Homo-Diels–Alder Addition of Hexafluorobut-2-yne to a Norbornadiene Rhodium(I) Complex: The Crystal Structure of the Adduct $[RhCl(norbornadiene)(C_4F_6)]_4$

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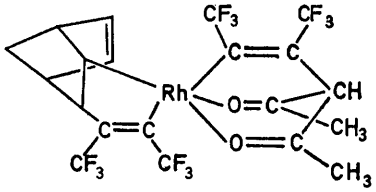
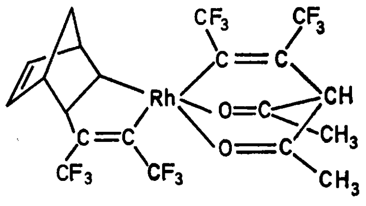
Summary Acetylacetonato(norbornadiene)rhodium(I) reacts with 2 mol. equiv. of hexafluorobut-2-yne to give a complex in which one molecule of the acetylene links the diene to the rhodium *via* a rhodiacyclopentene ring; however, hexafluorobut-2-yne and chloro(norbornadiene)-rhodium(I) dimer give a tetramer, $[RhCl(norbornadiene)(C_4F_6)]_4$, which is shown by *X*-ray studies to contain a novel homo-Diels–Alder adduct of the diene and the acetylene.

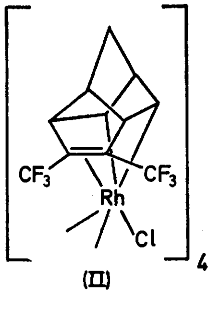
WE have shown[1] that hexafluorobut-2-yne undergoes 1:4 addition to the rhodium acetylacetonate ring in acetylacetonato(cyclo-octa-1,5-diene)rhodium(I). In the reaction the co-ordinated cyclo-octadiene is replaced by hexakistrifluoromethylbenzene. However, in a corresponding reaction of hexafluorobut-2-yne with acetylacetonato(norbornadiene)rhodium(I) diene displacement does not occur, and yellow crystals of (I), m.p. 177—179° (decomp.), are produced. In this adduct one molecule of hexafluorobut-2-yne has undergone the 1:4 addition [to the Rh(acac) system] as before,[1] deduced from i.r. and ^{1}H and ^{19}F n.m.r. spectroscopic evidence. Additional ^{19}F n.m.r. absorptions at $-8{\cdot}0$ (q, 3F, J_{F-F} 17 Hz) and $-5{\cdot}8$ p.p.m. (q, 3F, J_{F-F} 17 Hz) (relative to benzotrifluoride) and ^{1}H absorptions at τ 2·8 (1H), 3·6 (1H) 6·0 (1H), 6·4 (1H), 6·6 (1H), 6·9 (1H), and 8·0 (2H) (all broad peaks) are consistent with the formulation of the product as (Ia) or (Ib), in which a second molecule of hexafluorobut-2-yne completes a five-membered ring with the rhodium and one olefin bond of the diene. The ^{1}H resonances at τ 2·8 and 3·6 suggest that in solution the remaining olefinic bond is not co-ordinated.



(Ia)



(Ib)



(II)

Reaction of hexafluorobut-2-yne with chloro(norbornadiene)rhodium(I) dimer at 25° in benzene gives yellow crystals of an adduct (II) with empirical formula $[RhCl(C_7H_8)C_4F_6]_n$; the corresponding bromo-complex can also be obtained. Molecular weight determinations on (II) give values of n between 3 and 4. In contrast to (I), the ^{19}F n.m.r. spectrum of (II) contains a single absorption at $-4{\cdot}8$ p.p.m. at 35 °C which separates into two absorptions at $-5{\cdot}3$br (3F) and $-3{\cdot}6$br p.p.m. (3F) at -50 °C. ^{1}H n.m.r. absorptions occur at τ 6·61 (t, 2H), 6·9br (1H), 7·3br (1H), 7·6br (2H), and 9·35br (s, 2H). An *X*-ray single-crystal structure determination has demonstrated that (II) has the formulation shown; in the solid state n is 4. A

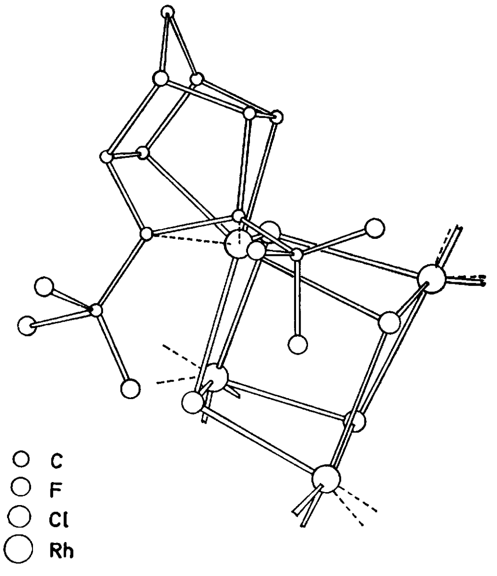


FIGURE. *A view (without hydrogen atoms) of part of the adduct* $[RhCl(C_{11}H_8F_6)]_4$, *showing the* Rh_4Cl_4 *cage and one of the homo-Diels–Alder adduct ligands. Partial bonds to the omitted adduct ligands are also shown. Average bond lengths* (Å) *with s.d.s:* Rh–Cl (trans *to* σ-C) 2·650 ± 0·009: *mean of* 8; Rh–Cl (trans *to* C=C) 2·427 ± 0·009: *mean of* 4; Rh–C (σ-bonded) 2·081 ± 0·036: *mean of* 8; Rh–C (*olefinic*) 2·151 ± 0·025: *mean of* 8; C=C (*co-ordinated*) 1·398 ± 0·011: *mean of* 4. *The e.s.d.'s of individual bonds are* Rh–Cl 0·005, Rh–C 0·02, C–C 0·035 Å.

hexafluorobut-2-yne molecule has undergone homo-Diels–Alder addition to the co-ordinated norbornadiene ligand in a similar manner to that reported for the free molecule.[2] However, the resulting polycyclic adduct remains co-ordinated to the metal *via* the C=C bond of the acetylenic fragment and two Rh–C σ-bonds arising from carbon atoms which would have completed a three-membered ring in the unco-ordinated adduct. The Rh atom may therefore be considered to have undergone oxidative insertion into this C–C bond, although no details of the reaction mechanism are yet available.

Crystal Data: $C_{44}H_{32}Cl_4F_{24}Rh_4$; $M = 1570{\cdot}2$; monoclinic, space group, $P2_1/c$, $a = 19{\cdot}48$, $b = 12{\cdot}21$, $c = 24{\cdot}63$ Å, $\beta = 109{\cdot}6°$, $U = 5578$ Å^3, $Z = 4$, $D_c = 1{\cdot}87$ g cm^{-3}; R for 5614 reflections (Cu-K_α) is 0·102 at the present stage of refinement (block-diagonal least-squares, Rh and Cl only anisotropic), data collected by Stoe automatic diffractometer.

Some details of the molecular geometry are shown in the Figure. The tetramer has almost perfect S_4 symmetry. Four Rh atoms define the apices of a tetrahedron and are bridged by four Cl atoms located over the tetrahedral faces in a similar manner to the Pt–Cl unit[3] in $[PtClMe_3]_4$; no Rh–Rh bonding is involved. The Rh–Cl distances demonstrate the larger *trans*-influence of σ-bonded carbon to that of a co-ordinated C=C bond;[4] the latter bond is lengthened as usual. Other C–C bond lengths are typical of a saturated system. No explanation of the temperature dependence of the ^{19}F n.m.r. spectrum is apparent from the crystal structure. Possibly a slight inequivalence of the two CF_3 groups is removed by partial dissociation of the tetramer in solution at room temperature.

The readiness with which co-ordinated norbornadiene undergoes homo-Diels–Alder addition may be compared with the more extreme reaction conditions necessary in the absence of a metal.[2] Some nickel complexes have been shown to catalyse the addition of acetylenes to norbornadiene[5] and similar adducts to (I) or (II) may be involved. Preliminary studies with $[RhCl(\text{cyclo-octa-1,5-diene})]_2$ suggest that an analogous adduct to (II) is formed.

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