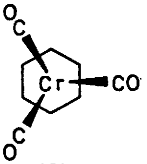
Orientation of $Cr(CO)_3$ and $Mn(CO)_3$ Groups in Tricarbonylchromiumbenzenecarboxylate and Tricarbonylmanganesecyclopentadienylcarboxylate Anions

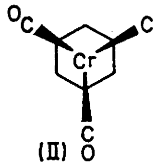
By M. A. BUSH, T. A. DULLFORCE, and G. A. SIM*

(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

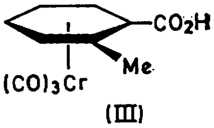
Summary The absolute configurations of (+)-tricarbonyl chromium-*o*-toluic acid, (−)-tricarbonylchromium-*m*-toluic acid, and (−)-tricarbonylmanganese-α-methylcyclopentadienylcarboxylic acid have been defined by the *X*-ray anomalous-dispersion method: the orientations of the tricarbonylchromium moieties in the toluate anions are interpreted in terms of the mesomeric and inductive effects of the CO_2^- group.



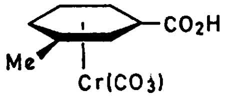
(I)



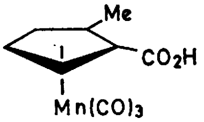
(II)



(III)



(IV)



(V)

A NUMBER of crystal-structure determinations have established that the orientation of the $Cr(CO)_3$ group in a substituted benzenechromium tricarbonyl is controlled by mesomeric electron repulsion or withdrawal by the substituent.[1] Whereas the benzene[2] and hexamethylbenzene[3] compounds have the staggered orientation (I), the anisole[4] and methyl benzoate[5] compounds display eclipsed orientations (II) in which the carbonyl–chromium vectors point towards the benzene positions *ortho* and *para* to the electron-repelling OMe-substituent and *meta* to the electron-withdrawing CO_2Me-substituent. We have now obtained results that establish that the $Cr(CO)_3$ derivatives of the *o*- and *m*-toluate anions adopt the staggered orientation (I) in the solid state (see Figures 1 and 2), and we conclude that the inductive electron repulsion of the CO_2^- group is enhanced and the mesomeric electron withdrawal diminished to the point of unimportance in these complexes by the powerful electron-withdrawing effect of the $Cr(CO)_3$ group.

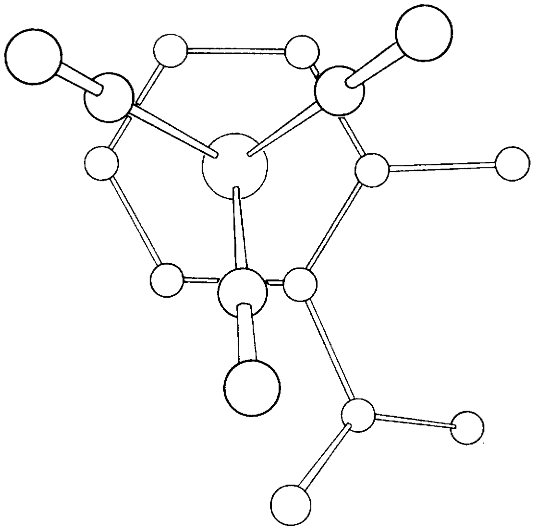


FIGURE 1. *Molecular structure of the tricarbonylchromium derivative of the* o-*toluate anion. Average values of bond distances are*: Cr–C(*benzene*) 2·21 ± 0·004 Å; Cr–C(*carbonyl*) 1·81 ± 0·007 Å; C–O 1·18 ± 0·008 Å.

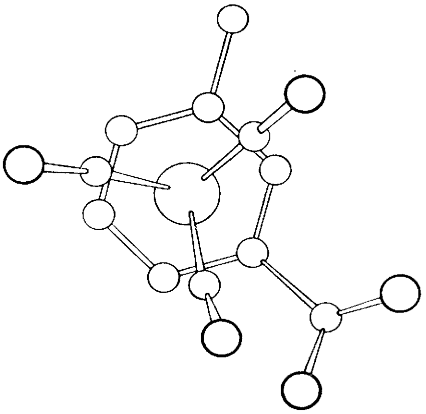


FIGURE 2. *Molecular structure of the tricarbonylchromium derivative of the* m-*toluate anion. Average values of bond distances are*: Cr–C(*benzene*) 2·20 ± 0·006 Å; Cr–C(*carbonyl*) 1·83 ± 0·009 Å; C–O 1·16 ± 0·012 Å.

We analysed the crystal structures of the (−)-α-phenethylamine salts of (+)-tricarbonylchromium-*o*-toluic acid (III) and (−)-tricarbonylchromium-*m*-toluic acid (IV)[6] and the (+)-α-phenethylamine salt of (−)-tricarbonylmanganese-α-methylcyclopentadienylcarboxylic acid (V)[7] in order to define unambiguously the absolute configurations of the optically-active organometallic compounds. The *X*-ray data were obtained by photographic methods, and the atoms located in electron-density distributions. The atomic parameters were adjusted by least-squares calculations with proper allowance for anomalous dispersion of Cu-K_α radiation by the Cr and Mn atoms, and the final values of R are 0·088 (*o*-toluic acid derivative, 1596 reflections), 0·096 (*m*-toluic acid derivative, 1520 reflections), and 0·110 (cyclopentadienylcarboxylic acid derivative, 2388 reflections, two formula units per asymmetric crystal unit). The analyses provide a firm basis for the kinetic resolution correlations employed in the assignments of absolute stereochemistries to (III), (IV), and (V), and also serve to confirm the accepted absolute configurations of (+)- and (−)-α-phenethylamine.[8,9]

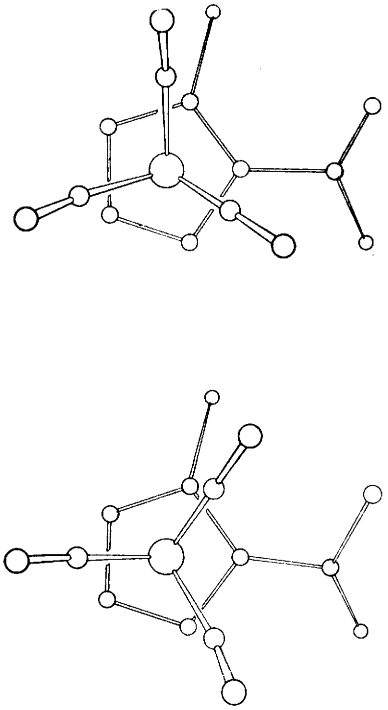


FIGURE 3. *Molecular structure of the tricarbonylmanganese derivative of the* α-*methylcyclopentadienylcarboxylate anion. Average values of bond distances are*: Mn–C(*cyclopentadienyl*) 2·12 ± 0·007 Å; Mn–C(*carbonyl*) 1·746 ± 0·009 Å; C–O 1·17 ± 0·012 Å.

Two distinct conformations of the tricarbonylmanganese-α-methylcyclopentadienylcarboxylate anion exist in the crystal (see Figure 3), and this observation provides additional evidence that the CO_2^- group has no orientational influence in tricarbonylmetal derivatives of aromatic carboxylate anions.

The α-phenethylammonium cations in the various crystal environments exhibit a common conformation in which the Me and NH_3^+ groups are approximately equidistant from, and on opposite sides of, the plane of the benzene ring. The bond lengths and valence angles are in good accord with values reported for related molecules.

We thank the S.R.C. for financial support (M.A.B. and T.A.D.), and Professor K. Schlögl for samples of the metallocene salts.

(*Received, November* 10*th*, 1969; *Com.* 1701.)

---

[1] G. A. Sim, *Ann. Rev. Phys. Chem.*, 1967, **18**, 57.
[2] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1314.
[3] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1298.
[4] O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc.*, (*A*), 1966, 822.
[5] O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc.* (*A*), 1967, 1619.
[6] H. Falk and K. Schlögl, *Monatsh.*, 1968, **99**, 578.
[7] H. Gowal and K. Schlögl, *Monatsh*, 1967, **98**, 2302.
[8] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, 1962.
[9] K. Schlögl, *Topics Stereochem.*, 1967, **1**, 39.