X-Ray Crystal Structure of Dicarbonylpentamethylcyclopentadienylchromium Dimer

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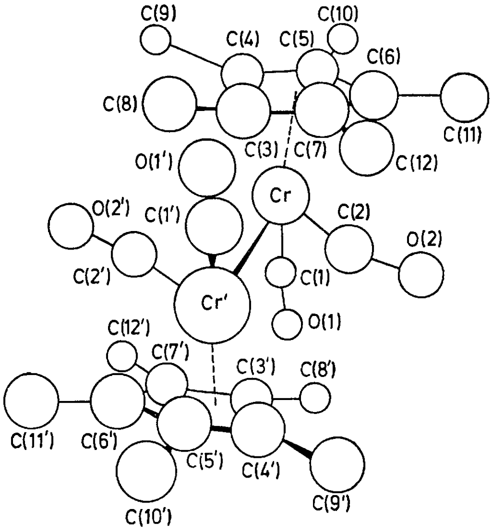
Summary Dicarbonylpentamethylcyclopentadienylchromium dimer, an unbridged binuclear π-complex with a metal–metal multiple bond, has a short Cr–Cr distance (2·276 Å) and terminal carbonyl groups.

Recently, short, strong metal–metal multiple bonds have been found in numerous inorganic compounds.[1] Crystallographic studies of binuclear π-complexes showed short metal–metal distances in $[(Bu^t)_2C_2Fe(CO)_2]_2$,[2] $[(C_5H_5)Nb(CO)Ph_2C_2]_2$,[3] and $(C_3H_5)_4M_2$ (M = Cr,[4] or Mo[5]) which were interpreted in terms of multiple bonds. Multiple bonds were also postulated for the dicarbonylpentamethylcyclopentadienylmetal dimers of Cr[6] (**1**) and Mo[7,8] (**2**), and dicarbonyl-(8,9-dihydroindenyl)molybdenum dimer (**3**).[8] Here we report the molecular structure of (**1**), an unbridged binuclear π-complex containing a multiple metal–metal bond.

The compound was prepared by the method of King and Efraty[7] and recrystallized from hexane. The crystals are monoclinic: $a = 8{\cdot}717$, $b = 14{\cdot}715$, $c = 9{\cdot}865$ Å, $\beta = 112{\cdot}0°$, $U = 1173$ Å^3, $Z = 2$, $D_m = 1{\cdot}408(15)$ g cm^{-3}, $D_c = 1{\cdot}408$ g cm^{-3}, space group $P2_1/n$. Since the unit cell contains two molecules, each lies at an inversion centre. Three-dimensional X-ray data were collected with an Enraf-Nonius CAD-3 diffractometer using Mo-K_α radiation. Data were collected to $\theta = 30°$ and 1803 independent reflections from a total of $3629(F^2 \geqslant \sigma)$ were used in the refinement. The structure was solved by the heavy-atom method. Currently, $R = 0{\cdot}098$.



FIGURE

The geometry of (**1**) is shown in the Figure. The most interesting features are the short Cr–Cr′ distance [2·276(2) Å] and the presence of two terminal CO groups per Cr, as determined by the C–Cr distances [Cr–C(1) 1·80(1); Cr′–C(1) 2·45(1); Cr–C(2) 1·78(1); Cr′–C(2) 2·62(1) Å]. Atoms Cr, Cr′, C(2), and C(2′) are coplanar (plane 1) as are atoms Cr, Cr′, C(1), and C(1′) (plane 2). Planes 1 and 2 are nearly perpendicular. Thus, the carbonyl groups are staggered with respect to the Cr–Cr′ axis, but not quite perpendicular to it as shown by the Cr′–Cr–C(CO) angles [72·9(3) and 79·3(3)° for C(1) and C(2) respectively]. The cyclopentadienyl ring centres (RC) are 2·21(1) Å from the nearest Cr atom and lie *ca.* 0·55 Å above and below plane 1. The rings are *trans* with respect to the Cr atoms and staggered with respect to each other as required by the centre of symmetry and by the Cr′–Cr–RC angle [158·6(6)°]. The cyclopentadienyl rings are normal: they are planar to 0·01 Å, adjacent C atoms are 1·42(2) Å apart, and the average internal ring angle is 108·0(12)°. All methyl groups are bent from the cyclopentadienyl plane [average RC–C(ring)–C(Me) angle 175·4(13)°] and are *exo* with respect to Cr. Last, the average C(Me)–C(ring) distance is normal [1·52(2) Å].

Mass spectra of (**1**) and single-bonded $[(C_5H_5)Cr(CO)_3]_2$[9] suggested a stronger Cr–Cr bond in (**1**). The Cr–Cr distance, when compared with that in metallic Cr (2·50 Å), also supports multiple bond character, while the diamagnetism of (**1**) in conjunction with the effective atomic number rule implies a triple bond. The Cr–Cr distance lies between that reported[10] for chromium(II) acetate (2·362 Å) and that[4] for $(C_3H_5)_4Cr_2$ (1·97 Å), both of which are said to contain quadruple bonds. This provides further evidence that care must be taken[5] when inferring bond multiplicity from bond length. We are attempting to explain the bonding in (**1**) using an idealized geometry of axial cyclopentadienyl rings and staggered carbonyls.

Chemically and thermally, (**1**) is quite stable. It is not sensitive to air and no decomposition is noted on heating in solution to 140 °C. Attempts to saturate the triple bond with σ- or π-donors such as Ph_3P and Ph_2C_2 were unsuccessful. The geometric features mentioned above make the triple bond rather inaccessible to attack by large groups. Penetration of small molecules from a few angles is possible as shown by the reaction of (**1**) with NO which yields $Me_5C_5Cr(CO)_2NO$.[11]

The unusual structural features reported here are most probably mirrored in the isostructural Mo analogue (**2**) and the related complex (**3**). However, (**2**) is less stable chemically than (**1**), while the corresponding tungsten compound has not been prepared. In contrast to inorganic systems, the available evidence indicates that for π-complexes, multiple bonds are more stable with first-row elements.

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