

### Preliminary communication

## A $\sigma$ -BRIDGING ALKYNE—DIMETAL COMPLEX. THE STRUCTURE OF $\mu$ -HEXAFLUOROBUTYNE—BIS(CARBONYL- $h^5$ -CYCLOPENTADIENYL-RHODIUM)

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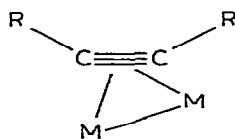
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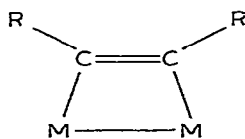
### Summary

The reaction between  $(h^5-C_5H_5)Rh(CO)_2$  and  $CF_3C\equiv CCF_3$  gives  $(h^5-C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ , and X-ray structural analysis of this shows that the bridging alkyne unit is  $\sigma$ -bonded to the two rhodium atoms, with a Rh—Rh distance (2.680 Å) indicating a metal—metal bonding interaction; there is a co-planar arrangement of the two rhodium atoms and the four carbon atoms of the alkyne within each molecule.

Numerous alkyne—transition metal complexes are known in which the alkyne unit adopts a  $\mu$ -bridging position between two metal atoms. X-ray diffraction studies [1,2] on several of these complexes have revealed the common structural features shown in I; the alkyne assumes a *cis*-bent geometry and is positioned normal to and above the metal—metal bond axis. An alternative possible bridging geometry, in which the alkyne unit is  $\sigma$ -bonded to the metal atoms is shown in II; the alkyne unit is *cis*-bent and is co-planar with the two metal atoms. This geometry has been proposed for the complex  $(Ph_4C_4)_2(PhC_2Ph)Mo_2(CO)_4$  [3] on the basis of the observed diamagnetism of the complex, and has been revealed in a structural study [4] of the tetrafluorobenzene complex  $Fe_2(CO)_8(C_6F_4)$ . A similar bonding geometry, in which there is no metal—metal bond, has been suggested for the complex ion



(I)



(II)

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$[\text{Co}_2(\text{CN})_{10}(\text{C}_2\text{H}_2)]^{6-}$  on the basis of spectroscopic properties [5] and has been revealed in preliminary structural studies on the complexes  $(\text{Ph}_3\text{P})_2\text{Au}_2(\text{CF}_3\text{C}_2\text{CF}_3)$  [6],  $\text{Fe}_2(\text{CO})_6(\text{SCF}_3)_2(\text{CF}_3\text{C}_2\text{CF}_3)$  [7], and  $(\text{Ph}_3\text{P})_2\text{Ir}_2(\text{NO})_2(\text{CF}_3\text{C}_2\text{CF}_3)_2$  [8].

In a recent study [9] of the reaction between hexafluorobut-2-yne and  $(h^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})_2$ , we isolated the complex  $(h^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$ . The observed spectroscopic properties of this complex were consistent with the bonding arrangements I and II, and no rational choice between the alternative geometries could be made. This complex is an intermediate in the formation of several other organorhodium complexes [9], and it is probable that unstable complexes of similar type are formed transiently in many other reactions of alkynes with carbonylmetal compounds. The importance of organotransition metal complexes as intermediates in organometallic and organic syntheses, coupled with uncertainty about the nature of  $(h^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$ , has prompted us to investigate the solid state structure of this complex.

We have used three-dimensional X-ray data collected by counter methods to determine the structure. The orange crystals of the compound are triclinic with space group  $P\bar{1}$ . The unit cell contains two molecules and has dimensions  $a = 9.322(5)$ ,  $b = 12.139(6)$ ,  $c = 8.671(5)$  Å,  $\alpha = 103.60(5)^\circ$ ,  $\beta = 68.98(5)^\circ$ ,  $\gamma = 109.87(5)^\circ$ . A total of 2101 structure amplitudes with  $F_o^2 > 3\sigma(F_o^2)$  were used in the solution of the structure. This solution was obtained by a combination of Patterson and difference Fourier methods. An anisotropic least-squares refinement has led to a value of  $R$  of 0.060 (where  $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ).

Figure 1 presents a drawing of the molecule. The two rhodium atoms are essentially co-planar with the four carbon atoms of the  $\text{CF}_3\text{C}_2\text{CF}_3$  ligand; the maximum displacement from the best least-squares plane through these atomic positions is 0.06 Å. The distance of 2.680(3) Å between the two metal atoms is consistent with a normal Rh—Rh bonding interaction [10]. One carbonyl group is attached to each rhodium atom, and the Rh—C—O bonds are approximately normal to the  $\text{Rh}_2\text{C}_4$ -plane. The two carbonyl groups within each molecule assume a *trans*-arrangement. This contrasts with the suggestion [9] of a *cis*-

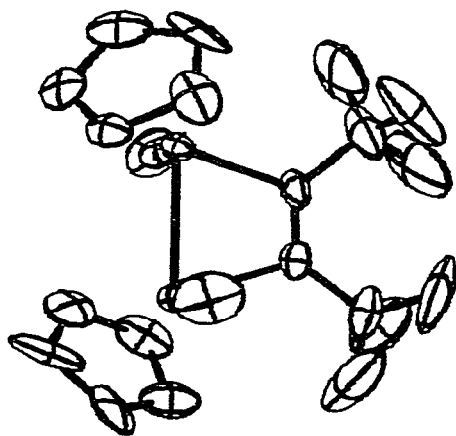


Fig. 1. Perspective view of the  $(h^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\text{CF}_3\text{C}_2\text{CF}_3)$  molecule. The 40% probability ellipsoids of thermal vibration are shown. Hydrogen atoms are omitted.

arrangement which was based on an interpretation of the infrared spectrum of the complex in solution, but it is consistent with the geometry in  $(h^5-C_5H_5)_2Rh_2(CO)_3$  [10]. The geometry within the  $h^5$ -cyclopentadienyl rings of  $(h^5-C_5H_5)_2Rh_2(CO)_2-(CF_3C_2CF_3)$  is regular within the accuracy of our determination. The rhodium to cyclopentadienyl plane distances are 1.91 and 1.89 Å; these distances are very similar to those found in other  $(h^5-C_5H_5)Rh$  complexes [11].

The geometry of the molecule is consistent with attachment of the  $CF_3C_2CF_3$  ligand to the rhodium atoms by two  $\sigma$ -bonds. The Rh—C bonding distances of 2.04(4) Å are similar to Rh—C( $sp^2$ ) distances observed for other molecules [12-14]. The  $CF_3C_2CF_3$  ligand is *cis*-bent with C—C— $CF_3$  angles of 130°; the C—C—Rh and  $CF_3$ —C—Rh angles are 110 and 120° respectively. Deviations from the normal olefinic angle of 120° are presumably due to constraints imposed by the Rh—Rh and Rh—C distances. The distance between the "ethenyl" carbon atoms of the ligand is 1.285(44) Å. This is intermediate between the normal C≡C and C=C distances of 1.20 and 1.35 Å respectively. A similarly short C=C distance has been reported [8] for the complex di- $\mu$ -hexafluorobut-2-enylene—bis(*cis*-triphenylphosphinenitrosyliridium(I)) but, in contrast, a normal C=C distance of 1.34(1) Å is reported [7] for the  $\mu$ -hexafluorobut-2-enylene—diiron complex,  $Fe_2(CO)_6(SCF_3)_2(CF_3C_2CF_3)$ . We can give no explanation of the apparent shortness of the C=C bond in  $(h^5-C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$ .

A complete report on the compound  $(h^5-C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$  will be published after completion of some chemical and spectroscopic studies.

All features of the molecular structure of  $(h^5-C_5H_5)_2Rh_2(CO)_2(CF_3C_2CF_3)$  are observed also for the closely related complex  $(h^5-C_5H_5)_2Rh_2(CO)_2(C_6F_5C_2C_6F_5)$ . This latter complex was prepared recently by Rausch and Gardner, and its crystal and molecular structure was determined by Dahl and Broach\* concurrently with our own structural investigation.

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