Tricarbonyl-1,6-methanocyclodecapentaenechromium

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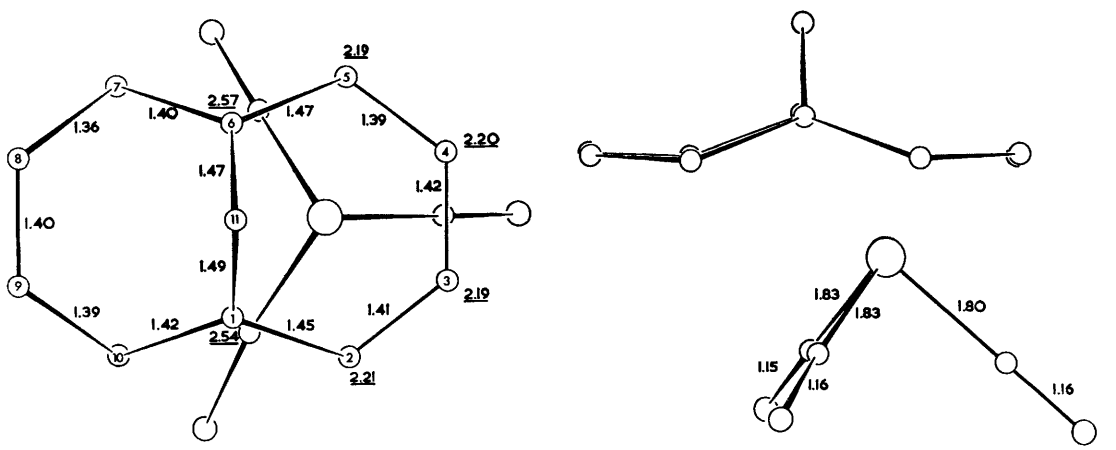
A DETAILED and accurate *X*-ray structure analysis of 1,6-methanocyclodecapentaene-2-carboxylic acid (I) has shown the molecule to be roughly planar and without pronounced alternation in bond-lengths around the perimeter.[1] The preparation of tricarbonyl-1,6-methanocyclodecapentaenechromium (II) and its n.m.r. spectrum have been reported recently.[2] We have undertaken the *X*-ray structure analysis of (II) both for comparison with (I) and with the two structures tricarbonyl-*exo*-phenyl-π-cycloheptatrienechromium[3] (III) and tricarbonyl-π-cycloheptatrienemolybdenum[4] (IV). Both (III) and (IV) exhibit alternation of bond-lengths.

The dark purplish-red crystals of (II) belong to the monoclinic system. The unit-cell parameters are $a = 13{\cdot}38$, $b = 7{\cdot}19$, $c = 24{\cdot}72$ Å, $\beta = 94{\cdot}59°$. $U = 2371$ Å^3 and $Z = 8$. The space-group is $I2/a$. This analysis is based on 749 unique reflexions ($R = 5{\cdot}4\%$). The molecular arrangement and bond-lengths are shown in the Figure. In the first place we note that the ligand is attached asymmetrically to the metal which is *trans* to the methylene bridge; the very large high-field shift of the methylene protons[2] is not therefore due to the close proximity of the metal atom. Secondly the chromium is not equally bonded to all the carbon atoms which form one "ring". Thus whilst four carbons are equidistant from the metal with separation 2·20 Å (the Cr–C distances are shown underlined in the Figure) the two central carbons are 2·55 Å away and are probably not involved in



FIGURE

bonding with the metal. The structure may therefore be one involving 34 electrons.

The overall shape of the ligand changes very little as a result of complex formation. It retains the "clerical hat" configuration previously determined and the *average* change in C–C distance is only $0{\cdot}01_8$ Å. There is virtually no change at all in that part not attached to the metal atom; there is a probably significant increase in the bond lengths C-1–C-2 and C-5–C-6 (from 1·41 to 1·46 Å) but the biggest change is in the "non-bonded" distanec C-1–C-6. The shortening from 2·26 Å in (I) to 2·14 Å is accompanied by a compression of the C-1–C-11–C-2 angle from 99·6° in the free ligand to 92·4° in the complex. Finally, when compared with (III) and (IV), the tricarbonyl group is rotated through 60°. Thus is achieved absence of short ligand–carbonyl separations. The idealised molecular symmetry of (II) is *m*.

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