

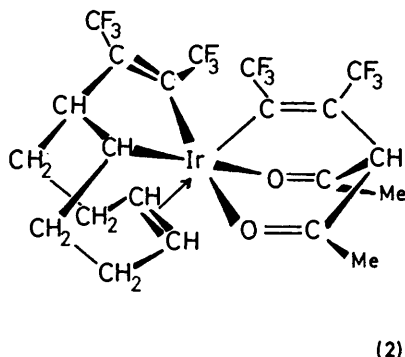
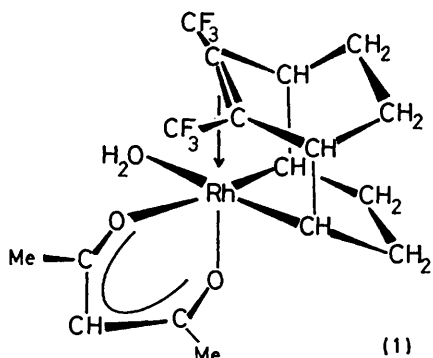
**1,4 Addition of Hexafluorobut-2-yne to Co-ordinated Cyclo-octa-1,5-diene:
Crystal Structures of the Adducts $[\text{Rh}(\text{acetylacetonato})(\text{C}_8\text{H}_{12})(\text{C}_4\text{F}_6)(1\frac{1}{2}\text{H}_2\text{O})]$
and $[\text{Ir}(\text{acetylacetonato})(\text{C}_8\text{H}_{12})(\text{C}_4\text{F}_6)_2]$**

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Summary Hexafluorobut-2-yne adds 1,4 to co-ordinated cyclo-octa-1,5-diene in the complex $[\text{Rh}(\text{cod})\text{Cl}]_2$, in contrast to the reaction of hexafluorobut-2-yne with

$[\text{Ir}(\text{acac})(\text{cod})]$ which gives an iridiacyclopentene ring system.

ALTHOUGH *homo* Diels–Alder addition to free¹ and co-ordinated² norbornadiene is known, related 1,4 addition to cyclo-octa-1,5-diene has not been reported. We now find that the reaction of hexafluorobut-2-yne with the



rhodium(I) complex $[\text{Rh}(\text{cod})\text{Cl}]_2$ leads to a 1,4 addition product. Treatment of $[\text{Rh}(\text{cod})\text{Cl}]_2$ with hexafluorobut-2-yne in benzene solution at room temperature for 24 h affords the yellow air-stable adduct $[\text{Rh}(\text{cod})(\text{C}_4\text{F}_6)\text{Cl}\frac{1}{2}\text{Et}_2\text{O}]_n$. This adduct readily reacts with sodium acetylacetonate in diethyl ether to give bright yellow crystals of a monomeric adduct (1) formulated $[\text{Rh}(\text{cod})(\text{C}_4\text{F}_6)(\text{acac})(\text{H}_2\text{O})]\cdot\frac{1}{2}\text{H}_2\text{O}$ from a single crystal X-ray structure determination. At room temperature the ^{19}F n.m.r. spectrum contains a sharp singlet at -3.68 p.p.m. (relative to benzotrifluoride) and there are ^1H n.m.r. absorptions at τ 4.69 (s, 1H), 6.20 (br, 4H), 8.06 (s, 6H), and 8.02–9.20 (10H), the absorption due to co-ordinated water being included under the peak at τ 6.20. However, at -90°C the ^1H n.m.r. spectrum contains absorptions at τ 4.69 (s, 1H), 6.08 (br, 2H), 6.42 (br, 2H), 8.04 (s, 3H), 8.22 (s, 3H), and 8.02–9.20 (10H) and the ^{19}F n.m.r. singlet broadens considerably. The i.r. spectrum contains a band at 3480 cm^{-1} $[\nu(\text{H}_2\text{O})]$.

Crystal data: $\text{C}_{17}\text{H}_{21}\text{F}_6\text{O}_3\text{Rh}\frac{1}{2}\text{H}_2\text{O}$, $M = 499.1$; monoclinic, space group $C2/c$, $a = 8.84$, $b = 19.34$, $c = 22.61$ Å, $\beta = 102.8^\circ$, $U = 3770.7$ Å³, $Z = 8$. Data were collected on a

† Satisfactory ^1H and ^{19}F n.m.r. and i.r. spectra have been obtained.

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⁵ A. C. Jarvis, R. D. W. Kemmitt, B. Y. Kimura, D. R. Russell, and P. A. Tucker, *J. Organometallic Chem.*, 1974, **66**, C53.

Stoe Weissenberg diffractometer using monochromatic $\text{Mo-K}\alpha$ radiation and were corrected for absorption. Block diagonal least-squares refinement reduced R to 0.091 for 1388 reflections.

The hexafluorobut-2-yne has added 1,4 across the co-ordinated cyclo-octadiene producing a new tricyclic system which is bonded to the metal by two Rh-C σ -bonds and by the C=C bond of the original acetylenic fragment. Mean bond lengths are $\text{Rh-C}(\text{CF}_3)$ 2.10 (2) and Rh-C 2.05 (2) Å. The two Rh-O (acac) bond lengths of 2.06 (2) Å *trans* to the π -bonded acetylenic fragment and 2.17 (2) Å *trans* to the Rh-C σ -bond reflect the greater *trans* influence of a σ -bonded carbon atom. The Rh-OH_2 bond length of 2.32 (2) Å is rather long [*cf.* 2.24 Å in $\text{Rh}(\text{AsMe}_3)_2[\text{C}(\text{CF}_3)_4\text{Cl}(\text{H}_2\text{O})^3]$] and the fluxional behaviour in solution, apparent from the n.m.r. spectra, is possibly due to lability of the water ligand. In the crystal structure an additional molecule of water on a diad axis is hydrogen bonded $[\text{O} \cdots \text{H-O}$ of 2.97 Å] to two molecules of the adduct.

An alternative mode of addition of hexafluorobut-2-yne to a co-ordinated cyclo-octa-1,5-diene molecule is observed in the adduct of empirical formula $\text{Ir}(\text{cod})(\text{acac})(\text{C}_4\text{F}_6)_2$ which can be isolated from the reaction of the acetylene with $[\text{Ir}(\text{acac})(\text{cod})]$ at 60°C in diethyl ether.† A single crystal X-ray structure determination shows the adduct to be (2).

Crystal data: $\text{C}_{22}\text{H}_{10}\text{F}_{12}\text{O}_2\text{Ir}$, $M = 723.6$; triclinic, space group $P\bar{1}$, $a = 13.445$, $b = 11.389$, $c = 8.472$ Å, $\alpha = 69.5$, $\beta = 114.1$, $\gamma = 104.2^\circ$, $U = 1101.8$ Å³, $Z = 2$. Data collected on a Stoe Weissenberg diffractometer using monochromatic $\text{Mo-K}\alpha$ radiation. R is 0.048 for 4642 reflections.

In this adduct one molecule of hexafluorobut-2-yne has inserted between the metal and one olefinic carbon atom to form an iridiacyclopentene ring. The second olefinic bond of the diene remains π -bonded to the metal. A second molecule of the acetylene has added 1,4 to the iridium acetylacetonato ring in a similar manner to previously reported additions to Rh^{I} ⁴ and Pd^{II} systems.⁵ This adduct contrasts with the product obtained by reaction of $[\text{Rh}(\text{acac})(\text{cod})]$ with hexafluorobut-2-yne where the acetylene trimerises and displaces the diene.⁴ Selected bond lengths are $\text{Ir-C}(\text{CF}_3)$ 2.016(9) (*trans* to O) and 2.049(7), Ir-O 2.192(7) [*trans* to $\text{C}(\text{CF}_3)$] and 2.223(6), $\text{Ir-C}(\text{olefinic})$ 2.333(8) and 2.267(9), and $\text{Ir-C}(\text{H})$ 2.057(8) Å. The π -co-ordinated olefinic C–C bond length is 1.37(2) Å.

These addition reactions presumably involve an intermediate metal acetylene complex. In the case of the reaction of hexafluorobut-2-yne with $[\text{Rh}(\text{cod})\text{Cl}]_2$, the close proximity of the co-ordinated acetylene to cyclo-octadiene, held in the correct conformation by the metal, would then facilitate 1,4 addition to give the observed product (1).

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