1:4 Addition of Hexafluorobut-2-yne to a Rhodium(I)–Acetylacetonate Ring

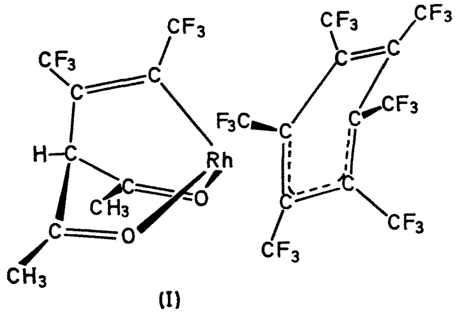
By D. M. Barlex, J. A. Evans, R. D. W. Kemmitt, and D. R. Russell*

(*Department of Chemistry, The University, Leicester* LE1 7RH)

Summary The crystal structure of the reaction product from four moles of hexafluorobut-2-yne and one of acetylacetonato(cyclo-octa-1,5-diene)rhodium(I) shows that one molecule of C_4F_6 adds 1:4 to the Rh(acac) ring.

Addition reactions of electronegative olefins and acetylenes to square-planar d^8 complexes have recently attracted considerable attention.[1] We now describe a new type of addition reaction which yields a Diels–Alder adduct of hexafluorobut-2-yne with a rhodium(I)–acetylacetonate ring.

Hexafluorobut-2-yne readily reacts with acetylacetonato-(cyclo-octa-1,5-diene)rhodium(I) in benzene to give 70%



(I)

yield of a yellow crystalline complex, the crystal structure of which has been determined. *Crystal data*: $C_{21}H_7F_{24}O_2Rh$ $M = 843{\cdot}1$; monoclinic, $P2_1/c$, $a = 9{\cdot}235$, $b = 8{\cdot}943$, $c = 30{\cdot}99$ Å, $\beta = 91{\cdot}15°$, $U = 2558{\cdot}8$ Å^3, $Z = 4$, $D_m = 2{\cdot}206$, $D_c = 2{\cdot}188$. R for 3628 reflections, all atoms (except hydrogen) anisotropic, is 0·067, data (Cu-K_α) collected by a Stoe Weissenberg diffractometer; an absorption correction was applied.

The molecular structure is shown in the Figure; the chemical composition is depicted as (I). Three molecules of C_4F_6 have trimerised and the resultant hexa(trifluoromethyl)benzene replaces cyclo-octadiene, co-ordinating to rhodium as a diene, as in the complex $Rh(\pi\text{-}C_5H_5)[C_6(CF_3)_6]$.[2] A fourth C_4F_6 molecule adds 1 : 4 to the Rh(acac) ring forming a bicyclo-system, similar to the bicyclo-product of the 1 : 4 addition of C_4F_6 to 1,2,4,5-tetramethylbenzene.[3] Although the C_4F_6 addition could be concerted, an alternative mechanism may involve formation of a C-bonded acetylacetonate[4] followed by insertion of C_4F_6 into the Rh-C bond[5] (we thank a referee for this suggestion). The reaction involves no change in formal oxidation state of rhodium, but its co-ordination number has increased by one. Analogous reactions with other dienophiles such as tetracyanoethylene and maleic anhydride are being investigated.

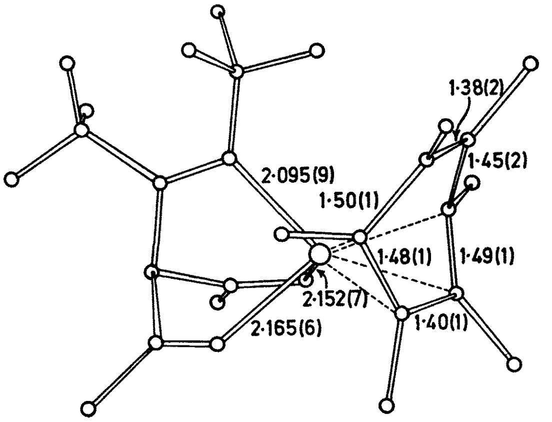


FIGURE. *The molecular geometry of* $Rh(C_9H_7F_6O_2)[C_6(CF_3)_6]$; *Bond lengths in* Å *with e.s.d. of last figure in parentheses. The fluorine atoms of* $[C_6(CF_3)_6]$ *have been omitted for clarity.*

The detailed geometry of the molecule is as one would expect. The hexa(trifluoromethyl)benzene ring is bent back with a dihedral angle of 42° (*cf.* 47·9° in $Rh(\pi C_5H_5)$-$[C_6(CF_3)_6]$). The four Rh–C(diene) distances are equal in the molecule (average $2{\cdot}116 \pm 0{\cdot}017$ Å), but the pattern of C–C distances around the ring can be interpreted as previously.[6] The relative orientation of the bicyclo-moiety with respect to the co-ordinated hexa(trifluoromethyl)benzene is such as to minimise repulsions between CF_3 groups.

We thank the S.R.C. for financial support, Johnson Matthey and Co. for a loan of rhodium, and Halocarbon Products for a gift of chemicals.

(*Received, February 2nd,* 1971; *Com.* 119.)

---

[1] J. P. Collman and W. R. Roper, *Adv. Organometallic Chem.*, 1968, **7**, 54.

[2] M. R. Churchill and R. Mason, *Proc. Roy. Soc.*, 1966, *A* **292**, 61.

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

[4] G. W. Parshall and F. N. Jones, *J. Amer. Chem. Soc.*, 1965, **87**, 5356; J. Lewis, R. F. Long and C. Oldham, *J. Chem. Soc.*, 1965 6740.

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

[6] R. Mason, *Nature*, 1968, **217**, 543.