signals at τ 2·77(m) (P*Ph*$_3$), 5·67(s) (C_5H_5). [d] Other signals at τ 2·72(m) (P*Ph*$_3$), 2·85(s) (O*H*), 4·64(m), 5·54(m), 6·28(m) (C_5H_4). [e] Other signals at τ 2·73(m) (P*Ph*$_3$), 5·03(s) (C_5H_5).

Although no bis-insertion product analogous to (II) was obtained using $C_2(CO_2Me)_2$, the reaction of complex (IV) with hexafluorobut-2-yne afforded a new complex (VI) containing one molecule of each acetylene. In contrast (I) did not yield a new complex with $C_2(CO_2Me)_2$.

The i.r. spectrum of (VI) shows a broad band at 1703 cm^{-1}, assigned to the two ester carbonyl groups, and a weaker band at 1582 cm^{-1}, assigned to ν(C=C). Except for the additional signals due to the methoxycarbonyl groups, the ^{1}H n.m.r. spectrum is similar to that of complex (II), while the ^{19}F n.m.r. spectrum contains two resonances at 54·35 and 50·35 p.p.m. From these spectra, the coupling constant data indicated that the proton was attached to the same carbon atom as one of the CF_3 groups; phosphorus–fluorine coupling was also observed.

The mass spectrum of complex (VI) contained a parent ion, and fragmentation occurs by loss of OMe or of PPh_3, so that both ions $[(C_5H_5)Ru(PPh_3)(C_4F_6H)C_2(CO_2Me)CO]^+$ and $[(C_5H_5)Ru(C_4F_6H)C_2(CO_2Me)_2]^+$ are observed. The structure of (VI) is similar to that of complex (II), containing a σ-butadienyl group, also attached to the metal by a π-bond from the $CH(CF_3){=}C(CF_3)$ group.

Other Reactions.—Following the successful incorporation of a further molecule of an acetylene into complexes (I) and (IV), we examined the reaction between complex (IV) and another type of reactive fluorocarbon molecule, hexafluoroacetone. The product was a 1 : 1 adduct of stoicheiometry $(C_5H_5)Ru(PPh_3)[C_2(CO_2Me)_2H]$-$(CF_3)_2CO$ (VII) formed by loss of a triphenylphosphine molecule. The molecular structure has been confirmed recently by an *X*-ray diffraction study.[14]

Two strong bands in the i.r. spectrum of (VII) at 1571 and 1664 cm^{-1} can be assigned to the ester carbonyl group and to an unco-ordinated double bond respectively, while the OH group gives rise to a band at 3146 cm^{-1}. The ^{1}H n.m.r. spectrum (Table 2) shows resonances at τ 2·72 (m) (15H, P*Ph*$_3$), 6·63 (s) and 6·83 (s) (3H each,

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[11] D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 1765.

[12] W. D. Bannister, B. L. Booth, R. N. Haszeldine, and P. L. Loader, *J. Chem. Soc.* (*A*), 1971, 930.

[13] A. N. Nesmeyanov, V. S. Kaganovich, L. V. Rybin, P. V. Petrovskii, and M. I. Rybinskaya, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1971, 1536.

[14] T. Blackmore, M. I. Bruce, F. G. A. Stone, R. E. Davis, and N. V. Raghavan, *J. Organometallic Chem.*, 1973, **49**, C35.

O*Me*), and 2·85. That the latter was due to a hydroxyl proton was shown by shaking a solution with D_2O upon which the signal disappeared. Double and triple resonance experiments showed that a signal at τ 3·92 was independent of the others, and is therefore assigned to the methine proton. Resonances due to the substituted cyclopentadienyl group occur at τ 4·64, 5·54, and 6·28 (rel. int. 1 : 1 : 2) and were shown to be coupled together. Substitution of the cyclopentadienyl ring by the $C(CF_3)_2OH$ group and formation of the intramolecular hydrogen bond prevents rotation of the ring. The ^{19}F n.m.r. spectrum contains two signals of equal intensity at 75·6 (qd) and 77·95 (q) p.p.m. The observed deformation of the hydrogen-bonded ester group contributes to the non-equivalence of the two CF_3 groups, only one of which (75·6 p.p.m.) is coupled with one of the ring protons.

The mass spectrum of (VII) showed that the complex was monomeric in the vapour phase, notable ions including $[P - C_2(CO_2Me)_2]^+$, $[Ru(PPh_3)C_2(CO_2Me)H]^+$, and $[C_5H_4C(CF_3)_2OHRu]^+$, suggesting that the vinyl ester group remains as an intact unit, and that the C_5 ring has been substituted.

Complex (VII) thus can be considered to be formed by electrophilic substitution of the C_5 ring of the cyclic ester complex (V) by hexafluoroacetone. None of the cyclic complex (V) was isolated from the reaction, suggesting that the triphenylphosphine is displaced by cyclisation after or at the same time as ring substitution occurs. Although triphenylphosphine forms an adduct with hexafluoroacetone,[15] we did not isolate this compound from the reaction mixture. Electrophilic substitution of aromatic systems by hexafluoroacetone has been noted,[16] although strong Lewis acids are generally required to effect this reaction; other cyclopentadienyl systems such as ferrocene require vigorous conditions (*e.g.*, 180° for 15 days in dimethoxyethane with no added catalyst).[16b] In (V), the tendency toward substitution will be enhanced by the presence of the phosphine ligands, leading to an excess of electron density on the metal, and by back-bonding, on the C_5 ring carbon atoms.

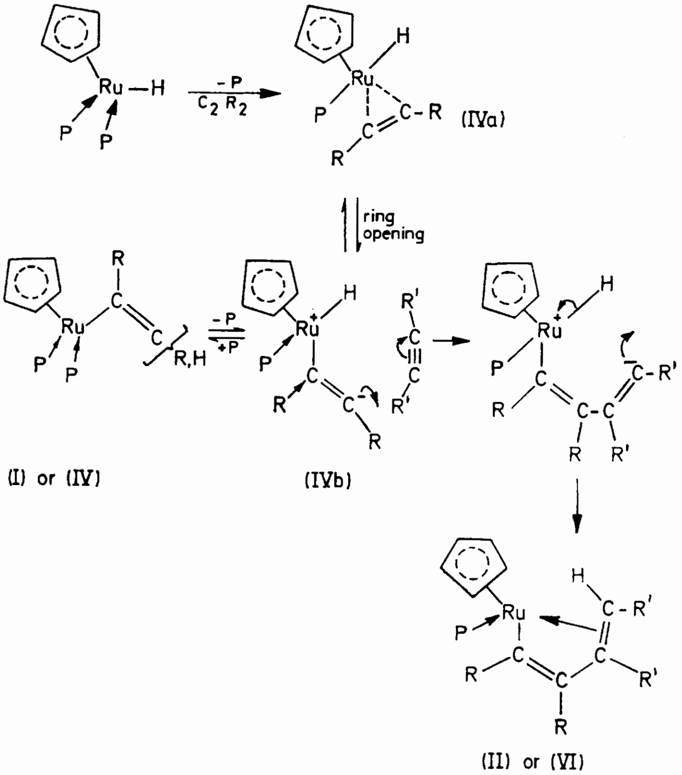
We have also examined the reaction between the hydride and the reactive olefin, $(CF_3)_2C{=}C(CN)_2$. On heating, a 1 : 1 adduct (VIII) is formed, which is a simple 1,2-insertion product. In the i.r. spectrum, a band at 2178 cm^{-1} is assigned to ν(CN). The ^1H n.m.r. spectrum contains resonances at τ 2·86 (m) (30H, P*Ph*$_3$), 5·89 (s) (5H, C_5H_5) and 7·26 [1H, $CH(CF_3)_2$]. The latter signal is a septuplet, the coupling of 8·2 Hz also being found in the CF_3 resonance which occurs at 68·3d p.p.m. in the ^{19}F n.m.r. spectrum. The mass spectrum contains ions formed by loss of CF_3, CN, HF, and PPh_3, although no parent ion was found. These data unambiguously establish the structure of the complex as the 1,1-bis(trifluoromethyl)-2,2-dicyanoethyl derivative shown.

DISCUSSION

Formation of complexes (I), (II), (IV), (VI), and (VIII) can be considered from two points of view. The first would envisage a straightforward *cis*-addition of the metal complex to the unsaturated molecule. However, this simple approach does not explain the possible formation of the *trans*-isomer (IV) from the diester. Although a simple *cis*-addition of the metal–alkenyl complex (I) across the acetylenic bond of $C_2(CF_3)_2$ would explain the formation of (II), two features point to the inadequacy of this simple explanation. So-called insertion reactions have not been described for metal–fluorocarbon σ-bonds, and more importantly, this type of reaction would not afford complex (VI). Instead the isomer formed would have been that in which the $C(CF_3){:}C(CF_3)$ moiety was adjacent to the metal. In an attempt to obtain this latter isomer, reaction between (I) and $C_2(CO_2Me)_2$ was investigated but only unreacted (I) was recovered.

A more detailed consideration of the mechanism of the 'insertion' reaction, shows that in many cases, a more accurate description is that of a hydride or alkyl migration to a co-ordinated unsaturated molecule. In the present case, we suggest that the first step involves co-ordination of the acetylene following dissociation of one of the phosphine ligands. We have previously noted[1] the ready displacement of one triphenylphosphine molecule by other, smaller donor ligands, such as CO or $PMePh_2$, probably for steric reasons.

The resulting π-complex (IVa) (see Scheme 1) then



SCHEME 1

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[15] F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, *Tetrahedron Letters*, 1966, 2151; R. F. Stockel, *ibid.*, p. 2833.

[16] (*a*) See C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, 1967, **1**, 168; (*b*) M. I. Bruce, B. J. Thomson, and F. G. A. Stone, unpublished results.

undergoes a hydride migration from the metal onto the β-carbon to give (I) or (IV), for example. This process may be facilitated by a partial opening of the three-membered ring to give a dipolar intermediate (IVb). Clark and Puddephatt [17] have reported the isolation of π-complexes of a related type from reactions between $PtClMeL_2$ (L = tertiary phosphine or arsine) and $C_2(CF_3)_2$, the structure of the adduct with L = $AsMe_3$ being confirmed by a single-crystal *X*-ray determination.[18] Subsequent reactions of this π-complex afford the *cis*-vinyl complexes. More recently, a free-radical mechanism has been proposed,[19] but we have no evidence for a reaction of this type.

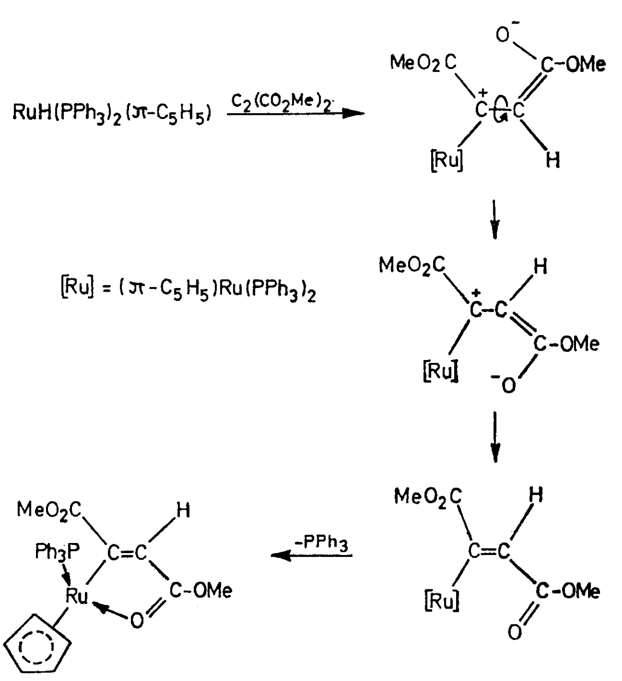
An attractive feature of our proposed mechanism is the explanation it offers for the formation of the bis-adducts. We suggest that the dipolar intermediate (IVb) mentioned above can under favourable circumstances attack a second molecule of acetylene in a nucleophilic reaction to give a butadienyl complex (see Scheme 1). If the second acetylene molecule differs from the first, as in the reaction between complex (IV) and $C_2(CF_3)_2$, the resulting product will retain the initial metal–carbon σ-bond, oligomerisation occurring *via* formation of a new carbon–carbon bond, as found in complex (VI).

We suggest that the hydride migration to and from the vinyl group, implied in the above mechanism, is related to the observation that on heating the σ-complex $Mo(H)[C(CO_2Me):CH(CO_2Me)](\pi\text{-}C_5H_5)_2$ affords the π-complex $Mo[\pi\text{-}CH(CO_2Me):CH(CO_2Me)](\pi\text{-}C_5H_5)_2$.[20]

A further example of a butadienyl-metal complex was reported after our initial communication, being obtained by acid cleavage of a palladiacyclopentadiene. In contrast to complexes (II) and (VI), the terminal double bond is not co-ordinated to the metal, being more nearly edge-on, with a possible Pd · · · H–C interaction with the vinylic proton.[21]

The probable difference in stereochemistry of the hydride adducts (I) and (IV), while explicable by arguments such as those above, may however indicate a different reaction mechanism. The *cis*-adduct can be formed by *cis*-addition to an initially formed π-complex, as discussed above; with the diester, however, *trans*-addition could result from direct attack of the ruthenium hydride on the acetylene, by a nucleophilic or free radical mechanism. The former has been suggested previously in a discussion of reactions between metal hydrides or anions and various fluorinated acetylenes.[22]

At this stage, we may also consider the problem of the structure of the methoxycarbonyl complexes. The earliest observations [10] on these complexes revealed their ready tendency to isomerise; moreover, the isolation of a *trans*-adduct from reactions of $C_2(CO_2Me)_2$ and related compounds with metal hydrides or alkyls is no proof that *trans*-addition occurs as the first step.[4,5] In the formation of (IV), a dipolar intermediate, with localisation of negative charge on the carbonyl oxygen rather than on the β-carbon atom (Scheme 2), would provide a ready mechanism for formation of the *trans*-isomer and for the *cis-trans*-isomerisations and cyclisations observed with complexes of this type, *viz.*



SCHEME 2

Some degree of stabilisation of the intermediate carbonium ion by the metal, perhaps involving some donation of electron density from the electron-rich metal centre, is to be expected, and could result in a lifetime long enough to allow rotation about the C–C bond as indicated. If a cyclic chelate complex, *e.g.* (V), can be formed, this factor may add to the driving force for the isomerisation. It is interesting to compare the structure of the proposed intermediate with those of several metal–carbene complexes which have been determined recently.[23]

EXPERIMENTAL

Spectra were recorded with Perkin-Elmer 257 (i.r.), Varian HA 100 (n.m.r.) and A.E.I. MS 902 (mass) instruments. Solvents were dried and distilled before use, and all reactions were routinely carried out under nitrogen. Chromatography was on columns of alumina (column A) or florisil (column F), initially packed in light petroleum.

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[18] B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Canad. J. Chem.*, 1972, **50**, 2276.

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[21] D. M. Roe, P. M. Bailey, K. Moseley, and P. M. Maitlis, *J.C.S. Chem. Comm.*, 1972, 1273.

[22] M. I. Bruce, D. A. Harbourne, F. Waugh, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 895.

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Analytical data are presented in Table 3, and various spectroscopic data are collected in Tables 1 and 2.

Reactions of $RuH(PPh_3)_2(\pi\text{-}C_5H_5)$.—(a) *With hexafluorobut-2-yne.* Hexafluorobut-2-yne (2·3 mmol), the complex hydride (300 mg, 0·45 mmol) and diethyl ether (35 ml) were sealed in a Carius tube at −196°, and left for 28 days at room temperature. The hydride quickly dissolved, and a clear golden-brown gel was formed. Extraction with ether, and slow addition of n-hexane to the concentrated extracts, gave a yellow crystalline solid. Recrystallisation from ether–n-hexane mixtures gave the *complex* $(\pi\text{-}C_5H_5)Ru(PPh_3)C_8F_{12}H$ (II) (39 mg, 12%), and the more soluble phosphorane $Ph_3P(C_4F_6)_2$ (III) (20 mg, 8%) identified by comparison with an authentic sample.[8]

In another experiment, hexafluorobut-2-yne (3 mmol), the hydride (400 mg, 0·58 mmol) and ether (25 ml) were sealed in a Carius tube and left for 6 days at room temperature. A golden-brown gel was produced as before, and this was evaporated to give a clear gel-like solid. Extraction with benzene, and evaporation gave an oily brown solid which was dissolved in dichloromethane and chromatographed (Column A). Elution with light petroleum gave a yellow band which was evaporated to an oily yellow solid. Crystallisation from light petroleum afforded yellow crystals of the *complex* $(\pi\text{-}C_5H_5)Ru(PPh_3)C_8F_{12}H$ (II) (44 mg, 10%). Benzene eluted a second yellow band. The solution was evaporated to dryness, and crystallisation from ether–n-hexane gave yellow crystals of the *complex* $CH(CF_3){:}C(CF_3)Ru(PPh_3)_2(\pi\text{-}C_5H_5)$ (I) (121 mg, 25%). In this experiment none of the cyclic compound $Ph_3P(C_4F_6)_2$ was isolated.

(b) *With dimethyl acetylenedicarboxylate.* Refluxing a mixture of $RuH(PPh_3)_2(\pi\text{-}C_5H_5)$ (300 mg, 0·45 mmol) and the acetylene diester (142 mg, 1 mmol) in ether (60 ml) for 5 h, followed by concentration of the solution and slow addition of n-hexane gave a pale yellow solid. Recrystallisation from an ether–n-hexane mixture gave yellow *crystals* of $(\pi\text{-}C_5H_5)Ru(PPh_3)_2C_2(CO_2Me)_2H$ (IV) (330 mg, 91%). Evaporation of the mother liquors gave an orange-red oil from which no further product could be obtained by crystallisation.

In another experiment, the hydride (600 mg, 0·92 mmol) and the diester (280 mg, 2·0 mmol) in ether (120 ml) were refluxed for 10 h. The orange-red solution was evaporated to a red oil. Crystallisation from ether–n-hexane mixtures gave a pale yellow *solid* which was recrystallised from ether–n-hexane, yielding (IV) (400 mg). The orange mother liquors were evaporated to give a red oil. This was dissolved in dichloromethane and chromatographed on alumina. Elution with benzene produced a red band which was evaporated to dryness and crystallised from light petroleum to give the red cyclic *complex* $(\pi\text{-}C_5H_5)Ru(PPh_3)C_2(CO_2Me)_2H$ (V) (23 mg, 4·6%). Elution with dichloromethane produced a yellow band which was evaporated to dryness and the solid crystallised from ether–n-hexane mixtures to afford a further batch of (IV) (130 mg), the total yield being 530 mg (74%).

TABLE 3

Analytical data

	Complex	M.p. (t/°C)	Found (Calculated) C	 H	 P	 F	 Other	M[a]
(I)	$(\pi\text{-}C_5H_5)Ru(PPh_3)_2C_4F_6H$	127—128 d	63·25 (63·25)	4·35 (4·25)	7·45 (7·25)	13·35 (13·35)		
(II)	$(\pi\text{-}C_5H_5)Ru(PPh_3)(C_4F_6)_2H$	194—196	49·65 (49·35)	2·9 (2·8)		30·1 (30·25)		754 (754)
(IV)	$(\pi\text{-}C_5H_5)Ru(PPh_3)_2C_2(CO_2Me)_2H$	158—160	67·85 (67·65)	5·2 (5·05)	7·5 (7·45)		(O) 7·85 (7·65)	
(V)	$(\pi\text{-}C_5H_5)Ru(PPh_3)C_2(CO_2Me)_2H$	126—127	60·75 (60·85)	4·75 (4·75)	5·4 (5·4)		(O) 11·1 (11·2)	572 (572)
(VI)	$(\pi\text{-}C_5H_5)Ru(PPh_3)(C_4F_6)[C_2(CO_2Me)_2]H$	151—152	54·15 (54·0)	3·8 (3·7)	4·1 (4·2)	15·45 (15·55)	(Ru) 13·65 (13·85)	734 (734)
(VII)	$[\pi\text{-}C_5H_4C(CF_3)_2OH]Ru(PPh_3)C_2(CO_2Me)_2H$	206—207	51·95 (52·05)	3·65 (3·70)	4·3 (4·2)	15·55 (15·45)		738 (738)
(VIII)	$(\pi\text{-}C_5H_5)Ru(PPh_3)_2C_2(CF_3)_2(CN)_2H$	181—182	62·3 (62·3)	4·15 (4·0)	6·75 (6·85)	12·6 (12·6)		

[a] Mass spectrometry.

(c) *With* 1,1-*dicyano*-2,2-*bis*(*trifluoromethyl*)*ethylene.* The olefin $(CF_3)_2C{=}C(CN)_2$ (250 mg, 1·17 mmol), and the hydride (400 mg, 0·58 mmol) in ether (40 ml) were refluxed for 1 h. A rapid colour change and apparent decomposition was observed. Evaporation of solvent was followed by chromatography in dichloromethane (Column A). Elution with benzene–dichloromethane mixtures (1 : 1) gave a yellow band from which the *complex* (VIII) (62 mg, 11%) was isolated by evaporation of solvent and crystallisation from ether–n-hexane mixtures. Methanol eluted a brown band which gave an intractable oil on evaporation and was discarded.

Reactions of Complex (*IV*).—(a) *With hexafluorobut-2-yne.* Hexafluorobut-2-yne (1·92 mmol), complex (IV) (400 mg, 0·48 mmol) and ether (30 ml) were sealed in a Carius tube and left at 60° for 10 days. The resulting orange gel was evaporated to dryness and extracted with dichloromethane. The filtered extracts were evaporated to *ca.* 4 ml and chromatographed (Column A). Elution with benzene gave an orange band which was collected, evaporated to dryness, and crystallised from light petroleum to give red crystals of the cyclic complex (V) (66 mg, 24%). Dichloromethane eluted an orange-yellow band which on evaporation gave an oily orange solid. Crystallisation from ether–n-hexane mixtures gave orange *crystals* of (VI) (74 mg, 21%).

(b) *With hexafluoroacetone.* Complex (IV) (480 mg, 0·58 mmol), hexafluoroacetone (2·9 mmol), and benzene (15 ml) were sealed in a Carius tube at −196° and then left in a 100° oven for 3 days. The tube was opened and the red solution was evaporated to a small volume and chromatographed (Column A). A single orange band was eluted from the column (benzene). Evaporation of solvent followed by crystallisation from an ether–n-hexane mixture gave the *complex* (VII) (307 mg, 72%).

Reaction of Complex (I) *with Hexafluorobut-2-yne.*—Complex (I) (46 mg, 0·054 mmol), hexafluorobut-2-yne (0·54 mmol), and ether (10 ml) were sealed in a Carius tube, left at room temperature for 14 days and then transferred to a 50° oven for 2 days. The tube was opened and the solvent removed by evaporation. Extraction with benzene followed by evaporation gave an oily solid, which was dissolved in dichloromethane and chromatographed (Column A). Elution with light petroleum–benzene gave a yellow solution from which (II) (7·2 mg, 18%) and $Ph_3P(C_4F_6)_2$ (3·1 mg, 10%) were obtained by evaporation of the solution and careful crystallisation from ether–n-hexane mixtures.

Pyrolysis of the Complex (IV).—The compound (110 mg, 0·13 mmol) in benzene (50 ml) was refluxed for 24 h to give an orange-red solution. Evaporation, extraction with dichloromethane and chromatography gave triphenylphosphine (20 mg, 58%) eluted with light petroleum, the complex (V) (43 mg, 39%) eluted with benzene, and unchanged starting material (45 mg, 60%) eluted with dichloromethane.

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