X-Ray Crystal and Molecular Structure of Tricarbonyltroponechromium

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Summary Tropone co-ordinated to chromium is not planar; the bond lengths show some alternation though this is less than in corresponding cycloheptatriene complexes.

THE X-ray structure of tropone has not yet been reported but it is generally thought to be planar. Tricarbonyltroponechromium (I) has recently been prepared[1] and we have determined its structure for comparison with other tropones and with cycloheptatriene complexes of chromium.

Crystal data: $C_{10}H_6O_4Cr$, $M = 242$, monoclinic, $a = 7{\cdot}145$ (4), $b = 9{\cdot}777(5)$, $c = 7{\cdot}231(3)$ Å, $\beta = 103{\cdot}68(4)°$, $U = 490{\cdot}75$ Å^3, $Z = 2$, space group $P2_1/m$ by systematic absences and analysis, 1493 reflexions with intensities $>3\sigma$ (counting statistics), four-circle diffractometer[2] data, Fourier methods, $R = 2{\cdot}98\%$ (refinement complete).

The shape of the complex, together with some bond-length and bond-angle data, is shown in the Figure. The complex contains a plane of mirror symmetry.

The seven-membered ring in (I) is more nearly planar than those in tricarbonylcycloheptatrienemolybdenum[3] (II) and tricarbonyl-*exo*-7-phenylcycloheptatrienechromium[4] (III). All these rings are distorted in the same sense; thus in (I) atoms C(1,4,5) occur out of the plane (i) defined by atoms C(2,3,6,7) and away from the tricarbonylchromium group. Plane (ii), defined by C(3,4,5,6), makes a dihedral angle of 4·4° with plane (i), a value marginally less than the corresponding ones in (II) and (III), 6·3 and 5·7°, respectively. A greater contribution to overall planarity comes from C(1). In (I), the plane defined by atoms C(1,2,7) makes a dihedral angle of only 28·5° with plane (i) compared to values of 45·7 and 45·8° reported for the others. In the case of the cycloheptatrienes, complex formation leads to a more planar arrangement than that found in the free ligand. In the absence of definitive structural information relevant to tropone itself, it is not possible to say whether complex formation has induced a greater degree of planarity or caused non-planarity to occur as it does in naphthalene and anthracene.[5] However, it is clear that in (I) the keto-group as a whole is not coplanar, even to a first approximation, with the ring. Further, the oxygen atom is not even coplanar with C(1,2,7) but is bent some 10° from this plane and towards the metal.

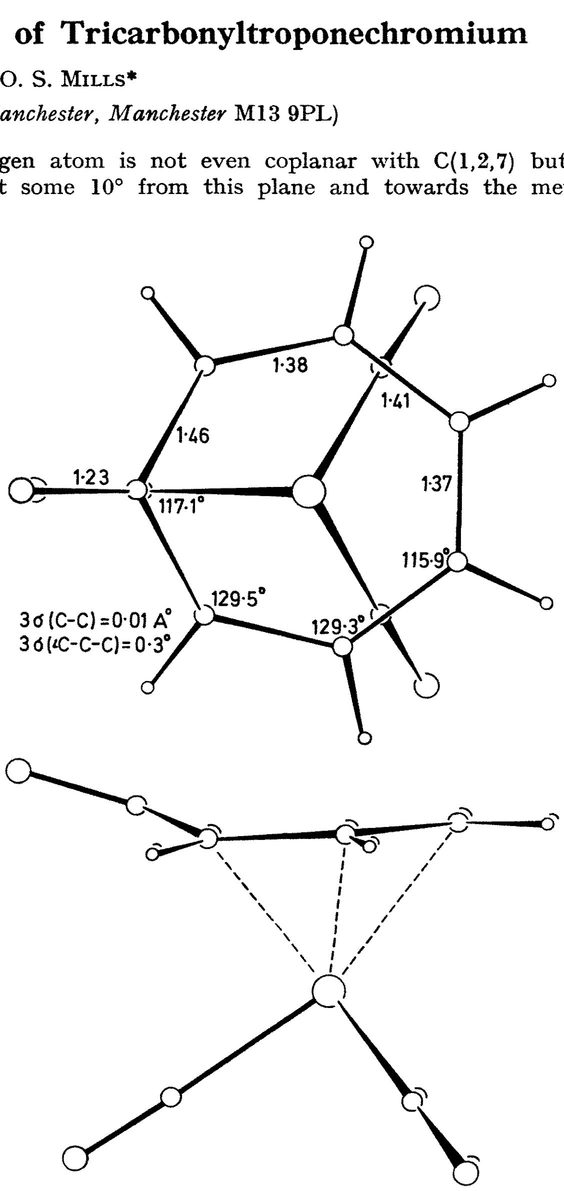
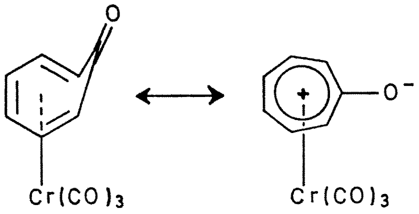
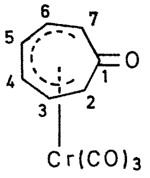


FIGURE. *Views of tricarbonyltroponechromium showing shape and dimensions.*

A similar out-of-plane distortion has been reported in the case of 4,9-methano[11]annulenone.[6] The tricarbonylchromium groups occupy similar positions, relative to the rings, in all three complexes. The Cr–C(3,4,5,6) separations are approximately equal, 2·21 Å, two more, Cr–C(2,7), are equal but longer, 2·30 Å, whilst Cr–C(1) is 2·64 Å. Whilst the latter is 0·24 Å less than in (III), we do not believe that the metal is bonded to this atom. In (II) and (III) the bond lengths in the ring, excluding the methylene carbon, reflect the localised polyene representation with lengths varying between 1·36 and 1·46 Å. By contrast, in (I) the variation is between 1·37 and 1·41 Å. Since the seven C–C lengths are not identical, the representation of the structure by (Ib) should be regarded as purely formal. Additionally, the C–O distance appears to be typically that for a carbonyl group.[7] Our results suggest a delocalisation such as in (Ic).



(Ia) (Ib)



(Ic)

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