The Stereochemistry of Tricarbonylcycloheptatrienechromium Derivatives

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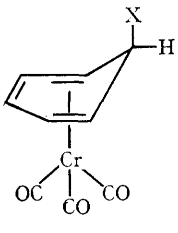
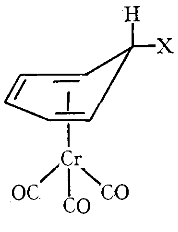
THE formation of a series of substituted tricarbonylcycloheptatrienechromiums by adding anions to tricarbonylcycloheptatrienechromium salts has been described.[1] This reaction invariably gives a single isomer, although two structures (I and II) are theoretically possible. These are designated *exo*- (I) and *endo*- (II) respectively and the *X*-ray data described below identify the above-mentioned products as the *exo*-isomers (I). A second and equally stereoselective method for their preparation is the nucleophilic displacement of the methoxy-group from tricarbonyl-*exo*-methoxycycloheptatrienechromium (I; X = OMe) by other substituents, X. By contrast, the *endo*-isomers (II) are the preferred products when substituted cycloheptatrienes (III) react with hexacarbonylchromium or with tricarbonyltripyridinechromium in the presence of boron trifluoride. Only in two cases (X = CN and X = C_6H_5) has the last mentioned method given both isomers (I and II). In other cases (X = Me, CH_2CO_2Et, $CH(CO_2Et)_2$, $CH_2C{\equiv}CH$) the *endo*-isomer (II) is formed with a high degree of stereoselectivity. We believe this must be attributed to the preferred "equatorial" conformation of the parent cycloheptatriene bearing a bulky substituent (III).

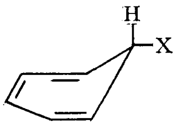
The preferred attack of nucleophiles on the tricarbonyltropyliumchromium cation from the side remote from the metal to give the *exo*-isomers (II) may likewise be the result of largely steric factors. It parallels the corresponding reactions of the biscyclopentadienylcobalt(III) ion. As in the latter case,[2] the *exo*-configuration of the product has been established by *X*-ray-crystallographic examination of phenyl derivative (I; X = C_6H_5). The crystals are monoclinic, space group $P2_{1/n}$, with unit cell dimensions a = 10·21 Å ± 0·02 Å, b = 14·01 Å ± 0·03 Å, c = 9·26 Å ± 0·02 Å and β = 105·33° ± 0·15°. The unit cell, U = 1378 Å^3, which contains four molecules, yields d_c = 1·465 g./c.c. (d_m = 1·47 g./c.c.). The structure was analysed from 1030 unique reflexions estimated from precession photographs taken with Mo-$K\alpha$ radiation. The agreement index, R, is 8·6% (excluding unobserved reflexions) and all hydrogen atoms have been located. The structure closely resembles that of tricarbonylcycloheptatrienemolybdenum.[3]



(I)



(II)



(III)

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[1] J. D. Munro and P. L. Pauson, *J. Chem. Soc.*, 1961, 3475; 3479.

[2] M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 1963, 112.

[3] J. D. Dunitz and P. Pauling, *Helv. Chim. Acta*, 1960, **43**, 2188.