The Molecular Structure of Dimethyl-π-cyclopentadienyl-methylcyclopentadienerhenium

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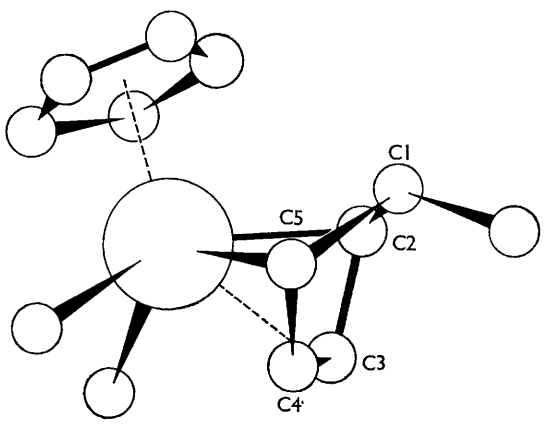
THE reaction of di-π-cyclopentadienylrhenium hydride with excess of n-butyl-lithium and then with excess of methyl iodide gives a compound of empirical formula $ReC_{13}H_{19}$. Spectroscopic studies indicated that this was probably dimethyl-π-cyclopentadienyl-methylcyclopentadienerhenium, although the lithiated derivative of di-π-cyclopentadienylrhenium has a lithium atom on each ring. An *X*-ray study of $ReC_{13}H_{19}$ has been undertaken to confirm the structure and for its interest in relation to other compounds containing cyclopentadiene rings or metal–alkyl bonds.

Crystal data: Monoclinic, space group $P2_1/c$. $a = 12{\cdot}59$, $b = 7{\cdot}751$, $c = 14{\cdot}35$Å, $\beta = 122{\cdot}92$, $Z = 4$. Intensities for 1860 independent reflections were measured by the integrating Weissenberg technique and the structure was readily solved by the heavy-atom method. It was refined initially by Fourier and differential syntheses, and then by several cycles of block diagonal least-squares refinement with an anisotropic temperature factor for the rhenium atom, and isotropic temperature factors for the carbon atoms. The present R value is 7·2%; standard deviations are ~ 0·03 Å for the rhenium–carbon bonds and ~ 0·05Å for the carbon–carbon bonds.

The suggested structure is correct (see Figure). The cyclopentadienyl ring is planar, but the cyclopentadiene ring is bent as has been found for similar compounds.[2] The angle between the planes through $C_2C_3C_4C_5$ and through $C_1C_2C_5$ is 38°, larger than any previously reported. Other compounds with bent cyclopentadiene rings have electron-withdrawing groups at C_1, but this structure disproves the suggestion[3] that such groups are necessary to produce a bent ring. The bond lengths of the cyclopentadiene ring are similar to those found in other compounds,[3] with a localised π-bond at C_3C_4(1·31Å) and two longer bonds C_2C_3 and C_4C_5(avg. 1·45Å). The metal atom forms one π-bond to C_3C_4 and two σ-bonds to C_2 and C_5.



The bonds from the methyl groups to the rhenium are 2·25Å (average). This gives a rhenium single bond radius of 1·48Å, longer than the 1·3Å estimated by Cotton for rhenium(IV) from chloro-complexes.[4] These bonds are markedly

[1] J. T. Moelwyn-Hughes, Ph.D. Thesis, Cambridge, 1962.; R. Cooper, M. L. H. Green, and J. T. Moelwyn-Hughes, *J. Organometallic Chem.*, in press.

[2] M. Gerloch and R. Mason, *Proc. Roy. Soc.*, 1964, *A*, **279**, 170; M. R. Churchill and R. Mason, *Proc. Roy. Soc.*, 1964, *A*, **279**, 194; L. F. Dahl and P. L. Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 752.

[3] N. A. Bailey, M. Gerloch, and R. Mason, *Nature*, 1964, **201**, 72.

[4] F. A. Cotton, *Inorg. Chem.*, 1965, **4**, 335.

shorter than the Mo–C(ethyl) bond (2·38Å) in tricarbonyl-π-cyclopentadienyl-ethylmolybdenum,[5] the only comparable structure containing metal–alkyl bonds that has been investigated. This difference may be connected with electron withdrawal by three carbonyl groups from the molybdenum, rather than by only one corresponding π-bond from the rhenium.

The two rings are approximately in eclipsed configuration. The bond lengths in the cyclopentadienyl ring vary in the same way and to the same degree as in dihydrodi-π-cyclopentadienylmolybdenum,[6] although the standard deviations are too large for the bonding to the metal atom to be deduced with confidence.

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[5] M. S. Bennett and R. Mason, *Proc. Chem. Soc.*, 1963, 273.
[6] M. Gerloch and R. Mason, *J. Chem. Soc.*, 1965, 296.