Crystal and Molecular Structure of π-Cyclopentadienyl-π-2,6-di-t-butyl-1,4-benzoquinonerhodium

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Summary In the title compound, the quinone ligand has a distinct boat-like conformation and is co-ordinated to the metal as a diolefinic ligand.

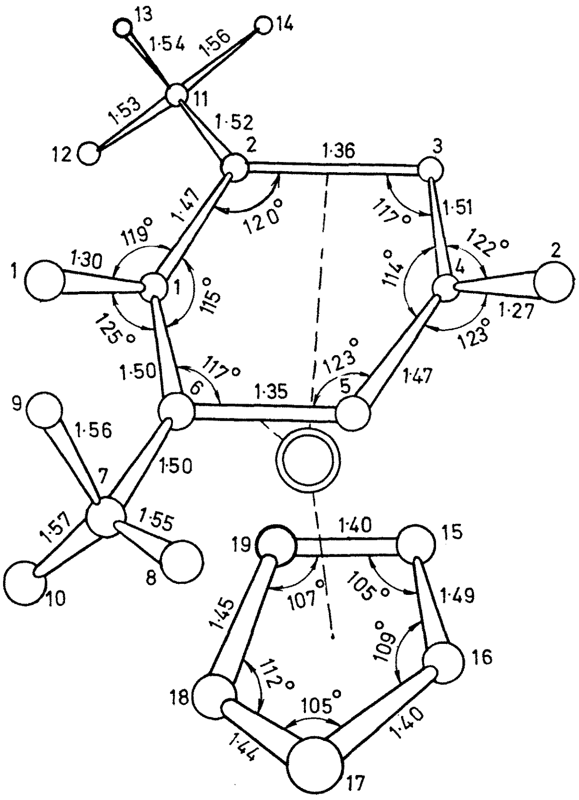
STUDY of the electrochemical reduction of rhodium and iridium π-complexes has shown[1] that co-ordination with metal fundamentally changes the reactivity of π-bonded quinones. To determine the geometry of quinone ligands in π-complexes of cobalt sub-group metals, we have undertaken the *X*-ray study of π-cyclopentadienyl-π-2,6-di-t-butyl-1,4-benzoquinonerhodium (I).[2]

The crystals of (I) are orthorhombic, $a = 15{\cdot}43$, $b = 22{\cdot}43$, $c = 9{\cdot}68$ Å, $D_m = 1{\cdot}52$, $D_c = 1{\cdot}54$ g.cm.$^{-3}$ for $Z = 8$, space group *Pbca*. Intensities of *ca.* 850 independent reflections were estimated visually disregarding absorption correction (equi-inclination Weissenberg goniometer, unfiltered copper radiation). The structure was determined by the heavy-atom method and refined by least-squares (full-matrix, isotropic temperature factors). At the present stage of refinement $R = 0{\cdot}14$ with an overall temperature factor $B = 3{\cdot}2$ Å^2. Standard deviations in bond lengths are 0·02—0·03 Å, in bond angles 2—3° depending on atomic numbers.

The geometry of the (I) molecule is shown in the Figure. The distances between the Rh atom and the carbon atoms of the quinone ring are not equal, four distances Rh–C(2), –C(3), –C(5), and –C(6) (2·16—2·20 Å) are significantly shorter than the other two distances Rh $\cdots$ C(1) (2·48 Å) and Rh $\cdots$ C(4) (2·38 Å). Thus the rhodium atom is co-ordinated by two olefinic bonds of the quinone ligand, attaining an 18-electron shell. The quinone ring, which is planar in free ligand molecules,[3,4] has in (I) a boat-like conformation with C(1) and C(4) furthest from the metal atom. The best plane going through C(2), C(3), C(5), and C(6) makes angles of 22° and 27° with planes C(3)C(4)C(5) and C(2)C(1)C(6), respectively. The greater value of the latter dihedral angle is due to steric repulsion of the C(1) =O fragment by bulky t-butyl groups situated in *ortho*-positions. In the only quinone π-complex studied previously by *X*-ray diffraction,[5] π-cyclo-octa-1,5-diene-π-duroquinonenickel (II), the quinone ligand also has a boat-like conformation but the deviation from planarity is much less (dihedral angles 6°).

The mean lengths of the two olefinic C(2)–C(3) and C(5)–C(6) bonds and the four single bonds in the quinone ligand (1·36 and 1·49 Å, respectively) are close to those found in free duroquinone (1·33 and 1·49 Å)[3] and benzoquinone (1·322 and 1·477 Å).[4] On the other hand, bond lengths for the quinone ligand in (II) differ much less (1·40 Å for double bonds, 1·45 Å for single bonds). This fact and the small deviation from planarity show that in (II) all six carbon atoms of the quinone ring interact with the nickel atom. Depending on the type of complex and the character of the metal, quinones may probably act in π-complexes either as diolefinic [*e.g.* complex (I)] or as arene [*e.g.* complex (II)] ligands. This variation of quinone ligand geometry and of interaction with metal atoms in (I) and (II) are reflected by a different degree of the C=O bond polarization in these complexes as compared with free quinones. Thus in (II) $\nu_{\text{C=O}}$ (1553 cm.$^{-1}$) is lower[5] by 133 cm.$^{-1}$ than in the i.r. spectrum of duroquinone itself. On the other hand, for (I) the lowering of $\nu_{\text{C=O}}$ relative to free 2,6-di-t-butyl-1,4-benzoquinone is much less (*ca.* 30 cm.$^{-1}$).[2] It is possible, however, that the difference of quinone ligand conformation in (I) and (II) may be due to steric overcrowding of this ligand by the bulky t-butyl groups. To rule out steric factors we have begun an *X*-ray study of π-cyclopentadienyl-π-duroquinonerhodium.

The planar π-cyclopentadienyl ligand (average C–C bond length 1·43 Å) is nearly parallel to the best plane through C(2), C(3), C(5), and C(6), making a dihedral angle of 6° with it. The mean Rh–C(cyclopentadienyl) distance (2·19 Å) does not differ from the distances between the rhodium atom and carbon atoms of the quinone ligand co-ordinated by double bonds, and from the value (2·18 Å) found[6] in (π-C_5H_5)Rh[$C_6(CF_3)_6$] which also is of a sandwich type. However, the Rh–C(cyclopentadienyl) distance in (I) is shorter than corresponding values in semi-sandwich complexes (π-C_5H_5)$_3$Rh$_3$(CO)$_3$,[7] (π-C_5H_5)$_2$Rh$_2$(CO)$_3$,[8] and (π-C_5H_5)Rh(C_2F_5)(CO)I[9] (2·24, 2·26, and 2·24 Å, respectively).



FIGURE

(*Received, April* 16*th*, 1969; *Com.* 520.)

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