1,4 Addition of Hexafluorobut-2-yne to Rhodium(I)–β-Ketoenolate Rings

By **D. M. Barlex, A. C. Jarvis, R. D. W. Kemmitt,*** and **B. Y. Kimura,** Department of Chemistry, The University, Leicester LE1 7RH

Hexafluorobut-2-yne reacts with the β-ketoenolate rhodium(I) complexes Rh(O–O)L_2 (O–O = acac or dpm; L_2 = cyclo-octa-1,5-diene or 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene) to give complexes in which the fluorocarbon adds 1,4 to the rhodium(I) β-ketoenolate ring. Also the hexafluorobut-2-yne is trimerised to hexakis(trifluoromethyl)benzene which remains co-ordinated to the rhodium so that the diene ligand is displaced. However, although a similar reaction occurs with Rh(dpm)(nbd), norbornadiene is not displaced from Rh(acac)-(nbd) and the diene becomes linked to the rhodium by the acetylene to form a rhodacyclopentene ring.

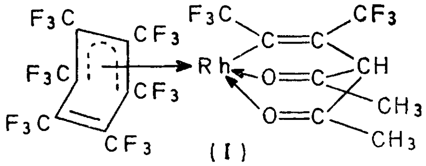
Hexafluorobut-2-yne reacts with Rh(acac)$(C_2H_4)_2$ and Rh(acac)$(C_2H_4)(C_2F_4)$ to give a complex which contains a 1,4 adduct of the acetylene and rhodium–acetylacetonate ring and a 1,2,3,4-tetrakistrifluoromethylcyclohexa-1,3-diene ligand. Attempts to isolate similar 1,4 addition products with Rh($CF_3COCHCOCF_3$)(cod), and Rh($CF_3COCHCOCF_3$)(nbd), have not been successful.†

RECENTLY we have shown[1] that hexafluorobut-2-yne adds 1,4 to the rhodium-acetylacetonate ring of acetylacetonato(cyclo-octa-1,5-diene)rhodium(I). In this reaction the acetylene also undergoes a cyclo-trimerisation reaction to form hexakis(trifluoromethyl)benzene which co-ordinates to the rhodium to give the complex (I). In order to investigate further the factors affecting this 1,4 addition reaction we have studied the reactivity of various olefin–rhodium(I)-β-ketoenolate systems containing electron-withdrawing and electron-donating substituents towards hexafluorobut-2-yne.

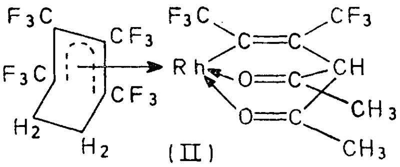
RESULTS AND DISCUSSION

Hexafluorobut-2-yne reacts with acetylacetonato-(cyclo-octa-1,5-diene)rhodium(I) in benzene solution at room temperature to yield a yellow crystalline rhodium complex, (I), the structure of which has been determined by a single-crystal *X*-ray study.[1] The i.r. spectrum of complex (I) shows bands at 1694 and 1662 cm^{-1} due to C–O of the β-diketone group and two weak bands at 1642 and 1600 cm^{-1} typical of C=C stretching frequencies. The band at 1600 cm^{-1} can be assigned to ν(C=C) of the vinylic system RhC(CF_3)=C(CF_3)– since a similar absorption is observed in complex (II) (see below), whilst the band at 1642 cm^{-1} can be assigned to ν(C=C) of the hexakis(trifluoromethyl)benzene ligand. In the complex Rh(π-C_5H_5){$C_6(CF_3)_6$}, ν(C=C) of the unco-ordinated double bond is observed at 1623 cm^{-1}.[2] The ^{19}F n.m.r. spectrum of a freshly prepared solution of (I) in acetone shows four poorly resolved resonances at −11·6 (9F), −9·8 (6F), −5·5 (6F), and −3·1 p.p.m. (3F) relative to benzotrifluoride. The broad bands at −11·6, −9·8, and −5·5 p.p.m. can be assigned to the CF_3 resonances of the hexakis(trifluoromethyl)benzene ligand, and by analogy with other systems[3-5] the high field quartet at −3·1 p.p.m. (J_{FF} 16 Hz) can be assigned to the β-CF_3 group of the vinylic system RhC($C^{\alpha}F_3$)=C($C^{\beta}F_3$)–. The low field resonance expected for the α-CF_3 group is hidden under the broad resonance at −11·6 p.p.m. In solution the complex (I) decomposes and resonances at −10·5 and −3·1 p.p.m. gradually become more prominent in the spectrum. The resonance at −10·5 p.p.m. appears as a singlet in a position characteristic of that of free hexakis(trifluoromethyl)benzene[6] which presumably results from dissociation of (I). A similar decomposition is observed in diethyl ether solutions.

The ^{19}F n.m.r. spectrum of (I) clearly shows that the hexakis(trifluoromethyl)benzene ligand is not fluxional and is rigidly bound to the rhodium at room temperature as is found for the complex Rh(π-C_5H_5){$C_6(CF_3)_6$}.[2] Recently, however, some hexakis(trifluoromethyl)benzene complexes of nickel(0) have been found to be fluxional.[7]



(I)



(II)

A similar product, (II) also results from the interaction of hexafluorobut-2-yne with acetylacetonatobis-(ethylene)rhodium(I). The i.r. spectrum of the yellow crystalline complex (II) shows a strong C–O absorption at 1695 cm^{-1} and a weak C=C stretching frequency at 1599 cm^{-1} which is consistent with the proposed structure. In addition the ^{19}F n.m.r. spectrum of a solution

---

† Abbreviations used in this paper, cod, 1,5-cyclo-octadiene; nbd, norbornadiene; acac, acetylacetonato; hfac, hexafluoroacetylacetonato; dpm, dipivaloylmethanato.

[1] D. M. Barlex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell, *Chem. Comm.*, 1971, 331.

[2] R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 1964, 2699.

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

[4] H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, 1967, **89**, 533.

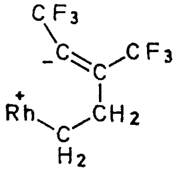
[5] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1970, **9**, 2670.

[6] J. F. Harris, R. J. Hander, and G. N. Sausen, *J. Org. Chem.*, 1960, **25**, 633.

[7] J. Browning, C. S. Cundy, M. Green, and F. G. A. Stone *J. Chem. Soc.* (*A*), 1971, 448.

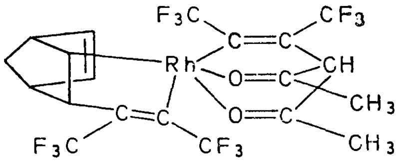
of complex (II) in acetone shows four signals at −11·3 (3F), −9·0 (6F), −3·3 (6F), and −2·8 p.p.m. (3F) (relative to benzotrifluoride). The unresolved multiplet at −11·3 and quartet at −2·8 p.p.m. can be assigned to the vinylic system $RhC(CF_3)=C(CF_3)^-$ and occur at positions similar to those found for complex (I). The two broad resonances at −9·0 and −3·3 p.p.m. are assigned to the CF_3 groups on the 1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,3-diene ligand. The four methylene protons of the cyclohexadiene ligand form an AA′BB′ system and measurement of the ^1H n.m.r. spectrum gives a geminal H–H coupling constant of 10 Hz. However, the vicinal couplings are not discernible and are probably less than 4 Hz.

By analogy with recent studies on the reactions of electrophilic acetylenes with ruthenium(0) and osmium(0) complexes[8] it seems reasonable to postulate that complex (II) is formed *via* an ionic intermediate which can react with a second mole of the acetylene to give a precursor of (II). The formation of this ionic intermediate is consistent with other studies which have shown that low-valent transition metal hydrocarbon complexes are susceptible to electrophilic attack by fluoro-olefins and -acetylenes.[9-11] An alternative mechanism involving a tetrakis(trifluoromethyl)rhodacyclopentadiene complex[8] seems less attractive since this would be expected to lead to the formation of complex (I). However, since a small quantity of hexakis(trifluoromethyl)benzene can also be isolated from the reaction it would appear that a rhodacyclopentadiene intermediate is involved in the formation of this by-product.

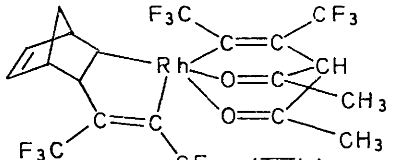


An alternative synthesis of (II) is also observed to take place when acetylacetonato(ethylene)(tetrafluoroethylene)rhodium(I),$Rh(acac)(C_2H_4)(C_2F_4)$ is treated with hexafluorobut-2-yne. A similar ionic intermediate is presumably involved in this reaction and it would appear that electrophilic attack by hexafluorobut-2-yne upon co-ordinated ethylene is favoured since tetrafluoroethylene is not incorporated into the product.

Some evidence for the mechanism of addition of hexafluorobut-2-yne to co-ordinated ethylene is obtained by the formation of complex (III) which can be isolated from the reaction of hexafluorobut-2-yne with acetylacetonato(norbornadiene)rhodium(I).[12] The structure of complex (III) follows from both its i.r. spectrum which shows C=O absorptions at 1703 and 1620 cm^{-1} and its ^{19}F n.m.r. spectrum which shows four quartets of equal intensity. By analogy with the complexes (I) and (II) the resonances centred at −12·9 and −3·4 p.p.m. are assigned to the CF_3 groups of the acetylene which has added to the acetylacetonato-group, whilst the peaks centred at −8·0 and −5·8 p.p.m. are assigned to the CF_3 groups of the acetylene which has linked the diene to the rhodium. The ^1H n.m.r. spectrum of (III) in deuteriated acetone shows in addition to the other expected resonances two singlets at τ 2·75 and 3·56 typical of a free olefinic linkage and it therefore seems possible that in solution the remaining olefinic bond of the diene is not co-ordinated. However, attempts to detect a vibration in the i.r. or Raman spectrum of (III) which can definitely be assigned to this olefinic linkage have not been successful. In $[RhCl(nbd)]_2$ the ^1H n.m.r. resonances of the olefinic hydrogens appear at τ 6·12.[13] The complex (III) could have either structure (IIIa) or (IIIb) but the present data does not differentiate between these two conformers.



(IIIa)



(IIIb)

In contrast to the above, treatment of acetylacetonato(hexachloronorbornadiene)rhodium(I) with hexafluorobut-2-yne gives complex (I) and it would appear that the presence of the chlorine substituents inhibits electrophilic addition to the diene.

Reactions of hexafluorobut-2-yne with the dipivaloylmethanato-complexes, (IVa—IVc) give the complex (V). In each reaction the diene ligand is displaced by hexakis(trifluoromethyl)benzene and there is no evidence for the formation of a complex analogous to (III). The ^{19}F n.m.r. spectrum of (V) is similar to that observed for complex (I).

In contrast to the ready addition of hexafluorobut-2-yne to the acetylacetonato- and dipivaloylmethanato-complexes we have not been able to obtain similar adducts with either hexafluoroacetylacetonato(cyclo-octa-1,5-diene)rhodium(I) or the corresponding norbornadiene complex. Possible mechanisms for these addition reactions include a concerted addition to the β-keto-

---

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

[9] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1964, 1752.

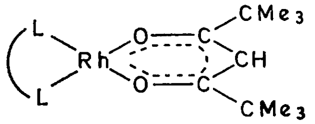
[10] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 1963, **2**, 713.

[11] A. Bond and M. Green, *Chem. Comm.*, 1971, 12.

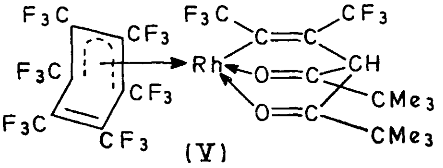
[12] J. A. Evans, R. D. W. Kemmitt, B. Y. Kimura, and D. R. Russell, *Chem. Comm.*, 1972, 509.

[13] K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometallic Chem.*, 1968, **15**, 195.

enolate system, or formation of a carbon bonded β-keto-enolate complex[14] followed by insertion of hexafluorobut-2-yne into the rhodium–carbon bond.[15] Since electron withdrawing substituents would tend to inhibit both concerted addition as well as insertion into a rhodium–carbon bond,[16] the inability to isolate products with hexafluoroacetylacetonato-complexes does not differentiate between these two mechanisms. However, the formation of these 1,4 addition products is consistent with the powerful dienophilic nature of hexafluorobut-2-yne.[17]



L-L = cod, (IVa); nbd, (IVb); 1,2,3,4,7,7, hexachlorobicylo-[2.2.1]hepta-2,5-diene, (IVc)



(V)

EXPERIMENTAL

M.p.s were determined on a Reichert hot-stage apparatus and are uncorrected. I.r. spectra (Nujol mulls) were recorded on Perkin-Elmer models 225 and 457 spectrometers. ^1H n.m.r. spectra and ^{19}F n.m.r. spectra (relative to benzotrifluoride at 56·4 MHz) were recorded on Varian Associates T60 and DA60 spectrometers respectively.

The complexes Rh(acac)(cod),[18] Rh(acac)(nbd),[18] Rh(acac)$(C_2H_4)_2$,[14] and Rh(acac)$(C_2H_4)(C_2F_4)$[14] were prepared as described in the literature. The complexes Rh(hfac)(cod), Rh(hfac)(nbd), Rh(dpm)(cod), Rh(dpm)(nbd), Rh(dpm)(hexachloronorbornadiene), were prepared by analogous procedures. Rh(hfac)(C_8H_{12}) (74%), m.p. 124° (Found: C, 36·7; H, 3·3; F, 27·0. $C_{13}H_{13}F_6O_2Rh$ requires C, 37·3; H, 3·1; F, 27·2%). Rh(hfac)(C_7H_8) (71%), m.p. 138° (Found: C, 35·4; H, 2·1; F, 28·3. $C_{12}H_9F_6O_2Rh$ requires C, 35·8; H, 2·2; F, 28·4%). Rh(dpm)(C_8H_{12}) (95%), m.p. 185° (Found: C, 57·6; H, 7·9. $C_{19}H_{31}O_2Rh$ requires C, 58·0; H, 7·9%). Rh(dpm)(C_7H_8) (88%), m.p. 124° (Found: C, 57·0; H, 7·2. $C_{18}H_{27}O_2Rh$ requires C, 57·4; H, 7·2%). Rh(dpm)$(C_7H_2Cl_6)$ (82%), m.p. 262° (Found: C, 37·0; H, 3·5. $C_{18}H_{21}O_2Rh$ requires C, 37·2; H, 3·6%). Rh(acac)$(C_7H_2Cl_6)$ (99%), m.p. 176—178° (Found: C, 28·0; H, 1·7; Cl, 42·3. $C_{12}H_{13}Cl_6O_2Rh$ requires C, 28·0; H, 1·8; Cl, 42·6%).

Reactions of Hexafluorobut-2-yne.—(a) *With acetylacetonato*(*cyclo-octa*-1,5-*diene*)*rhodium*(I). A solution of acetylacetonato(cyclo-octa-1,5-diene)rhum(I)odi (0·50 g, 1·6 mmol) in benzene (6 ml) was introduced into a Carius tube (150 ml). An excess of hexafluorobut-2-yne was condensed (−196°) into the tube. After 17 h at room temperature, the tube was opened and volatile material was removed. The orange precipitate was filtered off and washed with benzene (3 ml) and diethyl ether (2 × 3 ml) to give orange crystals of the adduct (I) (0·77 g, 56%), m.p. 260° (dec.) (Found: C, 29·6; H, 0·85; F, 53·4. $C_{21}H_7F_{24}O_2$ requires C, 29·7; H, 0·8; F, 53·7%). ν(C=O), 1694ms and 1662vw, ν(C=C), 1642w and 1600w cm^{-1}. The ^1H n.m.r. spectrum in $(CD_3)_2CO$ showed peaks at τ 3·23 (bs, 1H, 3-CH) and 7·50 (bs, 6H, CH_3). The ^{19}F n.m.r. spectrum (acetone) showed peaks at −11·6 (br, 9F), −10·5 [s, $C_6(CF_3)_6$, decomposition product], −9·8 (br, 6F), −5·5 (br, 6F), −4·7 (q, 3F, J 7 Hz, decomposition product of variable intensity), and −3·1 p.p.m. (q, 3F, J_{FF} 16 Hz). The complex is insoluble in benzene and light petroleum, slightly soluble in methylene chloride and diethyl ether, and soluble in acetone and tetrahydrofuran in which it slowly decomposes. Addition of a mixture of light petroleum (b.p. 40—60°) and diethyl ether to the filtrate obtained from the reaction and cooling to −78° afforded a small quantity of hexakis-(trifluoro-methyl)benzene which was identified by its i.r. and ^{19}F n.m.r. spectra.

(b) *With acetylacetonatobis*(*ethylene*)*rhodium*(I). Similarly a solution of Rh(acac)$(C_2H_4)_2$ (0·42 g, 1·6 mmol) in degassed sodium-dried benzene (10 ml) was shaken with an excess of hexafluorobut-2-yne for 3 days in a Carius tube. After a further 16 days at room temperature, the fine yellow precipitate was filtered off and washed with benzene and light petroleum (b.p. 40—60°). Recrystallisation from benzene gave pale yellow crystals of adduct (II) (0·51 g, 43%), m.p. 230° (dec.) [Found: C, 31·5; H, 1·5; F, 47·4; M (C_6H_6), 732. $C_{19}H_{11}F_{18}O_2$ requires C, 31·8; H, 1·5; F, 47·8%; M, 716], ν(C=O), 1695s cm^{-1}; ν(C=C), 1599w cm^{-1}. The ^1H n.m.r. spectrum (benzene) showed resonances at τ 5·05 (s, 1H, 3-CH), 8·70 (s, 6H, CH_3), and 7·22, 7·88, 9·22, 9·39 (br, 4H, CH_2CH_2, AA′BB′ spectrum, J_{HH} gem 10 Hz). At 100 MHz, J_{HH} gem 11 Hz. The ^{19}F n.m.r. spectrum (acetone) showed resonances at −11·3 (br, 3F), −9·0 (br, 6F), −3·3 (br, 6F), and −2·8 p.p.m. (q, 3F, J_{FF} 17 Hz). The complex is sparingly soluble in diethyl ether and benzene and very soluble in acetone in which it slowly decomposes. Addition of diethyl ether (5 ml) to the filtrate remaining from the preparation of (II) and cooling to −78° afforded a small quantity of a pale white solid which was identified as hexakis(trifluoromethyl)benzene by its i.r. and ^{19}F n.m.r. spectra. A further quantity of the adduct (II) was obtained by dissolution of the reaction residues in diethyl ether (3 ml) and keeping the solution at 0° for 15 h. The pale yellow crystals which formed were filtered, washed with cold diethyl ether and light petroleum (b.p. 40—60°) and recrystallised from benzene.

(c) *With acetylacetonato*(*ethylene*)(*tetrafluoroethylene*)*rhodium*(I). Similarly a solution of Rh(acac)$(C_2H_4)(C_2F_4)$ (0·39 g, 1·2 mmol) in degassed sodium-dried benzene (9 ml) was shaken with an excess of hexafluorobut-2-yne for 2 days. After a further 10 days at room temperature the yellow precipitate was filtered off and washed with benzene. Concentration of the filtrate gave a further yield of the adduct (II) which was recrystallised twice from diethyl ether–light petroleum (b.p. 60—80°). Yield 0·27 g, 32%.

(d) *With acetylacetonato*(*norbornadiene*)*rhodium*(I). Similarly a solution of Rh(acac)(nbd) (0·34 g, 1·2 mmol) in

---

[14] G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, 1965, **87**, 5356.

[15] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1970, **9**, 2670.

[16] M. L. H. Green, 'Organometallic Compounds,' vol. 2, G. E. Coates, M. L. H. Green, and K. Wade, Methuen, London, 1968.

[17] T. L. Cairns, C. G. Krespan, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1961, **83**, 3428.

[18] F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 3156.

degassed sodium-dried diethyl ether (20 ml) was shaken with an excess of hexafluorobut-2-yne for 2 h at room temperature. The yellow crystals which formed were filtered off and washed with diethyl ether and light petroleum (b.p. 40—60°). Concentration of the filtrate gave a further quantity of the adduct (III) and the total yield (0·22 g, 31%) was recrystallised from oxygen-free acetone–light petroleum (b.p. 60—80°). M.p. 177—179° (dec) [Found: C, 38·7; H, 2·5; F, 33·8; *M*(acetone), 633. $C_{20}H_{15}F_{12}O_2$ requires C, 38·8; H, 2·4; F, 36·9%; *M*, 618]. The complex is soluble in acetone and nitrobenzene. The same product is also obtained by repeating the reaction at 60°. ν(C=O), 1703s and 1620m; ν(C=C), 1669w and 1569w cm^{-1}. The ^1H n.m.r. spectrum ([$^2H_6$]acetone) showed resonances at τ 2·75 (br, 1H, =CH), 3·56 (br, 2H, =CH, 3-CH) 6·0 (br, 1H), 6·4 (br, 1H), 6·6 (br, 1H), 6·87 (br, 1H), 7·10 (s, 3H, CH_3), 7·28 (s, 3H, CH_3), and 8·0 (br, 2H, CH_2). The ^{19}F n.m.r. spectrum (acetone) showed resonances at −12·9 [br, q, 3F, *J*(CF_3–CF_3) 19 Hz], −8·0 [br, q, 3F, *J*(CF_3–CF_3) 17 Hz], −5·8 [q, 3F, *J*(CF_3–CF_3) 17 Hz], and −3·4 p.p.m. [q, 3F, *J*(CF_3–CF_3) 19 Hz].

(e) *With acetylacetonato*(*hexachloronorbornadiene*)*rhodium*(I). Similarly a solution of Rh(acac)($C_7H_2Cl_6$) (0·12 g, 0·024 mmol) in diethyl ether (20 ml) was heated at 60° with an excess of hexafluorobut-2-yne for 2 days. The resulting yellow solution was evaporated to a small volume and yellow crystals of the adduct (I) (0·04 g, 22%) were filtered off and characterised by m.p., i.r. spectrum, and ^{19}F n.m.r. spectrum.

(f) *With dipivaloylmethanato*(*cyclo-octa*-1,5-*diene*)*rhodium*(I). Similarly a solution of Rh(dpm)(cod) (0·43 g, 1·1 mmol) in diethyl ether (5 ml) and excess hexafluorobut-2-yne were heated at 60° for 15 h. Evaporation of the solution to a small volume gave orange crystals of adduct (V) (0·76 g, 74·5%), m.p. 224° (dec.) (Found: C, 34·7; H, 2·1; F, 49·1; $C_{27}H_{19}F_{24}O_2$ requires C, 34·7; H, 2·0; F, 48·8%). ν(C=O), 1660s, ν(C=C), 1640m and 1579w cm^{-1}. The ^1H n.m.r. spectrum ([$^2H_6$]acetone) showed resonances at τ 3·07 (s, H, 3-CH), and 8·67 (s, 18H, CH_3). The ^{19}F n.m.r. spectrum (acetone) showed resonances at −11·44 [br, 9F, 2-CF_3 plus RhC(CF_3)=C(CF_3)–], −9·76 (br, 6F, CF_3), −8·13 [q, 3F, *J*(CF_3–CF_3) 15·8 Hz, RhC(CF_3)=C(CF_3)–], and −5·53 p.p.m. (br, 6F, CF_3). An additional resonance at −10·5 p.p.m. can be assigned to free $C_6(CF_3)_6$. The complex is soluble in acetone and slightly soluble in diethyl ether, benzene, and methylene chloride.

(g) *With dipivaloylmethanato*(*norbornadiene*)*rhodium*(I). Similarly a solution of Rh(dpm)(nbd) (0·5 g, 1·3 mmol) in diethyl ether (5 ml) was shaken with an excess of hexafluorobut-2-yne at room temperature for 15 h. Evaporation of the solution to a small volume gave orange crystals of adduct (V) (0·83 g, 49·4%) which was identified by m.p., i.r. spectrum, and ^{19}F n.m.r. spectrum.

(h) *With dipivaloylmethanato*(*hexachloronorbornadiene*)-*rhodium*(I). Similarly a solution of Rh(dpm)($C_7H_2Cl_6$) (0·14 g, 0·02 mmol) in diethyl ether (5 ml) and an excess of of hexafluorobut-2-yne gave the adduct (V) (0·14 g, 62%).

(i) *With hexafluoroacetylacetonato*(*cyclo-octa*-1,5-*diene*)-*rhodium*(I). Similarly a solution of Rh(hfac)(cod) (0·5 g, 0·013 mmol) in benzene (10 ml) and an excess of hexafluorobut-2-yne were heated at 60° for 15 h. Evaporation of the solution gave a red oil which gave no fluorine resonances in its ^{19}F n.m.r. spectrum.

Similarly no pure product could be isolated from the reaction of Rh(hfac)(nbd) and hexafluorobut-2-yne.

We thank Johnson, Matthey Limited for a loan of rhodium trichloride, Mr. D. A. Atton for some experimental assistance, and the S.R.C. for financial support and a maintenance grant (to A. C. J.).

[2/1387 *Received*, 15*th June*, 1972]