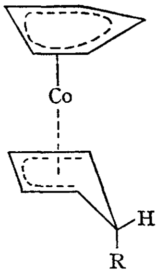
The Stereochemistry and Conformation of Hexamethylcyclohexadienylrhenium Tricarbonyl: a Complex exhibiting an Anomalously Low Carbon–Hydrogen Stretching Frequency

By PETER H. BIRD and MELVYN R. CHURCHILL*

(*Department of Chemistry, Harvard University, Cambridge, Massachusetts,* 02138)

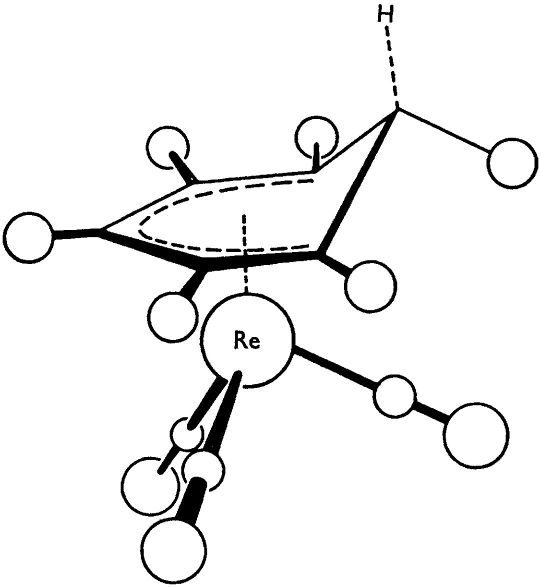
HYDRIDE ion attack on the $(\pi\text{-}C_5H_5)_2Co^+$ ion results in the formation of the cyclopentadiene complex, $\pi\text{-}C_5H_5CoC_5H_6$[1] which exhibits a broad, intense C–H stretch at 2742 cm.$^{-1}$. Deuteration studies have shown that this anomalously low C–H stretch involves the newly-formed hydrogen atom.[1] Substituted complexes, $\pi\text{-}C_5H_5CoC_5H_5R$, show no unusual C–H stretches, and crystallographic studies on two such species (R = Ph,[2] R = PhCO[3]) have demonstrated conclusively that the cyclopentadiene ligand is nonplanar, that the substituent occupies the *exo*-position (see I), and that the *endo*-hydrogen atom is some 3·05 Å from the metal.[2] However, no studies of complexes which possess the anomalous C–H stretch have yet been reported and there are *still* conflicting views as to whether it involves the *endo-* or *exo-*hydrogen.[4]



(I)

Attempts to study the crystal structure of π-$C_5H_5CoC_5H_6$ have failed, due to the X-ray sensitivity of this complex.[5] However, the cyclohexadienyl complex, $[C_6Me_6H]Re(CO)_3$, formed by hydride-ion attack on the hexamethylbenzene-rhenium tricarbonyl cation,[6] shows a similar broad, intense C–H stretch at low frequency (2790 cm.$^{-1}$). In order to obtain positive evidence on the origin of this stretch, a single-crystal X-ray analysis of hexamethylcyclohexadienylrhenium tricarbonyl was undertaken.

The complex crystallizes in space-group *Pbca* (No. 61) with $a = 13·512$, $b = 14·449$, $c = 15·552$ Å, $Z = 8$. The structure has been solved by conventional Patterson, Fourier, and least-squares refinement techniques. Complete three-dimensional data were collected on a Buerger Automated Diffractometer. The discrepancy index is $R_F = 0·20$ for all 2083 reflections, and $R_F = 0·12$ for the 1103 reflections with $|F^2| > 3\sigma(F^2)$. [The large number of extremely weak reflections is due to the proximity of the rhenium atom to the special position, $y = 1/4$.] The overall geometry of the molecule is shown in the Figure. The delocalized system formed by atoms C-2, C-3, C-4, C-5, C-6 is planar (r.m.s. deviation $=0·025$ Å), the mean Re–C distance being 2·35 Å. The rhenium atom is 1·86 Å below this plane whereas C-1, the saturated carbon atom of the cyclohexadienyl system, is 0·61 Å above the plane and the *endo*-methyl attached to C-1 is 0·48 Å above the plane. The dihedral angle between the planes formed by C-2, C-3, C-4, C-5, C-6 and C-2, C-1, C-6 is 50°.



FIGURE

This crystallographic analysis thus unambiguously demonstrates that the anomalous C–H stretch involves the *exo*-hydrogen atom. This result is consistent with previous crystallographic studies on cyclopentadiene complexes,[2,3] and is expected to be general for metal–cyclopentadiene and metal–cyclohexadienyl systems.

Although the saturated C-1 is 2·82 Å from the rhenium atom, it seems likely that the strange properties of the partially-hydridic[1] *exo*-hydrogen atom may result from some long-range interaction between the rhenium atom and carbon-1.

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