Cyclopentadienyl-ruthenium and -osmium Chemistry. Part 6.[1] Reactions of Alkylruthenium Complexes with Disubstituted Acetylenes

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Hexafluorobut-2-yne reacts with $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ in benzene to give the butadienyl complex $[Ru\{C(CF_3){:}C(CF_3)\cdot C(CF_3){:}CMe(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)]$. Using 1,2-dimethoxyethane as solvent, the vinyl complex $[Ru\{C(CF_3){:}CMe(CF_3)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ has been isolated. With $C_2(CF_3)_2$, the carbonyl complex $[RuMe(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ affords a diruthenium complex formulated as $[(\eta\text{-}C_5H_5)(OC)(Ph_3P)Ru\{C(CF_3){:}C(CF_3)\}Ru(CO)(\eta\text{-}C_5H_4\cdot C_6H_4\cdot PPh_2)]$, and the benzyl complex $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$ gives a product assigned a structure $[Ru\{CH_2C_6H_4\cdot C(CF_3){:}C(CF_3)H\}(PPh_3)(\eta\text{-}C_5H_5)]$. Dimethyl acetylenedicarboxylate reacts with $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ to give $[Ru\{C(CO_2Me){:}C(CO_2Me)\cdot C(CO_2Me){:}CMe(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)]$, $[Ru\{\eta^5\text{-}C_5(CO_2Me)_4H_3\}(\eta\text{-}C_5H_5)]$, and $[Ru\{C(CO_2Me){:}C(Me)\cdot C(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)]$; an analogous product to the latter is obtained from $C_2(CO_2Me)_2$ and $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$. The hydrido-complex $[RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ reacts with the acetylenic diester to give $[Ru\{C(CO_2Me){:}C(CO_2Me)H\}(PPh_3)_2(\eta\text{-}C_5H_5)]$, which reacts further with $C_2(CF_3)_2$ to give a ruthenocene derivative $[Ru\{\eta^5\text{-}C_5(CO_2Me)_2(CF_3)_2(OMe)\}(\eta\text{-}C_5H_5)]$. 4-Phenylbut-3-yn-2-one and $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ afford $[Ru\{C(Ph){:}C(Me)\cdot C(O)Me\}(PPh_3)(\eta\text{-}C_5H_5)]$ and $[Ru\{C(Ph){:}C\cdot C(O)\cdot CH_2\cdot C(Ph){:}C\cdot C(O)Me\}(PPh_3)(\eta\text{-}C_5H_5)]$.

WE have previously described[1-4] reactions of several ruthenium complexes $[RuR(PPh_3)_2(\eta\text{-}C_5H_5)]$ (R = H, Me, or CH_2Ph) with mono- and di-substituted acetylenes which afford complexes with vinyl, vinylidene, butadienyl, hexatrienyl, or cumulenyl groups σ-bonded to ruthenium. Where the organic substituent contains four or more carbon atoms, cyclisation occurs *via* η^2-bonding of one of the double bonds of the chain to ruthenium. Formation of many of the unusual products has been rationalised by postulating ready dissociation from the metal of one of the triphenylphosphine ligands, thereby providing a site for co-ordination of an acetylene molecule, and subsequent involvement of dipolar intermediates. In this paper we report additional studies in this area.

RESULTS

(a) *Hexafluorobut-2-yne (hfb).*—In benzene at 100 °C, hfb reacted with $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ to give the bis-insertion product (1) in low yield. This complex is the methyl analogue of one of the products obtained from $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$ and hfb, the molecular structure of which was established by *X*-ray crystallography.[4] However, with the hydridoruthenium complex a vinyl derivative $[Ru\{C(CF_3){:}C(CF_3)H\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ was also obtained. In contrast, no mono-insertion product was observed with $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ and hfb. The ^{19}F n.m.r. spectrum of (1) is very similar to that of $[Ru\{C(CF_3){:}C(CF_3)\cdot C(CF_3){:}C(CF_3)H\}(PPh_3)(\eta\text{-}C_5H_5)]$ showing four resonances. In the mass spectrum of (1) the ion at highest *m/e* (Table 1) corresponds to $[\text{Parent} - PPh_3]^+$.

When the reaction was carried out in 1,2-dimethoxyethane at 50 °C, surprisingly, a monocarbonylruthenium complex (2) [$\nu_{max.}$(CO) at 1 896, $\nu_{max.}$(C:C) at 1 576 cm^{-1}] was formed. In the ^1H n.m.r. a singlet resonance could be assigned to the methyl group. The mass spectrum of (2) contained a weak P^+ ion, together with other ions formed by loss of CO, CH_4, and C_4F_6. The two ^{19}F signals were broad, lack of any appreciable F–F coupling (double irradiation) suggesting a *trans* arrangement of the CF_3 groups. The formation of a *trans* adduct in this reaction contrasts with other reactions of related complexes with hfb, which have afforded the *cis*-vinyl complexes, and suggests that a different reaction pathway is followed.

Formation of (2), which occurs in low yield (*ca.* 6%), is probably due to the presence of traces of water in the dimethoxyethane. We have previously observed[5] a similar degradation of hfb on iridium in the reaction of $[IrCl(\eta\text{-}CF_3C_2CF_3)(PPh_3)_2]$ with water to give $[IrCl(CO)(PPh_3)_2]$. Interestingly, the monocarbonyl complex $[RuMe(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ does not react with hfb to give (2). No reaction occurs at 50 °C in 1,2-dimethoxyethane over a period of days. However, at 100 °C, a yellow crystalline diruthenium complex (3) is formed, characterised by analysis, the molecular ion in the mass spectrum, and i.r. and n.m.r. spectra. The i.r. spectrum shows bands at 1 938, 1 925 (CO), 1 610 (C:C), 1 250—1 100 (CF), and at 1 096 cm^{-1} (*ortho*-disubstituted phenyl[3]). In the ^1H n.m.r. spectrum the aromatic multiplet has a relative intensity of 29, and there are five signals for cyclopentadienyl protons (5 : 1 : 1 : 1 : 1). The two quartets in the ^{19}F spectrum indicate that the CF_3 groups are mutually *cis*. These spectral data can be accommodated by the structure shown. The chelating $\eta\text{-}C_5H_4C_6H_4PPh_2$ ligand has been previously established by *X*-ray crystallography in $[Ru(C_6F_4N{:}NC_6F_5)(\eta\text{-}C_5H_4C_6H_4PPh_2)]$ in earlier work[6] involving $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$.

Hexafluorobut-2-yne and the benzyl complex $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$ react to give lemon-yellow crystals of (4).[7] Characteristic features in the i.r. and ^1H and ^{19}F n.m.r.

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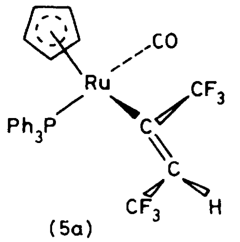
TABLE 1

Melting-point, analytical, and molecular-weight data

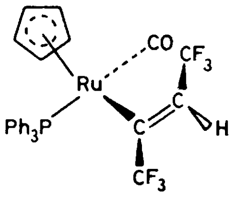
Complex	M.p. (θ_c/°C)	Analysis (%)[a] C	H	P	F	M[a,b]
(1)	160—165 (decomp.)					506[c] (768)
(2)	145—150 (decomp.)	52.7 (54.8)	3.15 (3.6)	4.6 (4.9)	16.8 (17.6)	
(3)	237—239	58.2 (58.1)	3.5 (3.6)	5.5 (5.8)		1 074 (1 074)
(4)	200—205 (decomp.)	58.9 (59.8)	3.9 (4.0)	4.7 (4.6)	17.6 (16.7)	682 (682)
(5)	190—191	54.6 (54.4)	3.4 (3.4)	5.0 (5.0)	18.6 (18.4)	620 (620)
(6)	152—154	59.4 (59.4)	5.0 (4.9)	2.9 (4.3)	18.3[d] (17.6)	466[c] (728)
(7)[e]	177—178	46.1 (46.5)	4.4 (4.4)		28.4[d] (27.5)	466 (466)
(8)	180—185 (decomp.)	61.5 (61.6)	5.0 (5.0)	5.3 (5.3)		586 (586)
(9)	204—206					662[c] (924)
(10)	182—184	65.6 (65.4)	5.1 (5.1)	5.2 (4.7)	10.0[d] (9.7)	662 (662)
(11)	142—144	60.3 (60.3)	4.6 (4.6)	5.3 (5.2)		572[f] (600)
(12)	116—119	39.9 (39.8)	2.7 (2.8)			514 (514)
(13)	168—170	69.7 (69.4)	5.5 (5.3)	5.0 (5.3)		588 (588)
(14)	240—243	71.8 (72.2)	5.1 (5.0)	4.7 (4.3)		

[a] Calculated values are given in parentheses. [b] Mass spectrometry, based on ^{102}Ru. [c] $[P - PPh_3]^+$. [d] Oxygen. [e] Ru, 18.7 (21.7%). [f] $[P - CO]^+$.

spectra of this complex include a band at 1 643 cm^{-1} (C:C), resonances at τ 6.78 and 8.86 assignable to a highly asymmetric benzylic methylene group, and two CF_3 resonances [47.1 and 59.9 p.p.m., with J(FF) 11.0 Hz] indicating a *cis*-$C(CF_3){:}C(CF_3)$ group. Reaction between hfb and $[RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ gives the vinyl adduct (5), paralleling formation of $[Ru\{C(CF_3){:}C(CF_3)H\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ from $[RuH(PPh_3)_2(\eta\text{-}C_5H_5)]$.[2] Complex (5) shows bands in the i.r. spectrum at 1 970 (CO) and 1 600 (C:C) cm^{-1} and in the ^{1}H n.m.r. a vinylic proton resonance (τ 3.35) with *gem*- and *cis*-fluorine couplings. Both the ^{1}H and ^{19}F n.m.r. spectra are temperature dependent, the low-temperature limiting spectra being obtained at *ca.* −95 °C, although the onset of crystallisation at this temperature resulted in loss of resolution. At < -60 °C four CF_3 resonances are observed, and these can be assigned to two isomeric complexes present in a 6 : 1 ratio. The complex present in major amount gives two resonances at 53.3 and 55.6 p.p.m., the low-field signal being coupled to the vinylic proton [J(HF) 9.0 Hz]. Proton decoupling gave two multiplets, approximately distorted quartets, with J(FF) 2.0 Hz. No ^{19}F–^{31}P coupling could be detected. The minor isomer is responsible for signals at 54.9 and 58.7 p.p.m., the former changing on irradiation of the vinyl proton, removing a coupling of *ca.* 6 Hz. The remaining fine structure arises from phosphorus coupling [J(HP) *ca.* 6 Hz]. At >80 °C the high-temperature limiting spectrum consists of a doublet of multiplets at 56.7 p.p.m., and a multiplet at 57.1 p.p.m. The ^{1}H n.m.r. spectrum does not change on heating, but at < -60 °C the cyclopentadienyl proton resonance at τ 4.86 is replaced by signals at τ 4.79 and 4.60, also with intensity ratio 6 : 1.



(5a)



(5b)

We believe that the dynamic process involves a sterically hindered rotation of the vinylic groups about the Ru–C bond, giving a pair of conformational isomers. A similar process has been described[8] for the complex $[MoH\{C(CF_3){:}C(CF_3)H\}(\eta\text{-}C_5H_5)_2]$ where the n.m.r. parameters resemble those found in the present case. The two isomers of the molybdenum complex are still observable at room temperature, and the limiting population differs. Structures (5a) and (5b) represent conformational isomers of the ruthenium complex, and the proximity of the CF_3 group to PPh_3 in (5a) perhaps suggests that this is the minor isomer.

(b) *Dimethyl Acetylenedicarboxylate* (*dma*).—Excess of dma reacts with $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ in refluxing diethyl ether to give four products. Two of these were identified as the organic compounds dimethyl fumarate and hexamethyl benzenehexacarboxylate by comparison with authentic samples. The other two products are assigned

TABLE 2

N.m.r. data [chemical shifts in τ (^1H) or p.p.m. upfield from $CFCl_3$ (^{19}F); coupling constants in Hz] in $CDCl_3$ unless stated otherwise

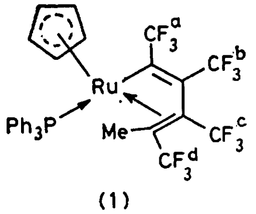
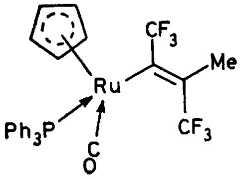
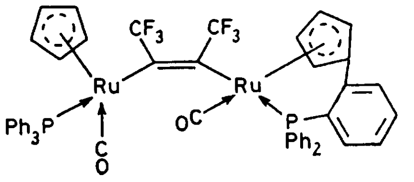
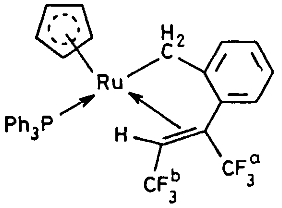
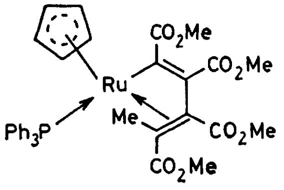
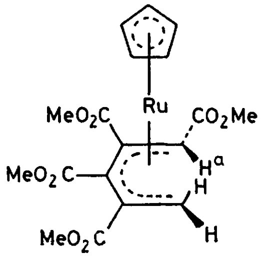
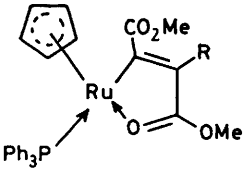
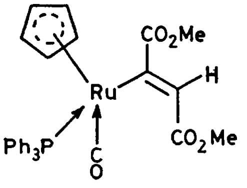
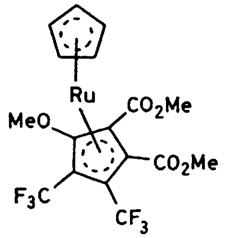
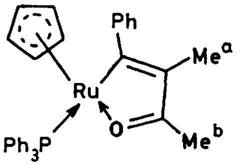
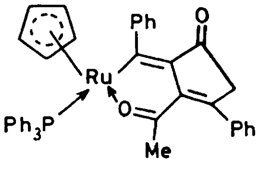
 (1)	2.58 (m)	Ph		
	5.02 (s)	C_5H_5		
	8.65 (d)	Me	J(PH)	9.0
	57.8 (m)	CF^a_3	$J(F^aF^b)$	10.8
	65.0 (q)	CF^b_3		
	56.2 (m)	CF^c_3	$J(F^cF^d)$	9.1
	49.4 (q)	CF^d_3		
 (2)	2.66 (m)	Ph		
	4.82 (s)	C_5H_5		
	8.77 (s,br)	Me		
	50.6 (m)	CF_3		
	51.5 (m)	CF_3		
 (3)	2.67 (m)	Ph		
	4.91 (s)	C_5H_5		
	4.80 (m), 4.94 (m), 5.18 (m), 6.10 (m)	C_5H_4		
	57.1 (q)	CF_3	J(FF)	9.0
	64.1 (q)	CF_3		
 (4) [in $(CD_3)_2CO$]	6.78 (d), 8.86 (d)	CH_2	J(HH)	17.5
	7.81 (dq)	$CH(CF_3)$	J(HF)(*gem*) J(PH)	11.0 16.0
	47.1 (q)	CF^b_3	J(HF)	11.0
	59.9 (q)	CF^a_3	J(FF)	11.0
 (6)	2.72 (m)	Ph		
	5.84 (s)	C_5H_5		
	6.25 (s), 6.31 (s), 7.08 (s), 7.11 (s)	CO_2Me		
	8.10 (s)	Me		
 (7) (in PhCl)	4.95 (s)	C_5H_5		
	6.14 (d), 9.00 (d)	CH_2	J(HH)	4
	6.22 (s), 6.24 (s), 6.36 (s), 6.37 (s)	CO_2Me		
	9.20 (s)	H^a		

TABLE 2 (*Continued*)

 (8) R = Me (9) R = CH$_2$Ph	R = Me			
	2.73 (m)	Ph		
	5.62 (s)	C$_5$H$_5$		
	6.50 (s, 6.76 (s)	CO$_2$Me		
	8.47 (d)	Me	*J*(PH)	1.5
	R=CH$_2$Ph			
	2.9 (m)	Ph		
	3.6 (m)	CH$_2$*Ph*		
	5.22 (s)	C$_5$H$_5$		
	6.47 (s), 6.51 (s)	CO$_2$Me		
	7.00 (d), 7.43 (d)	C*H*$_2$Ph	*J*(HH)	15.5
 (11) [in (CD$_3$)$_2$CO]	2.61 (m)	Ph		
	4.95 (s)	C$_5$H$_5$		
	6.44 (s), 7.11 (s)	CO$_2$Me		
	3.50 (d)	:CH	*J*(PH)	2.0
 (12)	5.03 (s)	C$_5$H$_5$		
	6.17 (s), 6.18 (s)	CO$_2$Me		
	6.22 (s)	OMe		
	53.7 (q)	CF$_3$	*J*(FF)	8.8
	54.8 (q)	CF$_3$		
 (13)	2.73 (m)	Ph		
	5.69 (s)	C$_5$H$_5$		
	8.48 (d)	Me(a)	*J*(PH)	~0.8
	8.51 (d)	Me(b)	*J*(PH)	2.6
 (14)	2.66 (m)	Ph		
	5.59 (s)	C$_5$H$_5$		
	7.26 (d), 7.60 (d)	CH$_2$	*J*(HH)	15.0
	8.56 (d)	Me	*J*(PH)	2.5

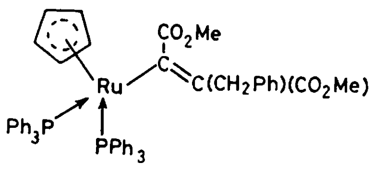
the butadienyl structure (6) and the η^5-pentadienyl structure (7), respectively. The former is believed to have a 1-σ,3—4-η^2-butadienyl structure mainly on the basis of its i.r. spectrum, which has bands at 1 653 and 1 620 (C:C) and at 1 704 and 1 690 cm^{-1} (C:O), but none between 1 500 and 1 600 cm^{-1} characteristic of co-ordinated ester CO groups. In the mass spectrum, the highest observable ion is at *m/e* 466, formed by loss of PPh$_3$ from the parent ion. The formation of (6) contrasts with the previously described [2] reaction between dma and [RuH(PPh$_3$)$_2$(η-C$_5$H$_5$)] from which only mono-insertion products were obtained, including one in which an oxygen of a terminal CO$_2$Me group is co-ordinated to ruthenium.

Complex (7) was isolated from the initial reaction in 1% yield, but on changing the solvent to refluxing 1,2-dimethoxyethane the yield increased to *ca.* 15%. The i.r. spectrum has four strong bands at 1 739, 1 730, 1 721, and 1 699 cm^{-1} (C:O), and a weak absorption at 1 659 cm^{-1} (C:C), but there are no bands in the 1 500—1 600 cm^{-1} region. The ^{1}H n.m.r. spectrum supports the proposed structure. There are five singlet signals (5 : 3 : 3 : 3 : 3) assignable to η-C$_5$H$_5$ and OMe groups, together with a doublet and a singlet resonance corresponding to 1 H each. In benzyl chloride solution a further resonance is observed, which is masked by the OMe resonances in CDCl$_3$ or (CD$_3$)$_2$CO solutions.

It seems likely that (7) forms *via* (6) and that the ruthenium promotes transfer of hydrogen from the methyl group to the other end of the butadienyl chain. The resulting ligand must be formally a five-electron donor, and the seven substituents restrict this to an acyclic pentadienyl system. The structure of (7) has recently been confirmed by an *X*-ray diffraction study.[9] The high shift of the *endo*-proton (τ 9.20) probably arises from extensive shielding by the metal atom. The mass spectrum is similar to that of (6), with the exception that there are no peaks resulting from fragmentation of PPh_3. Indeed, the observation that the highest *m/e* ion in the spectrum of (6) is $[P - PPh_3]^+$ suggests that thermal decomposition occurs on the probe to give (7) and free triphenylphosphine. In both spectra, a prominent ion is formed by loss of the fragment HCO_2Me, *i.e.* $[Ru(C_5H_5)\{C_4(CO_2Me)_3CH_2\}]^+$, further suggesting cleavage of the methyl group into $(CH_2 + H)$ components.

When 1,2-dimethoxyethane at reflux is used as solvent for the reaction of $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ with dma a third ruthenium complex (8) was isolated in low yield (*ca.* 2%). It is assigned the cyclic structure shown on the basis of i.r. bands due to free (1 695 cm^{-1}) and co-ordinated (1 576 cm^{-1}) ester CO groups, a C:C group (1 564 cm^{-1}), and the similarity of the ^1H n.m.r. spectrum to previously described [2] $[Ru\{C(CO_2Me){:}CH{\cdot}C(OMe){:}O\}(PPh_3)(\eta\text{-}C_5H_5)]$.

The benzyl complex $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$ reacts with dma in 1,2-dimethoxyethane to give the yellow crystalline complex (9), together with small amounts of its precursor (10), which readily loses PPh_3 to afford the chelate complex. The i.r. spectrum of (9) showed bands at 1 724s and 1 573 cm^{-1} (free and co-ordinated CO, respectively), and at 1 590w cm^{-1} (C:C), while for (10) bands occur at 1 702 (C:O) and 1 582 cm^{-1} (C:C). In the reaction between dma and $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$ there was also spectroscopic evidence for the formation of a complex $[Ru\{\eta^5\text{-}CH(CO_2Me)[C(CO_2Me)]_3CHPh\}(\eta\text{-}C_5H_5)]$ analogous to (7) (see Experimental section).



(10)

The pale yellow vinyl complex (11) [$\nu_{max.}$ at 1 951 (CO), 1 720, 1 689 (C:O), and 1 564 cm^{-1} (C:C)] is formed from $[RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ and dma in refluxing 1,2-dimethoxyethane. This complex is tentatively assigned the *trans* structure shown on the basis of the ^{31}P–^1H coupling (2 Hz) of the vinylic proton. In $[Ru\{trans\text{-}C(CO_2Me){:}C(CO_2Me)H\}(PPh_3)_2(\eta\text{-}C_5H_5)]$, *J*(PH) is *ca.* 1 Hz.[2]

Reaction between (11) and hfb afforded the ruthenocene derivative (12) [$\nu_{max.}$(C:O) at 1 728 cm^{-1}]. The n.m.r. data are in accord with the structure proposed, and the mass spectrum showed a parent ion (*P*) and ions corresponding to $[P - F]^+$, $[P - OMe]^+$, $[P - CO_2Me]^+$, $[P - CO_2Me - COMe]^+$, and $[Ru\{C_2(CO_2Me)_2\}(C_5H_5)]^+$.

(c) *4-Phenylbut-3-yn-2-one.*—The complex $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ reacts with PhC:CC(O)Me to afford a bright red complex (13) and a dark red compound (14). The i.r. bands observed in the spectrum of (13) at 1 594 and 1 572 cm^{-1} are assigned to C:C and co-ordinated CO, respectively. In the ^1H n.m.r. the two Me resonances are distinguished by coupling of Me^b to phosphorus [*J*(PH) 2.6 Hz, *cf.* the related complex [3] obtained from HC:CC(O)Me which has a corresponding *J*(PH) 2.5 Hz].

The i.r. spectrum of (14) contains a carbonyl band at 1 745 cm^{-1} which is at a higher frequency than that found in PhC:CC(O)Me, and suggests formation of a cyclic ketone or lactone. Other strong i.r. bands occur at 1 603 (C:C) and 1 584 cm^{-1} (co-ordinated C:O). The ^1H n.m.r. spectrum is as expected for the structure proposed, notable features including the resonances due to an asymmetric CH_2 group and the coupling between the acyl methyl protons and phosphorus. The mass spectrum shows ions corresponding to P^+, $[P - CO]^+$, $[P - PPh_2]^+$, and $[P - PPh_3 - COMe]^+$. The proposed structure of (14) contains a ligand formed by condensation of the two molecules of the acetylene.

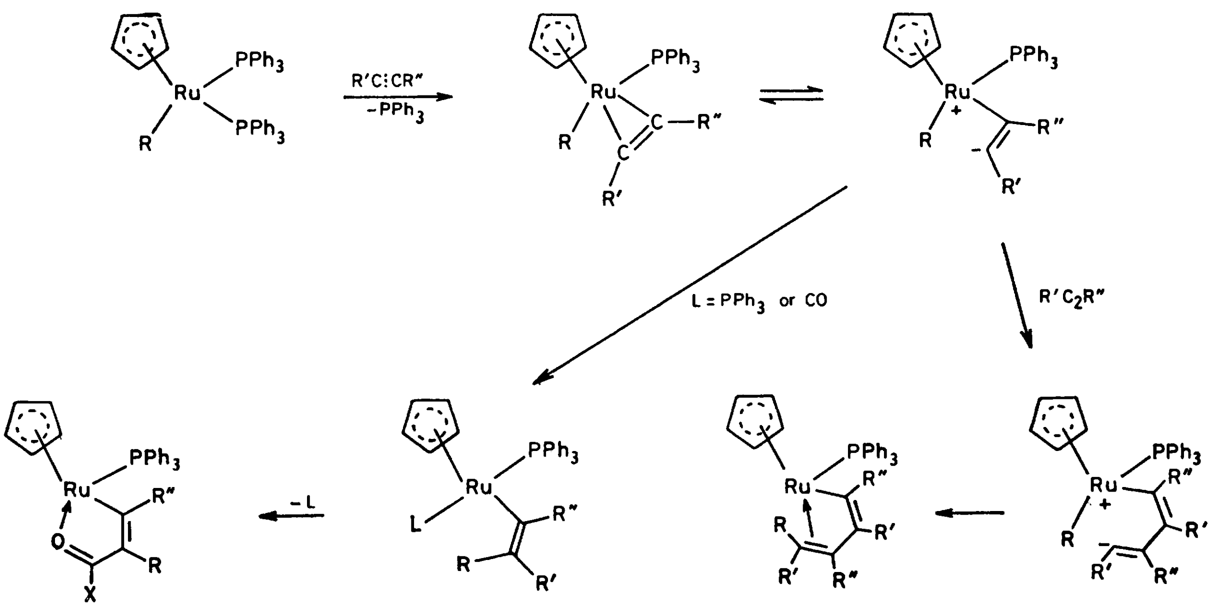
DISCUSSION

Oligomerisation of alkynes with transition-metal complexes is generally considered to proceed *via* initial formation of η^2-alkynemetal complexes or alternatively ' metallacyclopropenes '. Further reactions with alkyne molecules bearing electronegative substituents have been rationalised on the basis of the initial complex acting as a 1,3-dipole which may react with a second molecule of alkyne.[2,10] Many of the new compounds described in this paper can be accounted for on the basis of these ideas (Scheme 1); for example, formation of the vinyl derivatives (2), (5), (10), and (11), and the 1-σ,3—4-η^2-butadienyl complexes (1) and (6). Co-ordination of a carbonyl group as in (8), (9), (13), and (14) has several precedents.[2]

Possible routes to some of the unusual complexes (3), (4), (7), and (12) merit comment. Addition of metal alkyls to hfb to afford dimetal complexes such as (3) has been described previously for the gold complexes $[AuMe(PPhR_2)]$ (R = Me or Ph). For R = Ph, the complex $[(Ph_3P)Au\{C(CF_3){:}C(CF_3)\}Au(PPh_3)]$ was isolated.[11] However, with R = Me, an intermediate Au^I–Au^{III} complex was characterised and it was established [12] that formation of the final Au^I–Au^I product involved transfer of a methyl group from one gold atom to the other, followed by reductive elimination from the Au^{III} centre. This leads us to propose that formation of complex (3) proceeds *via* an unstable Ru^{II}–Ru^{IV} intermediate (Scheme 2), subsequent elimination of methane causing cyclometallation through a well established pathway.[13] This could be followed by phenyl-group migration from the Ru^{IV} centre to the cyclopentadienyl ring with concomitant loss of a second molecule of methane. Migration of aryl groups from metal to dienyl ligands [14,15] and linkage [6] of $C_6H_4PPh_2$ and $\eta\text{-}C_5H_5$ moieties has been previously observed.

Formation of (4) appears to be an example of a new reaction type involving activation of an σ-benzyl group, and is formally akin to metallation followed by insertion of hfb.

As mentioned above, formation of (13) is readily explicable *via* a conventional insertion reaction. However, speculation on the mode of formation of (14) seems unwarranted at this time. The mechanism of formation of the triphenylphosphine-free complexes (7) and (12) is



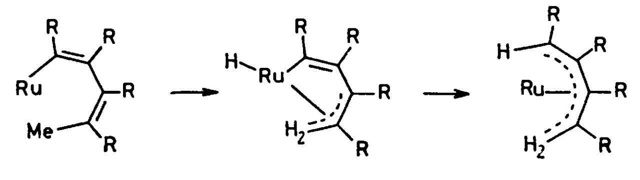
	R	R″	X
(8)	Me	CO$_2$Me	OMe
(9)	CH$_2$Ph	CO$_2$Me	OMe
(13)	Me	Ph	Me

	R	R′ = R″	L
(2)	Me	CF$_3$	CO
(5)	H	CF$_3$	CO
(10)	CH$_2$Ph	CO$_2$Me	PPh$_3$
(11)	H	CO$_2$Me	CO

	R	R′ = R″
(1)	Me	CF$_3$
(6)	Me	CO$_2$Me

SCHEME 1

also not clear but the most likely route to (7) *via* (6) is through an (η^3-allyl)hydridoruthenium(IV) species:

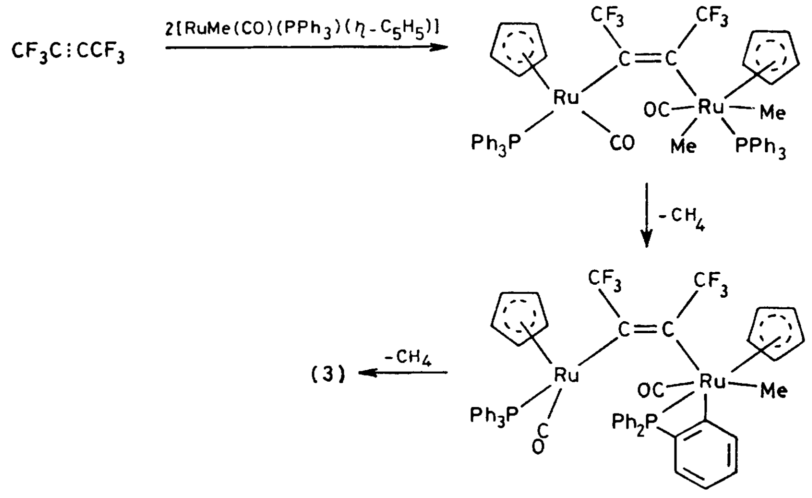


(6) Ru≡Ru(PPh$_3$)(η-C$_5$H$_5$)
R = CO$_2$Me

(7)

There are relatively few known acyclic η^5-pentadienyl metal complexes such as (7), and we are not aware of any produced by oligomerisation of an alkyne.

There are several examples of formation of η-cyclopentadienyl complexes from reactions of alkynes with transition-metal complexes,[16] but perhaps the closest analogy to the synthesis of complex (12) is the reaction of [{Fe(CO)$_2$(η-C$_5$H$_5$)}$_2$] with hfb which affords a ferracyclohexadienone complex identified by an *X*-ray diffraction study.[17] We do not favour a formulation for (12) involving acylbutadienyl or oxocyclohexadienyl ligands since the i.r. spectrum shows no acyl stretching frequency and the chemical shift of the Me protons is characteristic of an OMe rather than a CMe group. Structures containing acylbutadienyl and oxocyclohexadienyl ligands have been proposed or considered for products obtained from the reactions of [FeMe(CO)$_2$(η-C$_5$H$_5$)] and hfb.[17]



SCHEME 2

EXPERIMENTAL

Spectra were recorded on Perkin-Elmer 257 and 457 (i.r.), Varian Associates HA100 (^{1}H n.m.r. at 100 MHz; ^{19}F n.m.r. at 94.1 MHz), or A.E.I. MS902 instruments (mass at 70 eV *). Solvents were dried and distilled before use, and all reactions were carried out under an atmosphere of nitrogen. Chromatography was on columns of alumina or Florisil (columns A and F, respectively), initially packed in light petroleum (b.p. 40—60 °C). Analytical data for the new compounds are given in Table 1. Infrared spectra were obtained from Nujol mulls, except for those of the ν(CO) region [complexes (2), (3), and (11)], which were obtained from cyclohexane solutions.

Ruthenium complexes used as precursors were prepared as described previously, $[\mathrm{RuR(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (R = H,[18] Me,[2] or $\mathrm{CH_2Ph}$ [3]), or as follows.

(*a*) $[\mathrm{RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$.—The complex $[\mathrm{RuCl(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$ (0.98 g, 2.0 mmol) in 1,2-dimethoxyethane (100 cm^3) was treated with $\mathrm{Na[BH_4]}$ (0.28 g, 10 mmol), and the mixture was heated under reflux for 18 h. After filtration, and evaporation to dryness, the residue was extracted with benzene until colourless. Evaporation of the extract and recrystallisation from diethyl ether gave pale yellow *crystals* of $[\mathrm{RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$ (0.75 g, 83%), m.p. 125—127 °C (Found: C, 63.0; H, 4.6. Calc. for $\mathrm{C_{24}H_{21}OPRu}$: C, 63.1; H, 4.7%).

Alternatively, the complex could be prepared (210 mg, 70%) by treating $[\mathrm{Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (0.5 g, 0.64 mmol) in 1,2-dimethoxyethane (60 cm^3) with formaldehyde (20 cm^3, 37% w/v with MeOH). The mixture was treated under reflux for 18 h, filtered, and evaporated. The *product* was extracted with benzene and recrystallised from diethyl ether.

(*b*) $[\mathrm{RuMe(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$.—The complex $[\mathrm{RuMe(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (0.5 g, 0.71 mmol) in benzene (50 cm^3) was carbonylated (150 atm, 70 °C, 72 h). The solution was filtered, evaporated, and chromatographed (column F). Elution with benzene and recrystallisation from diethyl ether–light petroleum mixtures afforded pale yellow *crystals* of $[\mathrm{RuMe(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$ (121 mg, 36%), m.p. 206—209 °C (Found: C, 63.7; H, 5.1; O, 3.5; P, 5.4. Calc. for $\mathrm{C_{25}H_{23}OPRu}$: C, 63.7; H, 5.0; O, 3.4; P, 6.5%).

Reactions of Hexafluorobut-2-yne (hfb).—(*a*) *With* $[\mathrm{RuMe(PPh_3)_2(\eta\text{-}C_5H_5)}]$. The methyl complex (500 mg, 0.71 mmol) was heated with hfb (3.6 mmol) and benzene (10 cm^3) in a Carius tube for 3 d at 100 °C and left for 7 d at room temperature. The reaction mixture was filtered, evaporated to a small volume, and chromatographed (column F). A pale yellow fraction was eluted with diethyl ether–light petroleum (1 : 9), which from light petroleum yielded pale yellow *crystals* of the bis-insertion complex $[\mathrm{Ru\{C(CF_3){:}C(CF_3){\cdot}C(CF_3){:}CMe(CF_3)\}(PPh_3)(\eta\text{-}C_5H_5)}]$ (1) (26 mg, 4.8%).

In another experiment $[\mathrm{RuMe(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (900 mg, 1.27 mmol), hfb (6.0 mmol), and 1,2-dimethoxyethane (25 cm^3) were placed in a Carius tube at 50 °C for 2 h. All the solid dissolved to produce a deep red-brown solution, which was left for 9 d at room temperature. The contents were filtered, evaporated to dryness, and the residue was chromatographed in benzene (column F). A yellow solution was eluted with diethyl ether–light petroleum mixtures, which on evaporation yielded an oil. From a second chromatography (column F) a dark orange-yellow band, eluted with diethyl ether–light petroleum (1 : 1), afforded dark red *crystals* of the complex $[\mathrm{Ru\{C(CF_3){:}CMe(CF_3)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$ (2) (47 mg, 6%) after recrystallisation from diethyl ether–light petroleum.

(*b*) *With* $[\mathrm{Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)}]$. The benzyl complex (0.9 g, 1.15 mmol), hfb (3.25 mmol), and 1,2-dimethoxyethane (25 cm^3) were heated in a Carius tube at 50 °C for 48 h, producing an orange solution. The tube was opened, and the contents were filtered, evaporated to dryness, and chromatographed (column F). A yellow band was eluted with diethyl ether–light petroleum (1 : 3) and evaporated to an oil; crystallisation from diethyl ether–light petroleum at 0 °C overnight gave yellow *crystals* of $[\mathrm{Ru\{CH_2C_6H_4{\cdot}C(CF_3){:}C(CF_3)H\}(PPh_3)(\eta\text{-}C_5H_5)}]$ (4) (47 mg, 6.5%).

(*c*) *With* $[\mathrm{RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$. A Carius tube containing the hydride (465 mg, 1.02 mmol), hfb (5.5 mmol), and 1,2-dimethoxyethane (15 cm^3) was heated for 48 h at 60 °C and at 100 °C for 5 d. The resulting red solution was filtered, evaporated to dryness, the residue dissolved in the minimum volume of benzene, and chromatographed (column F). A pale yellow solution was eluted with diethyl ether–light petroleum (1 : 9), from which, on concentration and addition of more light petroleum, pale yellow *crystals* of $[\mathrm{Ru\{C(CF_3){:}C(CF_3)H\}(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$ (5) (130 mg, 21%) were obtained.

In another experiment the cyclic complex (10) (0.6 g, 0.91 mmol), hfb (5.0 mmol), and 1,2-dimethoxyethane (15 cm^3) were heated in a Carius tube for 2 d at 50 °C and at 100 °C for 7 d. The orange solution was filtered, evaporated to dryness, the residue dissolved in the minimum volume of benzene, and chromatographed (column F). With diethyl ether–light petroleum (1 : 9), a pale yellow solution was eluted which afforded a pale yellow microcrystalline *solid* (5) (35 mg, 6%).

(*d*) *With* $[\mathrm{RuMe(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$. The complex $[\mathrm{RuMe(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$ (450 mg, 0.95 mmol), 1,2-dimethoxyethane (15 cm^3), and hfb (4.75 mmol) were heated in a Carius tube at 60 °C for 2 d and 100 °C for 1 d. The resulting red solution was filtered, evaporated to dryness, the residue dissolved in the minimum volume of benzene, and chromatographed (column F). A pale yellow solution was eluted with diethyl ether–light petroleum (3 : 7), which afforded yellow *crystals* of $[\mathrm{(\eta\text{-}C_5H_5)(OC)(Ph_3P)Ru\{C(CF_3){:}C(CF_3)\}Ru(CO)\{\eta^5\text{-}C_5H_4{\cdot}C_6H_4{\cdot}PPh_2\}}]$ (3) (56 mg, 5%).

(*e*) *With* $[\mathrm{Ru\{C(CO_2Me){:}C(CO_2Me)H\}(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$ (11). The complex $[\mathrm{Ru\{C(CO_2Me){:}C(CO_2Me)H\}(CO)(PPh_3)(\eta\text{-}C_5H_5)}]$ (500 mg, 0.83 mmol), hfb (4.2 mmol), and 1,2-dimethoxyethane (15 cm^3) were heated at 50 °C for 60 h and at 100 °C for 7 d. The resulting dark brown solution was filtered, evaporated to dryness, and chromatographed in benzene (column F). A pale yellow solution was eluted with diethyl ether–light petroleum (3 : 1) which afforded the pale yellow *complex* $[\mathrm{Ru\{\eta^5\text{-}C(CO_2Me)C(CO_2Me)C(CF_3)C(CF_3)C(OMe)\}(\eta\text{-}C_5H_5)}]$ (12) (35 mg, 4%).

Reactions of Dimethyl Acetylenedicarboxylate (dma).—(*a*) *With* $[\mathrm{RuMe(PPh_3)_2(\eta\text{-}C_5H_5)}]$. A mixture of $[\mathrm{RuMe(PPh_3)_2(\eta\text{-}C_5H_5)}]$ (500 mg, 0.71 mmol) and dma (500 mg, 3.7 mmol) in diethyl ether (120 cm^3) was heated under

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J; 1 atm = 101 325 Pa.

reflux for 48 h. The solution was concentrated and addition of light petroleum gave an oily orange solid, which was dissolved in the minimum volume of benzene and chromatographed (column A). Elution with light petroleum and evaporation to dryness gave a volatile white solid, recrystallised from light petroleum and identified as dimethyl fumarate by comparison with an authentic sample (20 mg, 3.9%). Elution with diethyl ether–light petroleum (3 : 2) gave a pale yellow crystalline *complex* $[Ru\{\eta^5\text{-}CH(CO_2Me)C(CO_2Me)C(CO_2Me)C(CO_2Me)CH_2\}(\eta\text{-}C_5H_5)]$ (7) (4 mg, 1%). With diethyl ether–light petroleum (19 : 1), hexamethyl benzenehexacarboxylate, $C_6(CO_2Me)_6$ (51 mg, 10%), was obtained. On elution with diethyl ether, the orange microcrystalline complex $[Ru\{C(CO_2Me){:}C(CO_2Me)C(CO_2Me){:}CMe(CO_2Me)\}(PPh_3)(\eta\text{-}C_5H_5)]$ (6) (386 mg, 75%) was obtained.

In another experiment, a mixture of $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ (1.0 g, 1.56 mmol) and dma (1.05 g, 7.0 mmol) was heated in refluxing 1,2-dimethoxyethane (100 cm^3) for 16 h. The resulting orange solution was filtered, evaporated to dryness, and chromatographed in benzene (column A). Elution with diethyl ether–light petroleum (3 : 1) afforded dimethyl fumarate (51 mg, 5%). Elution with diethyl ether–light petroleum (1 : 1) gave orange crystals of the cyclic complex $[Ru\{C(CO_2Me){:}CMe{\cdot}C(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)]$ (8) (15 mg, 1.8%). Elution with diethyl ether–light petroleum (6 : 1) and recrystallisation from dichloromethane–diethyl ether gave pale yellow *crystals* of complex (7) (105 mg, 16%).

(*b*) *With* $[Ru(CH_2Ph)(PPh_3)_2(\eta\text{-}C_5H_5)]$. The benzyl complex (500 mg, 0.76 mmol) and dma (200 mg, 1.43 mmol) were heated under reflux in 1,2-dimethoxyethane (80 cm^3) for 18 h. The solution was filtered, evaporated to dryness, and chromatographed in benzene (column A). With diethyl ether–light petroleum (4 : 1) a red band yielded 1 or 2 mg of red *crystals* of the complex $[Ru\{C(CO_2Me){:}C(CH_2Ph)(CO_2Me)\}(PPh_3)_2(\eta\text{-}C_5H_5)]$ (10). The pale yellow band eluted with diethyl ether gave yellow *crystals* (from ether) of the chelate complex $[Ru\{C(CO_2Me){:}C(CH_2Ph)C(O)OMe\}(PPh_3)(\eta\text{-}C_5H_5)]$ (9) (235 mg, 56%). Further elution with diethyl ether afforded an orange fraction, shown by i.r. and mass spectrometry to be the complex $[Ru\{\eta^5\text{-}CH(CO_2Me)[C(CO_2Me)]_3CHPh\}(\eta\text{-}C_5H_5)]$ (5 mg, 2%), m.p. 222—226 °C (decomp.). I.r.: $\nu_{max.}$ at 1 740, 1 732, 1 717, 1 710 (C⁚O), 1 631 and 1 575 cm^{-1} (C⁚C). Mass spectrum (*m/e*): 542 $[P]^+$, 511 $[P - OMe]^+$, 483 $[P - CO_2Me]^+$, and 451 $[P - CH_2Ph]^+$.

(*c*) *With* $[RuH(CO)(PPh_3)(\eta\text{-}C_5H_5)]$. The carbonyl hydride (500 mg, 1.1 mmol) and dma (330 mg, 2.3 mmol) were heated under reflux in 1,2-dimethoxyethane (60 cm^3) for 16 h. The resulting orange solution was filtered, evaporated to dryness, the residue dissolved in the minimum volume of benzene, and chromatographed (column F). On elution with diethyl ether–light petroleum (2 : 3) a yellow solution afforded pale yellow *crystals* (from diethyl ether–light petroleum) of $[Ru\{C(CO_2Me){:}C(CO_2Me)H\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ (11) (190 mg, 29%).

Reaction between $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ *and* 4-*Phenylbut*-3-*yn*-2-*one*.—The methyl complex (500 mg, 0.71 mmol) and PhC⁚CC(O)Me (250 mg, 1.73 mmol) were heated together in 1,2-dimethoxyethane (50 cm^3) for 16 h. Chromatography (column A) gave unchanged $[RuMe(PPh_3)_2(\eta\text{-}C_5H_5)]$ (15 mg, 3%) [eluted with diethyl ether–light petroleum (1 : 9)], followed by a red band [diethyl ether–light petroleum (1 : 3)] which when concentrated and treated with light petroleum gave bright red *crystals* of $[Ru\{C(Ph){:}C(Me){\cdot}C(O)Me\}(PPh_3)(\eta\text{-}C_5H_5)]$ (13) (51 mg, 12%). Elution with diethyl ether–light petroleum (3 : 1) gave a dark red solution, which on concentration and addition of more light petroleum afforded dark red *crystals* of $[Ru\{C(Ph){:}C{\cdot}C(O){\cdot}CH_2{\cdot}C(Ph){:}C{\cdot}C(O)Me\}(PPh_3)(\eta\text{-}C_5H_5)]$ (14) (47 mg, 9%).

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