Insertion Reactions of Acetylenes with a Cyclopentadienyl-Ruthenium Phosphine Hydride: Structure of a Butadienyl-Ruthenium Complex

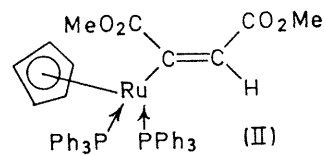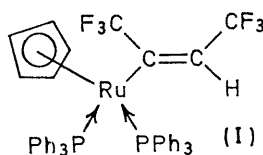By T. Blackmore, M. I. Bruce, and F. G. A. Stone*

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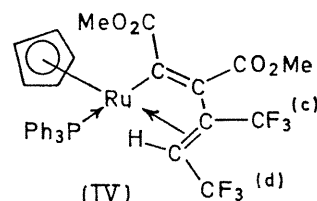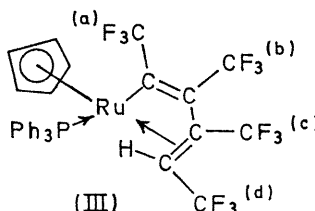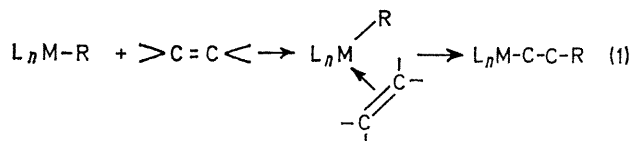
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Summary Reactions between $Ru(PPh_3)_2(\pi\text{-}C_5H_5)(\sigma\text{-}C_2R_2H)$ [(I; R = CF_3); (II; R = CO_2Me)] and hexafluorobut-2-yne give $Ru(PPh_3)(\pi\text{-}C_5H_5)(C_2R_2\cdot C_4F_6H)$ [(III; R = CF_3); (IV; R = CO_2Me)]; the crystal structure of (III) shows that it contains a buta-1,3-dienyl group, π-bonded to the metal *via* the double bond furthest from the carbon-ruthenium σ-bond, and the structure of (IV), as shown by its n.m.r. spectra, is unexpected in that the $CF_3C_2CF_3$ group has apparently inserted into the C–H bond of (II) rather than into the C–Ru bond.

ALTHOUGH the transition-metal complex catalysed polymerisation of unsaturated organic compounds is believed to proceed by co-ordination followed by insertion, *e.g.* reaction (1), the intermediates in such reactions have not often been

$$L_nM\text{-}R \;+\; {>}C{=}C{<} \;\longrightarrow\; L_nM\underset{\overset{\displaystyle |}{\underset{\displaystyle -C}{\overset{\displaystyle \|}{C-}}}}{\overset{\displaystyle R}{\diagup}} \;\longrightarrow\; L_nM\text{-}C\text{-}C\text{-}R \quad (1)$$

isolated. Consequently, the exact mechanisms of many of these reactions remain obscure. We present some evidence that reactions of this type, at least with alkynes bearing electron-withdrawing groups, may proceed by a different route.

The new hydride $Ru(PPh_3)_2(\pi\text{-}C_5H_5)H$ [1] reacts with excess of hexafluorobut-2-yne in ether solution to give three products, namely (I), (III), and the cyclic phosphorane $\overline{Ph_3P\cdot C(CF_3)\text{:}C(CF_3)\cdot C(CF_3)\text{:}C(CF_3)}$.[2]

Complex (I) shows an i.r. band at 1573 cm⁻¹, assigned to the $\nu(C{=}C)$ frequency of an $M\cdot C(CF_3)\text{:}C(CF_3)H$ group.[3,4]

The ¹H n.m.r. spectrum shows, in addition to signals from C_6H_5 and C_5H_5, a resonance at τ 5·22, assigned to C_4F_6H.

The ¹⁹F n.m.r. spectrum shows two equally intense resonances at 51·6 (quintet) and 57·4 br p.p.m. (upfield from

TABLE

Coupling constant data

	$J[CF_3(a)\text{-}CF_3(b)]$	$J[CF_3(c)\text{-}CF_3(d)]$	$J[H\text{-}CF_3(d)]$	$J[P\text{-}CF_3(a)]$	$J[P\text{-}CF_3(d)]$	$J(PH)$
(III)	8·8	10·0	10·3	2·0	0·5	14·5 Hz
(IV)	—	10·0	10·0	—	<1	14·5

internal $CFCl_3$). The coupling constants $[J(CF_3\text{-}CF_3), 14·4; J (CF_3\text{-}H, gem) 11·0; J (CF_3\text{-}H, trans), 0 Hz]$ show that the complex contains a $cis\text{-}CF_3(Ru)C{=}C(H)CF_3$ group.[4]

The second ruthenium complex (III) is a pale yellow, air-stable compound, of composition $Ru(PPh_3)(\pi\text{-}C_5H_5)C_8F_{12}H$; $\nu(C{=}C)$ at 1640 cm⁻¹. The proton attached to the fluorocarbon group resonates at τ 7·98 (m), and four resonances appear in the ¹⁹F n.m.r. spectrum at 50·1 [CF_3(d), quintet of doublets], 55·1 [CF_3(a), quartet of doublets], 57·2 [CF_3(b), complex multiplet, broad], and 64·9 p.p.m. [CF_3(c), broad multiplet]. Decoupling experiments and coupling constant data allowed the assignment of the resonances as shown;

important couplings are listed in the Table. The mass spectrum shows a parent ion cluster centred at m/e 754, and fragmentation occurs by loss of F and HF, and of PPh_3. The fluorinated C_8 unit shows considerable stability, and no evidence for the loss of a C_4F_n ($n \leqslant 6$) group was found.

The structure deduced from the spectroscopic data has been confirmed by a single-crystal X-ray study. Crystals of (III) from ether are monoclinic, space group $P2_1/C$, with $a = 9.324$, $b = 22.498$, $c = 14.985$ Å, $\beta = 113.08°$, $Z = 4$.

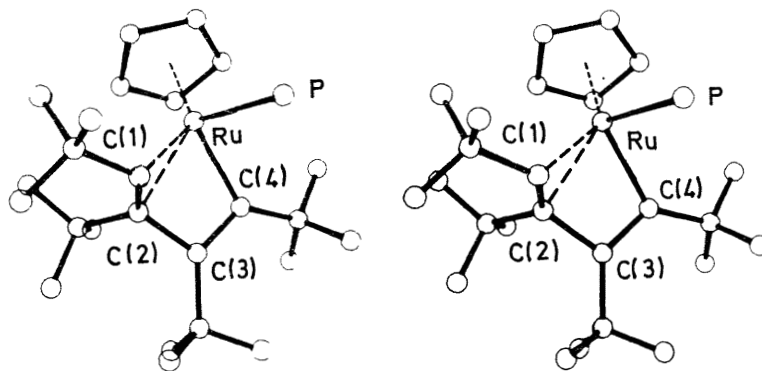(1) might explain the oligomerisation. However, there is no reported instance of an insertion reaction involving a fluorocarbon–metal σ-bond. Further information was provided by the reaction between complex (II), formed from the hydride and $C_2(CO_2Me)_2$, and hexafluorobut-2-yne, which would be expected to give $Ru(PPh_3)(\pi\text{-}C_5H_5)[\sigma\text{-}C(CF_3):C (CF_3).C(CO_2Me):C(CO_2Me)H]$ if equation (1) applies.

The ^1H n.m.r. spectrum of the product (IV) of this reaction shows ester methyl resonances at τ 6·45 and 6·98

FIGURE.　*Structure of complex* (III).

Using the 3572 observed reflections out of 4761 measured with Cu-K_α radiation, the structure was solved by the heavy atom method, after location of the Ru and P atoms from a Patterson map. The structure has been refined, including all hydrogen atoms, to a conventional R value of 0·048 and a weighted R value of 0·034.

The molecular geometry is shown in the stereoscopic drawing (Figure) from which the phenyl groups have been omitted. The Ru atom is π-bonded to atoms C(1) and C(2), at distances of 2·19 and 2·16 Å, respectively. The Ru–C(4) σ-bond distance is 2·05 Å, while the non-bonded Ru $\cdots$ C(3) distance is 2·65 Å. As is characteristic in metal complexes, the C(1)=C(2) bond is considerably lengthened, to 1·42 Å; this may be contrasted with the normal ethylenic bond distance of 1·33 Å for C(3)=C(4). The C(2)–C(3) distance is 1·51 Å. The five cyclopentadienyl C–C distances average $1·40 \pm 0·016$ Å, the 18 phenyl C–C distances average $1·38 \pm 0·018$ Å, and the 12 C–F distances average $1·34 \pm 0·015$ Å, where the deviations given are the root-mean-square deviations from the group averages. A description of the structure determination and further details of molecular geometry will be published later (A. G. and R. E. D.).
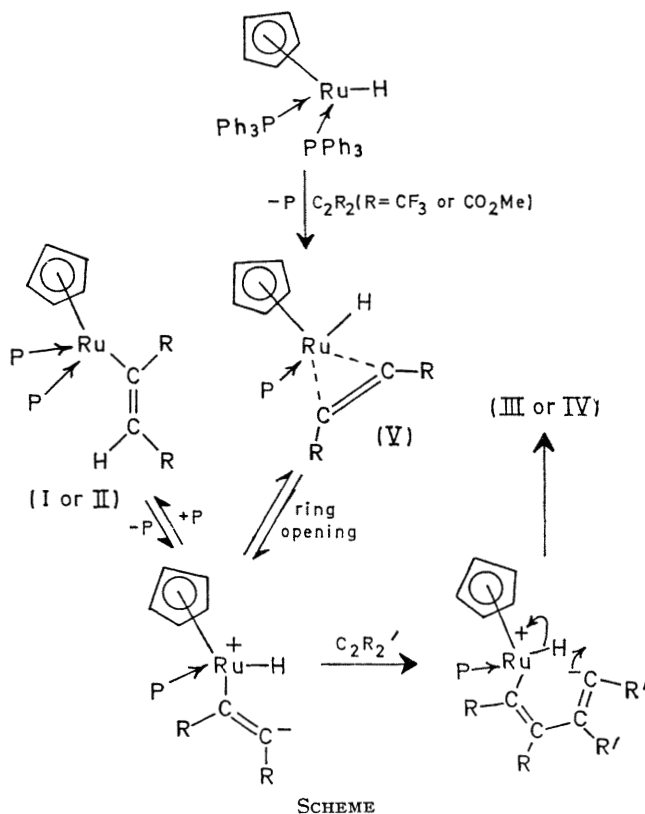
A related bonding situation has been described recently in the complex $Rh(PPh_3)[Ph_2PC_6H_4(C_2Ph_2)_2]$.[5] Complex (III) also bears a formal resemblance to a compound obtained from $(PhCN)_2PdCl_2$ and but-2-yne. This was postulated[6] to contain a trimer of the acetylene, formed by successive insertion of butyne molecules into the Pd–Cl bond, followed by co-ordination of a free double bond. This was facilitated by the ready displacement of a benzonitrile ligand. In the present study, conversion of (I) into (III) was achieved by reaction with more acetylene, the ready dissociation of one of the phosphine ligands in (I) apparently encouraging co-ordination of a second molecule of hexafluorobut-2-yne.

Since the CF_3 groups of the fluoroacetylene, and of complex (I), cannot be distinguished in the resulting complex (III) a mechanism similar to that described in equation

[cf. τ 6·34 and 6·98 for (II)], and a single proton resonance at τ 7·82 [cf. τ 7·98 in (III)]. The ^{19}F n.m.r. spectrum shows two

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resonances at 50·4 (quintet) and 54·4 p.p.m. (quartet of quartets). These results, together with the coupling

constant data (see Table), support assignment of structure (IV) for this complex, in which the incoming acetylene has apparently inserted into the C–H bond of the $Ru.C(CO_2Me):C(CO_2Me)H$ group.

There is no direct precedent for this type of reaction, but the results suggest the mechanism shown in the Scheme. Ready dissociation of one phosphine ligand from $Ru(PPh_3)_2(\pi-C_5H_5)H$, already demonstrated with CO and other phosphines,[1] encourages formation of a mono-alkyne π-complex (V). Reco-ordination of the phosphine ligand results in insertion of the alkyne into the metal–hydrogen bond to give the vinyl complexes (I) and (II), expected from equation (1) (with R = H). However, the intermediate shown, which may be formed by ring-opening,[7] can also attack a second alkyne molecule, leading to the formation of (III) or (IV).

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