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STRUCTURE AND REACTIVITY OF THE (η^6-MESITYLENE)(η^2-MALEIC ANHYDRIDE) CHROMIUM-DICARBONYL COMPLEX

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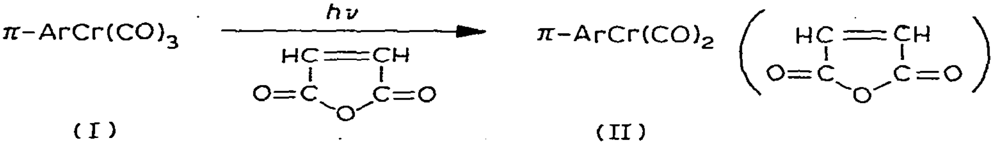
Summary

The structure of (η^6-mesitylene)(η^2-maleic anhydride) chromium-dicarbonyl was studied and it was established that the olefin ligand is symmetrically bonded with the chromium atom, the double bond turns out to be practically parallel to the benzene ring plane, the double bond length (1.433(10) Å) considerably exceeding its value in the non-coordinated molecule of maleic anhydride (1.303 Å). The five-membered heterocyclic is not completely planar, the oxygen atom deviates by 0.09 Å from the mean plane of the remaining four atoms of the cycle.

The hydrogen isotope exchange reaction of the complex in CF_3COOD was investigated and it was established that replacement of the CO ligand by the stronger electron accepting ligand maleic anhydride leads to an approximately 20-fold decrease of the rate constant of this reaction.

Introduction

Heberhold and Yablonski showed in 1968 [1] that under UV irradiation in the presence of maleic anhydride, the CO ligand of the π-arenechromiumtricarbonyl complex I is replaced by the maleic anhydride molecule which acts as a two-electron ligand to forming complex II.



(I) (II)

Using spectral data it was established that maleic anhydride is π-coordinated to the chromium atom via the olefin fragment —CH=CH—. In the IR-spectra of complex II, bands of the CH=CH group disappear in the 1500 cm^{-1} range characteristic of the non-coordinated maleic anhydride, and new bands appear in the long-wave region, which can be attributed to the CH=CH vibrations of the coordinated maleic anhydride [1].

Electronic effects of maleic anhydride in transition metal complexes can be estimated from IR- and ^1H NMR-spectra. Force constants of terminal CO-groups $k(C\equiv O)$ from the IR-spectra of complexes II are increased by 0.3—0.5 mdyn $Å^{-1}$ in comparison with force constants of CO-groups in the corresponding complexes I. In the ^1H-NMR spectra aromatic proton signals of the π-arene ring of complexes II are shifted downfield by approximately 0.5 ppm [1,2]. These data indicate that the maleic anhydride is a stronger electron accepting ligand than the CO group. Since the structure and reactivity of such complexes are not described in the literature, we studied these characteristics of complex II with Ar = mesitylene by the methods of an X-ray structure analysis and an isotopic exchange of hydrogen in an acid medium.

Results and discussion

The molecular geometry of the complex $(\eta^6\text{-}C_6H_3Me_3)(\eta^2\text{-}C_4H_2O_3)Cr(CO)_2$ (III) is shown in Fig. 1. The Cr atom has an octahedral coordination, the benzene ring acting as a tridentate, and the carbonyl groups and the ethylene bond as monodentate ligands. Participation of the bulky maleic anhydride molecule in coordination leads to a noticeable distortion of the C_{3v} local symmetry of the Cr atom environment which results in a decrease of the OC—Cr—CO bond angle to 81.5(3)° in comparison with the ideal value of 90°. A similar distortion of the coordination polyhedron is noted also in the other mono-olefin chromium complex, $[2,5\text{-}Me_2C_6H_3CH_2OCH_2CH=CH_2]Cr(CO)_2$ (IV) [3], where the OC—Cr—CO angle is equal to 84.6°. Besides, as in molecule IV, the steric crowding of complex III leads to an increase of the average Cr—C(arene) distance to 2.268(6) Å compared to the values of 2.20—2.22 Å usually observed in molecules of the type (arene)CrLL′L″ (e.g. [4]), and also to inequality of individual values of Cr—C(arene) distances.

The benzene ring is planar (the maximum deviation of atoms from the mean ring plane does not exceed 0.015 Å), but the methyl substituents C(9), C(10) and C(11) are displaced from this plane away from the Cr atom by 0.05, 0.06 and 0.03 Å, respectively. The average bond lengths C—C(arene) of 1.407(9) Å and C—Me of 1.487(10) Å are close to the usual values.

The olefin ligand is symmetrically bonded with the Cr atom and the average Cr—C distance of 2.176(7) Å is close to that found in molecule IV (2.220 Å). It is to be noted that, as in IV, the C(12)=C(13) double bond turns out to be practically parallel to the benzene ring plane (the angle is 1.3°). The length of the double bond C(12)=C(13) of 1.433(10) Å considerably exceeds the standard value of a non-coordinated olefinic bond (1.337 Å) and its length (1.303 Å) in the non-coordinated maleic anhydride molecule (V) [5]. This elongation is characteristic of transition metal complexes with olefin ligands and is due to the back donation contribution to the metal—ligand interaction.

The other bond lengths and the bond angles in the maleic anhydride molecule remain almost unchanged on coordination: C—C 1.44(1) (III) and

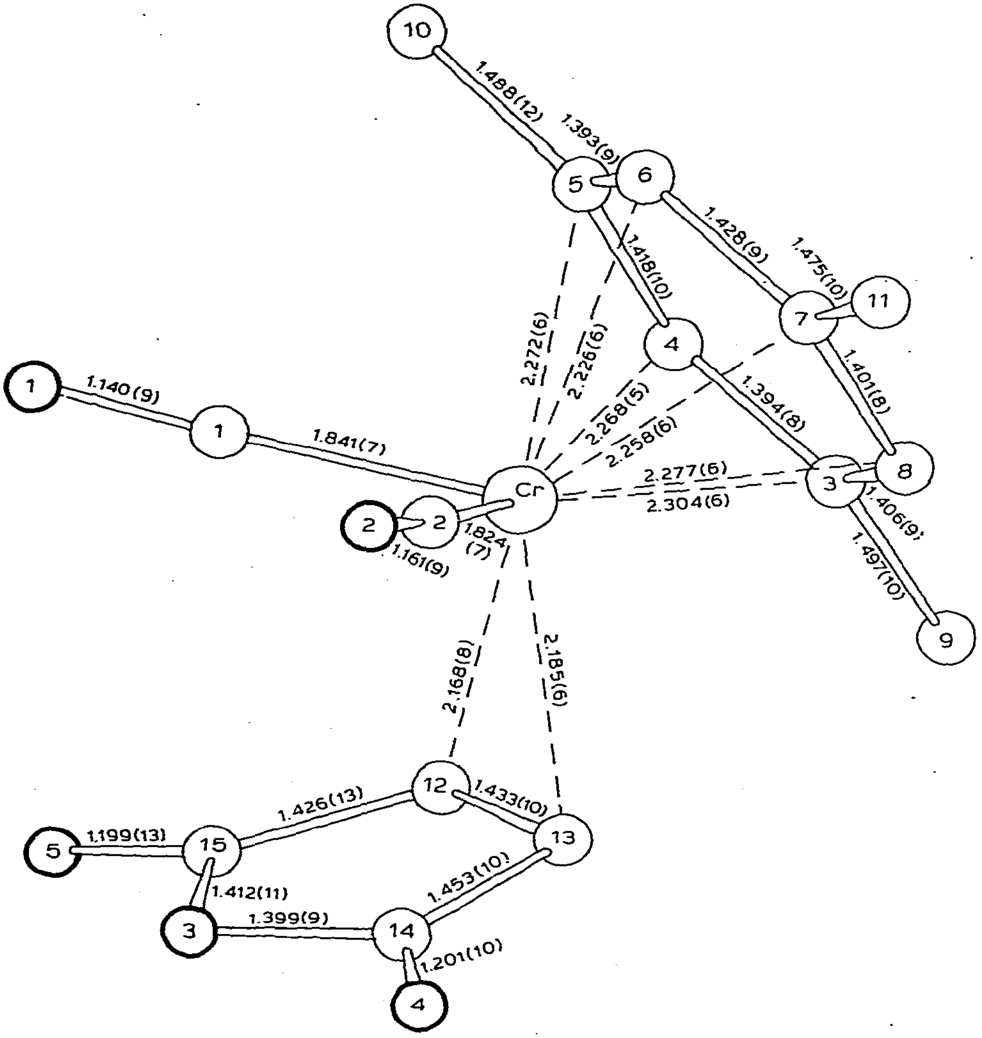


Fig. 1. Geometry of molecule III.

1.470(V); C—O 1.406(10) and 1.388; C=O 1.20(1) and 1.189 Å; C—C—C 106.9(7) and 108.6; C—C—O (cycle) 109.0(7) and 107.7; C—O—C 107.7(6) and 107.5°.

The five-membered heterocycle is not completely planar since the O(3) atom is displaced by 0.09 Å from the average plane of the remaining four atoms of the cycle (in molecule V this displacement is 0.03 Å), and the C(14)=O(4) and C(15)=O(5) bonds are inclined to this plane at angles of 1.6 and 3.3° respectively.

It is also interesting to note the non-orthogonality of the C(15)C(12)C(13)-C(14) group and the CrC(12)C(13) plane (the dihedral angle is 108.3°) which is indicative of a certain $sp^2 \rightarrow sp^3$ rehybridization of the C(12) and C(13) atoms participating in the π-interaction and was noted previously, e.g. for platinum ethylene complexes. Here the ethylene molecule loses planarity which is accompanied by deviation of hydrogen atoms from the metal atom [6].

TABLE 1

ATOMIC COORDINATES (X10^5 FOR Cr AND X10^4 FOR THE OTHER ATOMS) AND ANISOTROPIC TEMPERATURE FACTORS (X 10^2 FOR Cr AND X10 FOR THE REST) [a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	18904(6)	2495(8)	25000	243(3)	289(3)	247(3)	10(2)	16(3)	17(5)
O(I)	−491(5)	−401(9)	2245(7)	31(2)	96(4)	106(6)	−17(2)	−3(3)	−2(4)
O(2)	1173(6)	3108(7)	1447(5)	73(3)	45(3)	49(3)	19(2)	−4(2)	15(2)
O(3)	375(4)	2507(6)	4040(4)	54(2)	54(3)	56(3)	14(2)	18(2)	−7(2)
O(4)	1535(6)	4009(7)	3613(5)	91(4)	38(3)	64(3)	8(2)	1(3)	−7(2)
O(5)	−305(8)	255(9)	4608(7)	92(5)	86(4)	97(6)	−12(3)	64(5)	−9(4)
C(1)	421(6)	−196(8)	2374(7)	35(2)	40(3)	59(5)	−3(2)	6(3)	8(3)
C(2)	1460(5)	2020(8)	1879(5)	33(2)	48(3)	33(3)	2(2)	1(2)	−3(2)
C(3)	3431(4)	−1140(7)	2926(5)	30(2)	41(3)	32(2)	10(2)	1(2)	6(2)
C(4)	2618(5)	−2162(6)	2615(6)	39(2)	28(2)	38(3)	10(2)	4(3)	3(3)
C(5)	2126(5)	−2014(7)	1673(5)	46(3)	24(3)	32(2)	1(2)	2(2)	−7(2)
C(6)	2431(5)	−775(7)	1076(5)	37(2)	39(3)	25(2)	0(2)	−2(2)	1(2)
C(7)	3254(5)	302(7)	1376(5)	29(2)	37(3)	27(2)	4(2)	4(2)	1(2)
C(8)	3740(5)	84(8)	2301(4)	27(2)	41(3)	33(3)	8(2)	1(2)	2(2)
C(9)	3998(7)	−1350(11)	3894(6)	48(4)	57(4)	38(3)	11(3)	−11(3)	7(3)
C(10)	1293(9)	−3155(10)	1333(8)	71(5)	41(3)	52(4)	−18(3)	−3(4)	−9(3)
C(11)	3594(7)	1566(10)	713(6)	46(3)	48(4)	39(3)	−6(3)	9(3)	11(3)
C(12)	1566(7)	431(9)	4066(6)	66(4)	51(4)	31(3)	21(3)	16(3)	4(3)
C(13)	2180(6)	1764(8)	3763(5)	44(3)	39(3)	27(2)	6(2)	−4(2)	−3(2)
C(14)	1415(7)	3054(9)	3783(5)	59(4)	40(4)	30(3)	12(3)	1(3)	−6(2)
C(15)	477(8)	923(11)	4282(6)	73(5)	60(4)	47(3)	−2(4)	31(3)	−4(3)

[a] The temperature factor is in the form $T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2\,B_{23}klb^*c^*)]$.

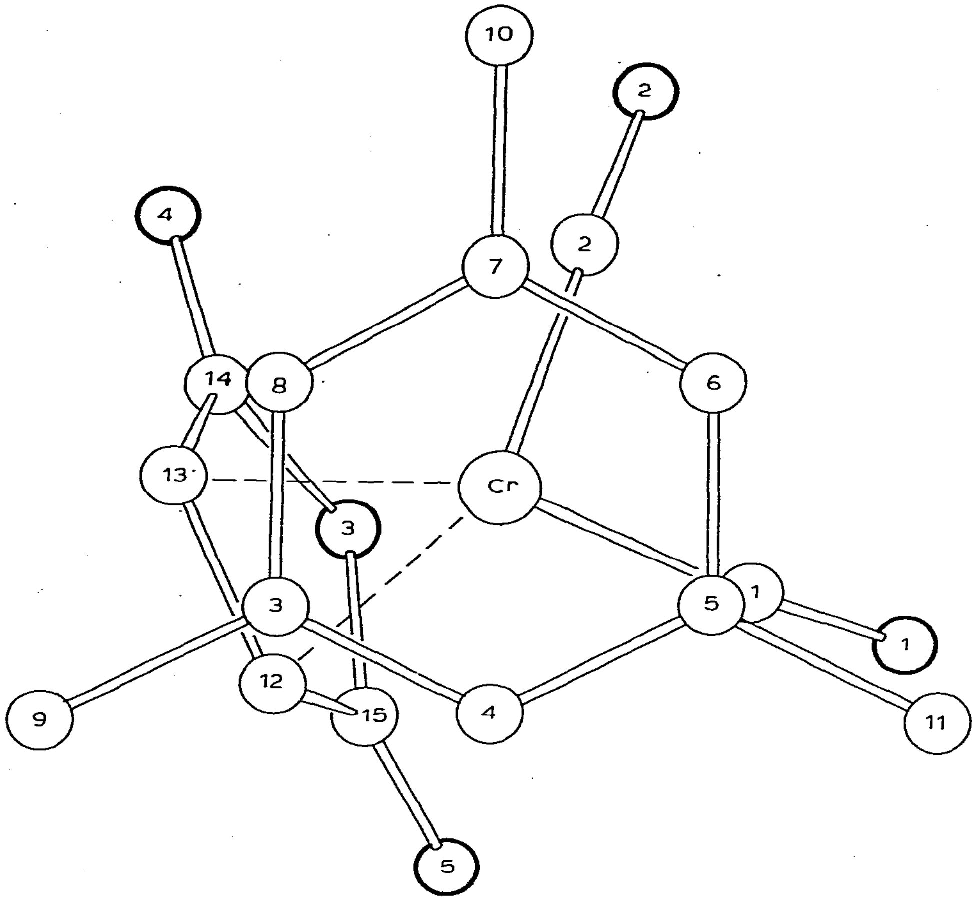


Fig. 2. Projection of molecule III in the benzene ring plane.

The projection of molecule III on the benzene ring plane is shown in Fig. 2. It is evident that the relative orientation of the arene and the other three ligands corresponds to a conformation intermediate between eclipsed and staggered forms (closer to the former). An analysis of intramolecular non-bonded distances in the ideal staggered conformation and the one found in the crystal has shown that the observed deviation from the staggered form can be explained only by the influence of the crystal field.

The dihedral angle between the six-membered cycle and the mean plane of the five-membered one is equal to 69.6°. As for the π-interaction of the double bond with the Cr atom, an alternative orientation of the maleic anhydride molecule is equivalent to that found in the crystal and can be obtained from the latter by reflecting this molecule in the CrC(12)C(13) plane. However, this alternative orientation is prohibited by the short non-bonded intramolecular contacts.

The metal-carbonyl groups are linear, the average bond lengths Cr—C of 1.832(7) and C—O of 1.150(9) Å do not differ from those found in other arenechromium-tricarbonyl complexes.

An increase of the maleic anhydride double bond length by more than 0.1 Å

TABLE 2

BOND ANGLES ω (°)

Angle	ω	Angle	ω	Angle	ω
C(1)CrC(2)	81.5(3)	C(8)C(3)C(4)	118.9(6)	C(13)C(14)O(3)	109.2(6)
CrC(1)O(1)	175.4(7)	C(9)C(3)C(4)	121.3(6)	C(14)O(3)C(15)	107.7(6)
CrC(2)O(2)	177.0(6)	C(9)C(3)C(8)	119.8(6)	O(3)C(15)C(12)	108.8(7)
C(3)C(4)C(5)	121.2(6)	C(10)C(5)C(6)	120.7(6)	C(15)C(12)C(13)	107.9(7)
C(4)C(5)C(6)	118.7(6)	C(10)C(5)C(4)	120.6(6)	O(4)C(14)C(13)	131.7(7)
C(5)C(6)C(7)	121.4(6)	C(11)C(7)C(6)	120.4(6)	O(4)C(14)O(3)	119.1(7)
C(6)C(7)C(8)	117.8(5)	C(11)C(7)C(8)	121.8(6)	O(5)C(15)O(3)	118.8(9)
C(7)C(8)C(3)	121.9(6)	C(12)C(13)C(14)	105.9(6)	O(5)C(15)C(12)	132.4(9)

on coordination with a chromium atom indicates a considerable contribution of the back donation from the metal to this ligand. It was interesting to evaluate to what extent this effect would influence the reactivity of the π-arene ligand. With this purpose we carried out hydrogen isotope exchange reactions (HIE) of complex III in deuterotrifluoroacetic acid at 70°C. Simultaneously, the HIE reaction of mesitylenechromium-tricarbonyl (I) was studied under the same conditions. The HIE rate of complex III turned out to be approximately 20 times lower than that of complex I ($K_{\mathrm{HIE(III)}} = 8.5 \times 10^{-8}\ \mathrm{s}^{-1}$, $K_{\mathrm{HIE(I)}} = 186.0 \times 10^{-8}\ \mathrm{s}^{-1}$).

The decrease of the electrophilic HIE rate of the π-arene ligand in the complex III indicates that maleic anhydride has stronger electron acceptor properties than the carbonyl ligand and these results agree with data from IR- and PMR-spectroscopy [1].

Experimental

Complex III was obtained by the method described in ref. 1.

Crystals of III grown from CH_2Cl_2 are orthorhombic, *a* 12.2011(8), *b* 8.6346(3), *c* 13.575(1) Å, *V* 1430.2 Å^3, mol.wt. = 326.3, D_{calc} 1.524 g/cm^3; $Z = 4$, space group $P2_1/n$. Intensities of 1834 reflections with $I \geqslant 3\sigma$ were measured with the 4-circle automatic Hilger-Watts diffractometer (λ Cu-K_α, graphite monochromator, $\theta/2\theta$-scan); absorption was neglected. The structure was solved by the heavy atom technique and refined by least squares in full-matrix anisotropic approximation, hydrogen atoms located by the difference synthesis were included in the calculation of *F* but were not refined. The final value of the *R* factor is 0.040. Atomic coordinates and temperature factors are listed in Table 1, bond angles in Table 2.

HIE of complex III was carried out in CF_3COOD at 70°C in sealed ampoules by the techniques developed previously [7]. The rate constant was calculated by the first order equation.

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