Crystal and Molecular Structure of π-(*exo*-2-Acetoxybenzonorbornenyl)-*exo*-tricarbonylchromium

By H. LÜTH, I. F. TAYLOR, JUN., and E. L. AMMA*

(*Department of Chemistry, University of South Carolina, Columbia, South Carolina* 29208)

Summary The stereochemistry of the product of acetolysis of benzonorbornenyl methanesulphonate has been shown by single-crystal *X*-ray diffraction to be π-(*exo*-2-acetoxybenzonorbornenyl)-*exo*-tricarbonylchromium.

BLY and STRICKLAND have studied the acetolysis of chromium tricarbonyl-complexed neophyl methanesulphonates and found the rates are accelerated by metal-participation to yield π-aryl tricarbonyl migrated products.[1] In addition, to determine whether the π-bonded moiety precedes or follows the migrating aryl they have examined the acetolysis of benzonorbornenyl methanesulphonates (2-, 3-, and 5-OMs). However, it is essential that the stereochemistry of one of the compounds be rigorously established by single-crystal *X*-ray means and the others can then be related. We now report the crystal structure of the title compound (I).

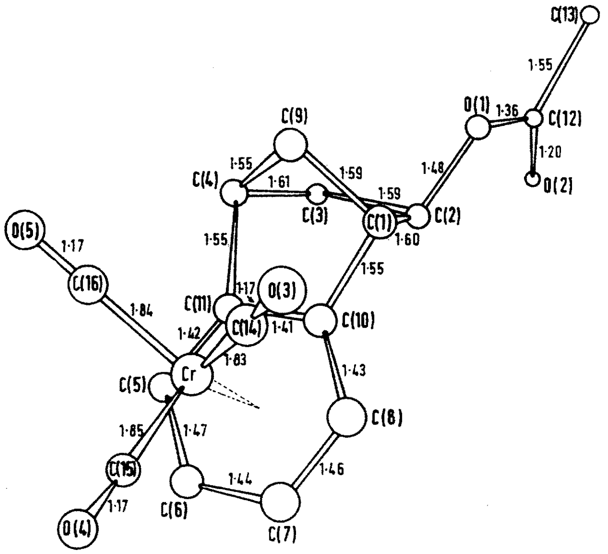

FIGURE *A perspective view of the* π-(exo-2-*acetoxybenzonorbornenyl*)-exo-*tricarbonylchromium showing the* exo–exo *configuration and the important intramolecular distances. The e.s.d.'s of bond distances are* ±0·014 Å *or less.*

Prof. R. S. Bly provided a needle crystal (0·12 × 0·06 × 0·54 mm) which was coated with hydrocarbon grease and sealed into a thin-walled glass capillary. The crystals were found to be monoclinic, $P2_1/a$;[2] $a = 21{\cdot}898 \pm 0{\cdot}003$, $b = 6{\cdot}911 \pm 0{\cdot}001$, $c = 10{\cdot}428 \pm 0{\cdot}002$ Å, $\gamma = 102{\cdot}2 \pm 0{\cdot}1°$ with $\lambda = 0{\cdot}71068$ Å, with $Z = 4$, $D_m = D_c = 1{\cdot}46$g cm^{-3}, $\mu = 7{\cdot}14$ cm^{-1} with Mo-K_α. From a total of 2255 independent *hkl* reflections for $2\theta < 65°$ measured on a Picker automated diffractometer, 1057 were found to be statistically above background and used in the structure determination. The structure was solved by conventional heavy-atoms methods and refined by full-matrix least-squares with unit weights to a final *R*† of 0·065 and weighted *R* of 0·070.

The structure is made up of discrete molecules of (I) separated by only van der Waals distances with no intermolecular contacts less than 3·8 Å. A perspective view of the molecule is seen in the Figure. The stereochemistry is *exo*-tricarbonylchromium and *exo*-acetoxy. The orientation of the chromium tricarbonyl fragment is such that the carbon atoms of the benzene ring are in staggered configuration relative to the carbonyl groups. This is the same configuration that has been found in hexamethylbenzenechromium tricarbonyl,[3] benzenechromium tricarbonyl,[4] phenanthrenechromium tricarbonyl,[5a] and naphthalenechromium tricarbonyl.[5b,c] We do not view this as a result of any particular electronic interaction between the ring and the chromium tricarbonyl moiety, but rather a steric consequence of the hydrogen atom on C(9). The O(3)–H distance is 3·23 Å. The molecule, excluding the acetate group, has an approximate mirror plane of symmetry passing through O(4), C(15), Cr,C(9) and bisecting the C(6)–C(7), C(11)–C(10), and C(3)–C(2) bonds. The Cr–C and C–O distances within the Cr(CO)$_3$ entity are normal. The Cr–C ring distances are as expected from results of similar compounds.[3–5] The benzene ring is planar, well within experimental error (± 0·01 Å). All other distances and angles are more or less normal. It would be useful to compare distances in this complex with benzonorbornenyl derivatives[6] and other norbornene derivatives, but in general, the e.s.d.'s reported in the literature are such that comparisons are meaningless.[7]

We acknowledge financial support from the National Science Foundation.

(*Received, October 12th,* 1970; *Com.* 1763.)

---

† $R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$; weighted $R = \{\Sigma\omega[|F_o| - |F_c|]^2\}^{\frac{1}{2}}/[\Sigma\omega|F_o|^2]^{\frac{1}{2}}$.

[1] R. S. Bly and R. C. Strickland, *J. Amer. Chem. Soc.*, in the press.
[2] "International Tables for X-Ray Crystallography," vol. I, eds. N. F. M. Henry and K. Lonsdale, The Kynoch Press, Birmingham, 1965.
[3] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, 4, 1298.
[4] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, 4, 1314.
[5] (a) H. Deuschl and W. Hoppe, *Acta Cryst.*, 1964, 17, 800; (b) K. W. Muir, G. Ferguson, and G. A. Sim, *J. Chem. Soc.* (B), 1968, 467; (c) V. Kunz and W. Nowacki, *Helv. Chim. Acta*, 1967, 50, 1052.
[6] T. Sato, M. Shiro, and H. Koyama, *J. Chem. Soc.* (*B*), 1968, 935.
[7] G. Dallinga and L. H. Toneman, *Rec. Trav. chim.*, 1968, 87, 795.