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Preliminary communication

MOLECULAR STRUCTURE OF AN ARENEOLEFINDICARBONYLCHROMIUM CHELATE COMPLEX WITH (2,5-DIMETHYLBENZYL)ALLYL ETHER AS THE CHELATE LIGAND

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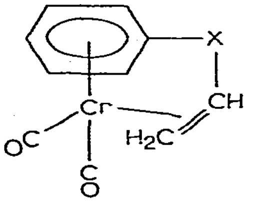
Summary

(2,5-Dimethylbenzyl)allyl ether produces two diastereomeric pairs of enantiomers with η^8 coordination of the $Cr(CO)_2$ group; the structure of the principal enantiomeric pair is established by complete X-ray analysis.

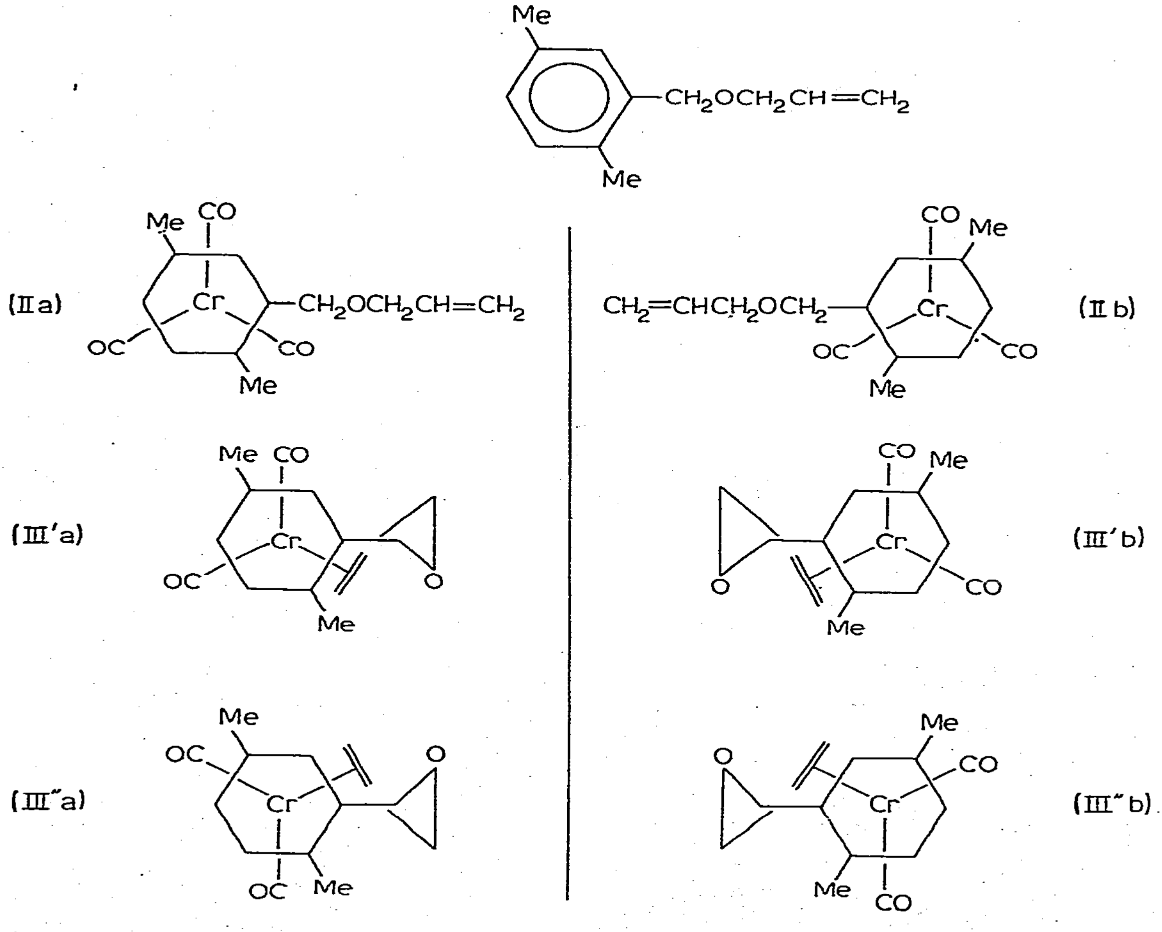
We have previously reported [1] the preparation of new chelate areneolefindicarbonylchromium complexes (I). In this work we studied the molecular structure of complexes with (2,5-dimethylbenzyl)allyl ether as chelating ligand, in order to elucidate the olefinic group orientation relative to the arene and to determine the chelate ring conformation. (2,5-Dimethylbenzyl)allyl ether was chosen because it has two prochiral groups; which made it possible to form a mixture of diastereomeric areneolefindicarbonylchromium complexes.



(I)

The corresponding arenetricarbonylchromium complex was obtained by reaction of the areneolefin with $Cr(CO)_6$ in boiling diglyme. In this case a racemic mixture of complexes II is formed; yield 79%, oil, $\nu(C{\equiv}O)$ 1899, 1969 cm^{-1} (cyclohexane). Under UV irradiation a CO ligand is replaced by an olefinic group. Another nonclassical chiral center appeared in the molecule and the isomeric mixture III′ and III″ was formed. III′a and III′b, III″a and III″b are enantiomeric pairs, while compounds III′ and III″ are diastereoisomers and the latter are also geometric isomers (Scheme 1). The total yield of the mixture of complexes III is 66%, m.p. 132—134°C (decomp.), $\nu(C{\equiv}O)$ 1870, 1925 cm^{-1}. According to PMR spectra the ratio III′/III″ is 5:1. The enantiomeric pair III′a, III′b is considerably less soluble and this fact enabled us to obtain the pure racemate by recrystallization from acetone. M.p. 134—135°C (with decomp.).

The molecular stereochemistry of racemate (III′a, III′b) is established by an X-ray structural study. The crystals are monoclinic, space group $P2_{1/c}$ with $a = 6.626(1)$, $b = 12.140(3)$, $c = 15.893(4)$Å, $\beta = 98.12(2)°$, $V = 1265.4(6)$Å^3, mol.wt. = 284.3, $D_m = 1.48$, $D_c = 1.49$ g.cm^{-3} and $Z = 4$, $\mu = 9.4$ cm^{-1} (λMoK_α). Intensities of the 1452 reflections greater than 2 σ were measured with an automatic "Syntex $P\ 2_1$" (Mo-radiation, graphite monochromator, $\theta/2\theta$ scan).



SCHEME 1

The structure was solved by the standard heavy-atom method and refined to $R = 0.032$ by the block-diagonal least squares technique in anisotropic approximation (isotropic for hydrogen atoms) localized by difference Fourier.

The coordination of the chromium atom is deduced from that found in benzene tricarbonylchromium (IV) [2] by replacement of one CO group by the ethylenic double bond. Due to its greater volume this ligand causes a decrease in the OC—Cr—CO angle to 84.6(2)° (Fig. 1). In III mutual orientation of the arene ligands and the three other ligands is staggered and similar to that found in IV and some of its derivatives (Fig. 2).

The distances, Cr—C(arene) to carbon atoms having substituents are somewhat longer (2.229—2.278 (3)Å) than to the other three carbons (2.199—2.216(3)Å). The distances to atoms bearing Me-groups are the longest and accordingly the benzene ring acquires a boat-like conformation with bending of the C(3) and C(6) corners out of the boat plane by 0.030 and 0.040 Å respectively. Substituents are also bent out of this plane: Me groups C(7) by 0.075, C(8) outwards by 0.193(4) Å and the methylene group C(9) towards the chromium atom by 0.030(13)Å. In IV the benzene ring is planar with almost equal Cr—C(arene) distances 2.220—2.240 Å.

The molecule III is one of the first chromium π-complex with a mono-olefinic ligand to be studied by X-ray analysis. In other structurally investigated olefinic complexes, namely Dewar benzene $(Me_6C_6)Cr(CO)_4$ (V) [3] and norbornadiene $(C_7H_8)Cr(CO)_3 \cdot PPh_3$ (VI) [4], coordinated double bonds are incorporated in rigid bicyclic systems. The double bond in III is coordinated symmetrically and the Cr—C distances 2.228 and 2.213Å are significantly shorter than in V (2.33 and 2.34Å) and VI (2.225—2.376Å). However the length of the C(11)—C(12) double bond itself (1.378(5)Å) is

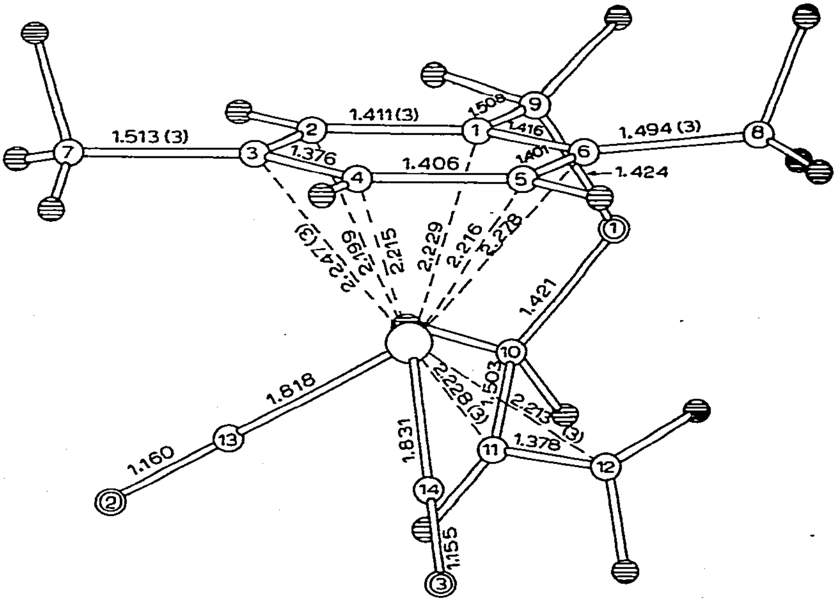


Fig.1. Molecular geometry of $3,5\text{-}(CH_3)_2C_6H_3CH_2OCH_2CH{=}CH_2 \cdot Cr(CO)_2$.

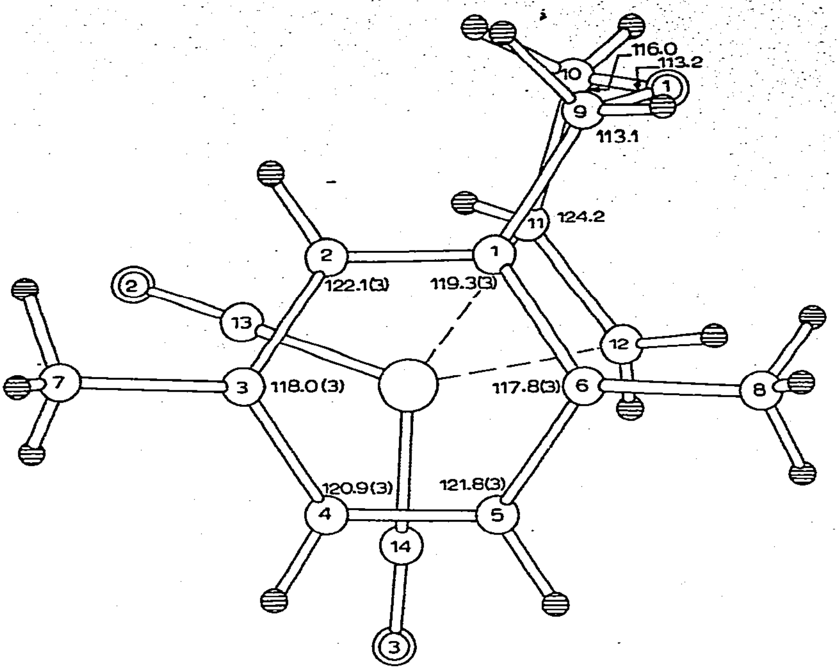


Fig.2. Projection of atoms onto the benzene ring plane.

comparable with values found in related compounds (1.36A in V and 1.350 and 1.407Å in VI). It is essential to note that the double bond is almost parallel (angle 1.3°) to the C(1)—C(6) bond of the arene ligand (Fig. 2). Evidently, in molecules of the other enantiomeric pair (III″a, III″b) the double bond should be parallel to the neighbouring arene bond C(1)—C(2).

The C(1), C(9), O(1), C(10), C(11) bridge connecting the benzene ring and the double bond is notably strained. Bond angles in this bridge are increased (e.g. O—CH_2—C angles to 113—116°) and torsional angles are far from ideal (+ 66.1, − 98.5 and −30.4° for the C(9)—O(1), O(1)—C(10) and C(10)—C(11) bonds respectively).

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