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Preliminary communication

REACTION OF IODOCARBONYLRHODIUM IONS WITH METHYL IODIDE. STRUCTURE OF THE RHODIUM ACETYL COMPLEX: $[Me_3PhN^+]_2[Rh_2I_6(MeCO)_2(CO)_2]^{2-}$

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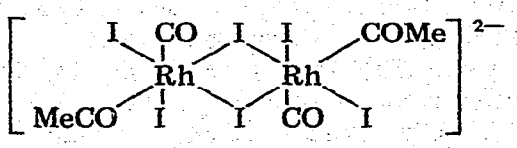
Summary

A rhodium acetyl complex $[Me_3PhN^+]_2[Rh_2I_6(MeCO)_2(CO)_2]^{2-}$ has been prepared and structure determined by X-ray diffraction: the Rh—C (acetyl) bond length is 2.062(23) Å and the dimeric anion is held together by Rh—I—Rh bridges with unequal Rh—I bond lengths.

The addition of methyl iodide to $[Rh(CO)_2I_2]^-$ ions yields an acetyl complex of rhodium. An X-ray examination of the trimethylphenylammonium salt of this complex has been undertaken to determine its structural and geometrical features. The complex is the di-μ-iodotetraiododiacetyldicarbonyldirhodium(III) ion, $[Rh_2I_6(MeCO)_2(CO)_2]^{2-}$ (I).



(I)

Deep red crystals of the trimethylphenylammonium salt of (I), $(C_9H_{14}N^+)_2(C_6H_6I_6O_4Rh_2)^{2-}$, are monoclinic, space group $P2_1/c$ with a 9.663(8), b 15.050(12), c 12.399 Å (10), and β 92.42(10)°, $Z = 2$. The intensities were measured on a linear diffractometer with Mo-K_α radiation: a Busing and Levy [1, 2] type absorption was applied (μ 6123 m^{-1}). The structure was determined by a combination of direct methods and Fourier syntheses; it was refined by least squares with individual anisotropic temperature factors till R for 2867 planes was 0.100.

Fig. 1 shows the anion, which has a crystallographic centre of symmetry, projected onto the I(1)I(2)I(3) plane. The coordination round the rhodium atoms is approximately octahedral and the two octahedra are joined by a double halogen bridge across the symmetry centre. The independent Rh—I (bridge) distances are 2.679(2) and 3.001(2) Å, so that the octahedra are only loosely held together. The two Rh—I terminal bonds may be compared with the Rh—I bonds in $RhI_2Me(PPh_3)_2$, 2.643 Å [3], and in π-$C_5H_5Rh(CO)C_2F_5I$, 2.653 Å [4]: the appropriate radius sum is 2.60 Å. A similar discrepancy in Rh—halogen (bridge) distances in $[RhCl_2(C_8H_{15}O_2)(4\text{-}CH_3C_5H_4N)_2]_2$ has been ascribed to the *trans* influence of a saturated carbon ligand [5]. However, no lengthening of Rh—Cl *trans* to Ph in chlorophenyl(tetraphenylporphine)rhodium was observed [6]

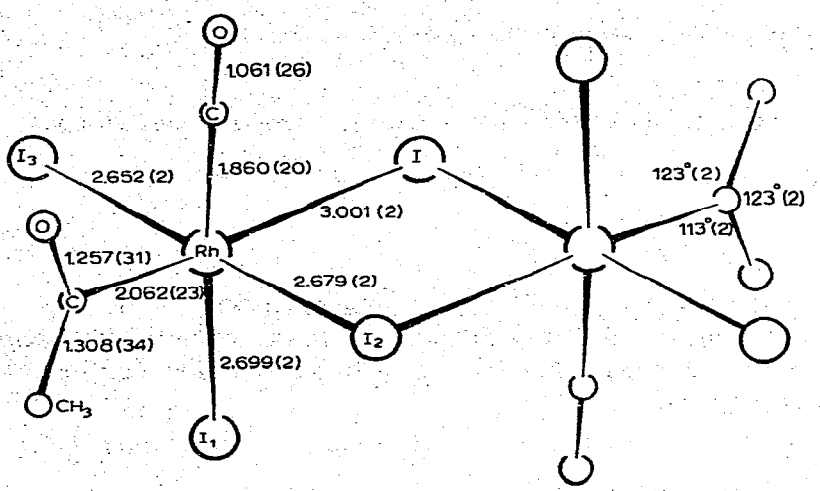


Fig. 1.

The Rh—C (acetyl) bond length is 2.062(23) Å, close to the value found for the Rh—C (methyl) bond in $RhI_2Me(PPh_3)_2$, 2.08 Å [3], and in $Rh_2I_2Me_4(SMe_2)_3$, 2.08 Å [7]. A similar distance has also been found for Rh—C(perfluoroalkyl) in π-$C_5H_5RhI(CO)C_2F_5$, 2.08 Å [4], and for Rh—C(Ph) in chlorophenyl(tetraphenylporphine)rhodium 2.05 Å [6]. There are no significant differences in these Rh—C σ bond lengths, a result which is in contrast to the variations observed in Mo—C σ bonds. Thus in π-$C_5H_5Mo(CO)_2(PPh_3)COMe$ the Mo—C(acetyl) bond length is 2.264 Å [8], in $[\pi\text{-}C_{10}H_8Mo(CO)_3Me]_2$ the Mo—C(methyl) bond length [9] is 2.383 Å, in π-$C_5H_5Mo(CO)_3C_3F_7$ the Mo—C(perfluoroalkyl) bond length is 2.288 Å [10], and in π-$C_7H_7Mo(CO)_2C_6F_5$ the Mo—C(perfluorophenyl) bond length is 2.244 Å [11].

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