Crystal Structure of Decachlororuthenocene. Noncoplanarity of Carbon and Chlorine Atoms Arising from Valence Forces

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Summary X-Ray crystal-structure analysis shows that the decachlororuthenocene molecule is eclipsed with nearly perfect D_{5h} symmetry and that the chlorine atoms are systematically displaced outward *ca.* 0·1 Å from nearly exactly planar C_5 rings, apparently through the action of directed valence.

Two subjects of continuing interest in the structural chemistry of bis(cyclopentadienyl)metal compounds are the twist of the rings with respect to each other and the departures of substituent atoms from coplanarity with the ring atoms.[1] From a precise X-ray crystal-structure analysis, we find that the molecule of decachlororuthenocene[2] is exactly eclipsed within the errors of our determination and that the chlorine atoms are displaced outward by 0·094—0·126 Å (average 0·106 Å) from the nearly perfectly planar rings of carbon atoms (see Figure). Although these displacements are small, they are systematic and *ca.* 100 times the estimated standard deviation of a chlorine atom

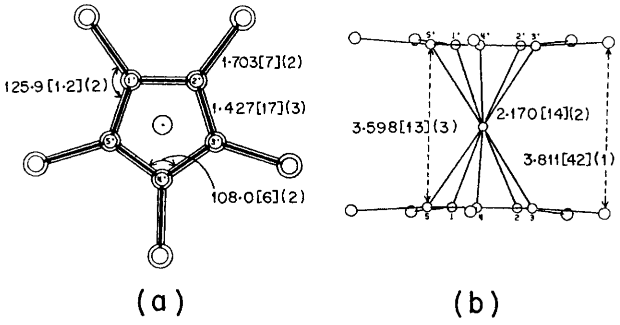

FIGURE. *The decachlororuthenocene molecule viewed* (*a*) *perpendicular and* (*b*) *parallel to the ring planes. The means of chemically equivalent distances* (Å) *and angles* (*deg.*) *are shown, with ranges* [*in brackets*] *and standard deviations of individual values* (*in parentheses*).

co-ordinate. Of greatest interest is the fact that the displacements appear to be a manifestation of directed valence.

Comparison of the Cl ··· Cl′ distances (average 3·811 Å) between opposing atoms with the usually accepted distance of 3·60 Å for a van der Waals contact Cl ··· Cl does not suggest intramolecular repulsion as the cause of the displacements. Nor is intramolecular repulsion suggested by comparison of the Cl ··· Cl′ distances with those of the intermolecular Cl ··· Cl contacts actually found in this crystal, of which there are 25 at distances less than 3·838 Å, the greatest of the Cl ··· Cl′ distances. Of these 25, 10 are less than 3·70 Å, four are between 3·61 and 3·64 Å, and one is at 3·33 Å. Since abnormal repulsive stress would be expected only in the closest one of these contacts, there is no reason to expect it in the intramolecular contacts at *ca.* 3·80 Å. In fact, no unusual stress would be expected even if the chlorine atoms were coplanar with the C_5 rings, which are 3·60 Å apart. Intramolecular repulsion seems, therefore, to be excluded as the cause of the displacements.

Detailed consideration of the packing of the molecules shows no kind of regularity in packing such that the displacements might reasonably be ascribed to intermolecular attractive and repulsive forces. It is of interest that the repulsion presumably associated with the contact at 3·33 Å is directed so as to oppose the outward displacements of the two chlorine atoms involved, which are related by inversion through a symmetry centre. We conclude that the chlorine atoms are held out of the ring planes by valence forces, not by any intermolecular forces or by intramolecular repulsion.

We have found similar systematic displacements of the chlorine and oxygen atoms in an *X*-ray structure analysis of 1,1′-diethoxyoctachloroferrocene,[3] which also is eclipsed (twist angle *ca.* 1·3°). These displacements are also ascribed chiefly to directed valence, though the average Cl ··· Cl′ distance of 3·511 Å suggests that repulsion may be involved to a slight degree. We know of no other π-cyclopentadienyl compounds which display such systematic outward displacements and no others in which displacements are clearly attributable to directed valence.

A slight effect of tightening of the Ru–ring bonding as a result of the multiple substitution by chlorine atoms is indicated by the value 2·170 Å for the average Ru–C distance in comparison with the value 2·21 Å in ruthenocene.[4] The average C–C distance of 1·427 Å in the cyclopentadienyl rings is not significantly different from the average in ruthenocene. The average C–Cl distance of 1·703 Å agrees with the value 1·70 ± 0·01 given by Sutton[5] as the average from a number of chlorine derivatives of aromatic compounds.

Crystal data: $C_{10}RuCl_{10}$, $M = 576{\cdot}4$, triclinic, $a = 8{\cdot}5193(3)$, $b = 13{\cdot}8812(5)$, $c = 7{\cdot}3770(3)$ Å, $\alpha = 95{\cdot}839(3)°$, $\beta = 101{\cdot}063(3)°$, $\gamma = 89{\cdot}216(3)°$, $U = 851{\cdot}7$ Å^3, $Z = 2$, $D_c = 2{\cdot}243$ [at $23{\cdot}6 \pm 0{\cdot}5°$ C, $\lambda(\text{Cu-}K_{\alpha 1}) = 1{\cdot}54051$ Å]. F(000) = 548; space group $P\bar{1}$ (C_i^1, No. 2). The structure is based on the intensities of 6181 independent reflections (Mo–K_α radiation) recorded with a diffractometer and corrected for absorption ($\mu = 24{\cdot}4$ cm^{-1}). The solution was obtained by inspection of a Patterson map; the refinement, by full-matrix least-squares, included adjustment of anisotropic thermal parameters for all atoms and corrections for a very slight degree of extinction. The final discrepancy index $R(F)$ is 0·048.

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