

PECULIARITIES OF COORDINATION OF SILAOXAPHENANTHRENE WITH THE TRICARBONYLCHROMIUM GROUP. CRYSTAL AND MOLECULAR STRUCTURE OF TRICARBONYL[1-4*a*(10*a*)- η -10,10-DIMETHYL-10-SILA-9-OXA-9,10-DIHYDROPHENANTHRENE]CHROMIUM AND TRICARBONYL[5-8*a*(4*b*)- η -10,10-DIMETHYL-10-SILA-9-OXA-9,10-DIHYDROPHENANTHRENE]CHROMIUM

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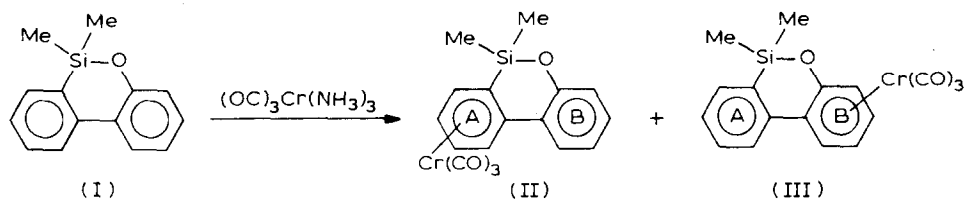
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Summary

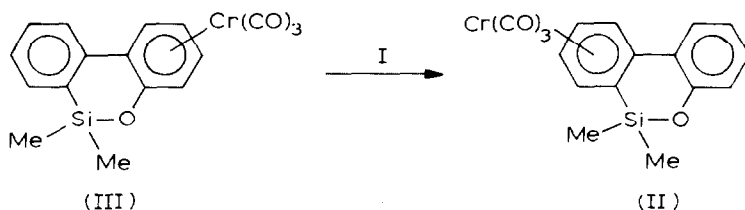
An X-ray crystal structural analysis of two tricarbonylchromium complexes formed by 10,10-dimethyl-10-sila-9-oxa-9,10-dihydrophenanthrene (I) and having the same composition $[\overset{\text{C}}{6}\overset{\text{H}}{4}(\overset{\text{Si}}{\text{Me}}_2\overset{\text{O}}{\text{C}}_6\overset{\text{H}}{4})\text{Cr}(\text{CO})_3$ (II and III) was carried out. The complexes are isomers in which wherein different aromatic fragments of the ligand are coordinated with the Cr atom. The silicon-substituted fragment is linked with the metal atom in complex II, the oxygen-substituted fragment is coordinated in complex III. In both cases the tricyclic system of the ligand is nonplanar with the dihedral angle between benzene rings being 20.4° in II and 15.5° in III. The chromium atom is displaced from the centre of the coordinated ring in the direction opposite to the ring junction carbon atoms by 0.032 \AA in II and 0.064 \AA in III. The final *R*-factors are 0.029 and 0.027 for structures II and III, respectively.

Introduction

Two different tricarbonylchromium complexes were obtained by the reaction of $(\text{OC})_3\text{Cr}(\text{NH}_3)_3$ with 10,10-dimethyl-10-sila-9-oxa-9,10-dihydrophenanthrene (I) in



SCHEME 1



SCHEME 2

boiling dioxane [1] (Scheme 1).

Complexes II and III have close melting points, solubilities and chromatographic mobilities on Al_2O_3 and silica. The molecular ion with $[M]^+ = 362$ is found in the mass spectra of both II and III. Its further fragmentation shows similarities between the mass-spectral behaviour of both complexes [2].

It is noteworthy that complex III was not isolated in the reaction of $\text{Cr}(\text{CO})_6$ with (I) under more severe conditions (140°C , dibutyl ester, 18 h), but the yield of II was 70% [1]. Thus complex II is more stable than the isomeric complex III. Actually, boiling of the solution of III in BuO_2 leads to considerable decomposition with the liberation of the free ligand and with the formation of II in small quantities. The transformation $\text{III} \rightarrow \text{II}$ proceeds nearly quantitatively on boiling a mixture of III and the free ligand (Scheme 2).

In order to unambiguously establish the structure of complexes II and III and to elucidate structural peculiarities of their molecules, an X-ray crystal structure investigation was carried out. Its results are reported in the present paper.

Results and discussion

A general view of molecules II and III with main bond lengths is shown in Fig. 1 and 2, respectively. The aromatic ring A of the silicon-substituted ligand is coordinated in complex II. However, the oxygen-substituted ring B is coordinated in complex III.

In both complexes the siloxaphenanthrene ligand represents a non-planar system involving two planar aromatic rings and the strongly distorted central heterocycle. The deformation of the latter is similar in both molecules. The O and C(11) * atoms are coplanar with the benzene ring B. The Si and C(12) atoms are displaced out of this plane away from the Cr atom. In molecule II the displacements of Si and C(12) atoms are 0.87 and 0.44 Å, respectively and the distance Cr–Si is 3.68 Å. In molecule III these values are 0.71, 0.34 and 3.31 Å (Cr–O distance), respectively. A similar ligand conformation was found recently in (4-chromanone)chromium(0) tricarbonyl [3]. In this complex as in II and III in the bicyclic oxygen-containing heterocycle the carbon atom bonded to oxygen is in fact coplanar with the coordinated aromatic ring, but two adjacent carbon atoms of the ring are displaced in different directions.

The dihedral angle between the coordinated and non-coordinated aromatic rings A and B is 20.4° in molecule II and 15.5° in molecule III. A similar value of the

* Atom numbering in molecules II and III is shown in Fig. 1 and 2.

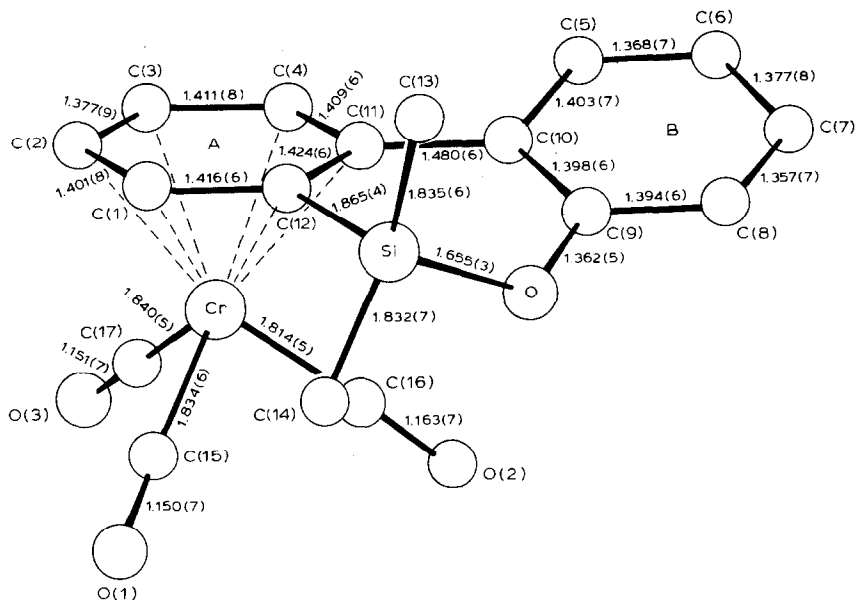


Fig. 1. Structure of the molecule II.

dihedral angle between benzene rings (15°) is also found in the structure of 9,10-dihydrophenanthrenetricarbonylchromium [4]. The average C–C bond lengths in aromatic rings of both complexes are presented in Table 1, which shows an elongation of these bond lengths by the same value (Δ).

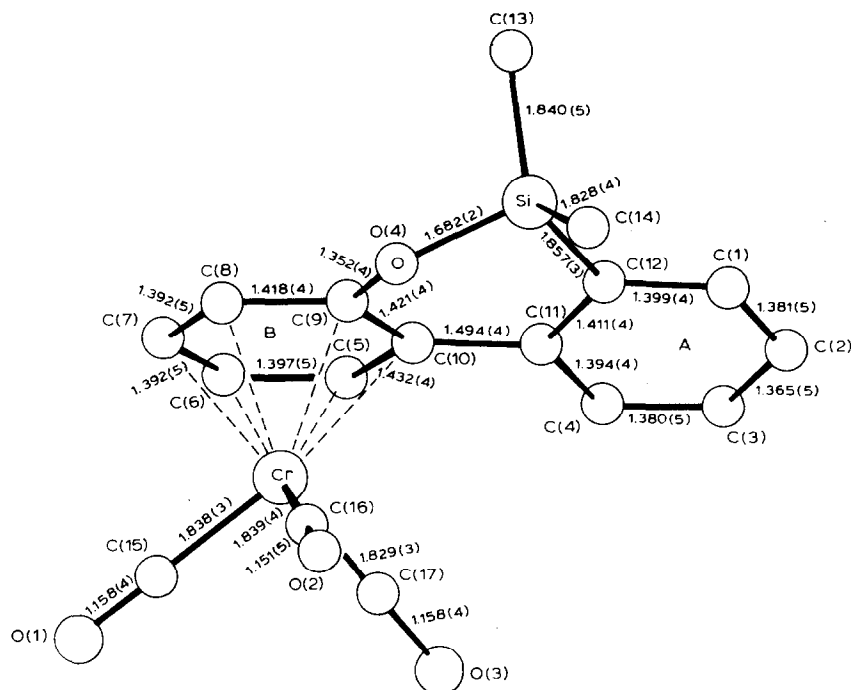


Fig. 2. Structure of the molecule III.

TABLE 1

AVERAGE C-C BOND LENGTHS IN AROMATIC RINGS OF MOLECULES II AND III (Å)^a

Compound	Ring A	Ring B	Δ
II	1.406(2)	1.383(2)	0.023
III	1.388(2)	1.409(2)	0.021

^a The mean square values of the observed e.s.d.'s are given in parentheses.

The Cr-C (carbonyl) bond lengths in both isomers II and III are close to the values found in $C_6H_6Cr(CO)_3$ (av. 1.841 Å [5]).

The orientation of $Cr(CO)_3$ groups relative to the aromatic rings is shown in Fig. 3. In molecule II it is nearly eclipsed, and in III nearly staggered. The rotation angles (α , β and γ , see Fig. 3) of CO groups with the carbon atoms of the coordinated aromatic rings are given in Table 2.

One of the characteristic structural features of (Arene) $Cr(CO)_3$ complexes (Arene = polycyclic system of anthracene, phenanthrene, naphthalene type [6] or $(CH_3O)_3C_6H_3$, $(C_2H_5)_2NC_6H_5$ [7]) is a remarkable difference in Cr-C_{Arene} bond lengths. This feature is also observed in both complexes investigated here (see Table 3). It is noteworthy that the displacement of the Cr atom (the difference between the

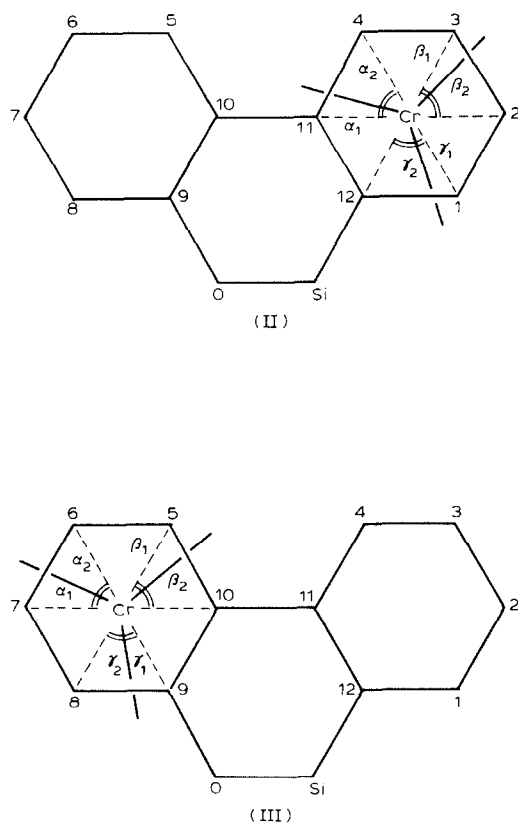


Fig. 3. Projections of molecules II and III on the plane of the coordinated aromatic ring.

TABLE 2

ROTATION ANGLES OF CO GROUPS IN MOLECULES II AND III WITH CARBON ATOMS OF AROMATIC RINGS

Rotation angle	II	III
α_1	5.7	15.7
α_2	54.3	44.3
β_1	3.6	19.9
β_2	56.4	40.1
γ_1	5.0	18.1
γ_2	55.0	41.9

TABLE 3

 Cr-C_{Arene} BOND LENGTHS d (Å) IN II AND III^a

Complex II		Complex III	
Bond	d	Bond	d
Cr-C(1)	2.203(5)	Cr-C(5)	2.209(3)
Cr-C(2)	2.224(6)	Cr-C(6)	2.217(4)
Cr-C(3)	2.197(6)	Cr-C(7)	2.208(3)
Cr-C(4)	2.216(5)	Cr-C(8)	2.227(3)
Av.	2.210(5)	Av.	2.215(3)
Cr-C(11)	2.249(4)	Cr-C(9)	2.280(3)
Cr-C(12)	2.236(4)	Cr-C(10)	2.277(3)
Av.	2.242(4)	Av.	2.278(3)
$\Delta = \text{Cr-C}(11,12)_{\text{av.}} - \text{Cr-C}(1-4)_{\text{av.}} = 0.032$		$\Delta = \text{Cr-C}(9,10)_{\text{av.}} - \text{Cr-C}(5-8)_{\text{av.}} = 0.063$	

^a The mean square values of the observed e.s.d.'s are given in parentheses.

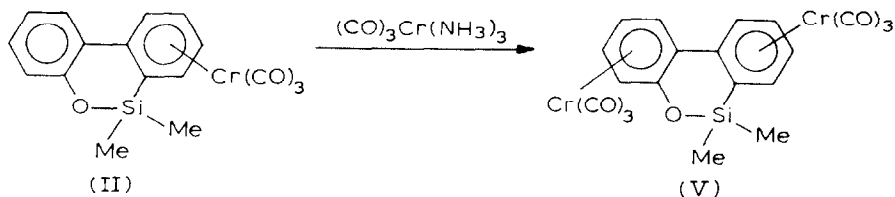
TABLE 4

 BOND LENGTHS IN THE CENTRAL C_{Arene}-O-Si-C_{Arene} BRIDGE OF MOLECULES II, III AND IV (Å)

Compound	C _{Arene} -O	O-Si	Si-C _{Arene}
II	1.363	1.655	1.865
III	1.352	1.682	1.857
IV	1.37	1.62	1.81

average values of two long and four short Cr-C_{Arene} bond lengths) is greater in complex III (0.064 Å) than in complex II (0.032 Å). It may be supposed that the effect of the shift of the Cr atom away from the ring-junction carbon atoms reflects a different influence of Si or O heteroatoms on the coordinated aromatic ring.

Therefore, it seems interesting to compare the geometry of C_{Arene}-O-Si-C_{Arene} bridges in both II and III and in the uncoordinated molecule of silaoxaphenanthrene (I). X-ray data for I are not available, but the structure of a similar molecule, viz. 10,10-dichloro-10-sila-9-oxa-9,10-dihydrophenanthrene (IV), was studied [8]. The conformation of the central bridge in II and III is remarkably different from



SCHEME 3

that found in IV, where both Si and O heteroatoms are displaced from the planar part of the heterocycle in opposite directions. Bond lengths in the central bridge in II, III and IV are given in Table 4.

Similar changes of bond lengths are observed in both complexes, where the Si-C_{Arene} and Si-O bonds are longer than in IV. The longest Si-O bond in series II-IV is observed in complex III, where the C_{Arene}-O bond length has the smallest value. These changes in bond lengths show that the conjugation of the oxygen atom with the aromatic ring B is more pronounced in complex III, where this ring is coordinated, than in the uncoordinated ligand and complex II, due to the electron-acceptor action of the Cr(CO)₃ group. Thus it may be assumed that this effect increases the reactivity of the coordinative Cr-Arene bond in complex III, so that the arene exchange (see Scheme 2) proceeds in the III → II direction. These results are in good agreement with the earlier data by Saillard [7] and Cais [6] on correlation between the geometry of (Arene)Cr(CO)₃ complexes and the reactivity of Cr-Arene bonds in their molecules.

In the scope of the present investigation it was also interesting to explore the possibility of the formation of a bis-tricarbonylchromium complex with siloxarophenanthrene. Indeed, such a complex is obtained by the action of $(\text{CO})_3\text{Cr}(\text{NH}_3)_3$ on II (Scheme 3).

The complex V is soluble only in polar organic solvents and has a limited stability in solution at ambient temperature in contrast with the binuclear complexes of another Si-containing system, 9,9,10,10-tetramethyl-9,10-disiladihydroanthracene, studied earlier [9]. Distortions of molecular geometry of V may be expected to be more pronounced than in mononuclear complexes II or III.

Crystallization of V was possible at low temperatures only. An X-ray study of a single crystal of V was carried out and indicated a *trans*-arrangement of two Cr(CO)₃ groups relative to the ligand mean plane. Unfortunately, disordering of the O and Si atoms was detected in the C_{Arene}-O-Si-C_{Arene} bridging fragment of molecule V. Therefore a detailed analysis of the geometry of V was not possible.

Experimental

All syntheses were carried out under an inert gas atmosphere in absolute solvents. Mass spectra were measured with an MS-30 spectrometer (electron ionisation energy of 70 eV). The synthesis of the starting ligand I was carried out according to ref. 10.

Tricarbonyl [1-4a(10a)-η-10,10-dimethyl-10-sila-9-oxa-9,10-dihydrophenanthrene]-chromium (II) and tricarbonyl [5-8a(4b)-η-10,10-dimethyl-10-sila-9-oxa-9,10-dihydrophenanthrene]chromium (III)

A mixture of 2.26 g (10 mmol) of I, 2.81 g (15 mmol) of $(\text{CO})_3\text{Cr}(\text{NH}_3)_3$ and 70 ml of dioxane was boiled for 8 h. The mixture was cooled to 20°C and filtered; its volatile components were evaporated in vacuo. The residue was repeatedly extracted with hexane, the extracts were evaporated and chromatographed on an alumina column. The colored band was eluted in three fractions using hexane/acetone 4/1, 2/1 and 1/1 mixtures, respectively. The second fraction was chromatographed again in an analogous manner. 1.25 g of complex II (from the first fraction of the eluate) and 0.81 g of complex III (from the third fraction of the eluate) were obtained. Crystals of II and III suitable for an X-ray analysis, were obtained by crystallization from ether/heptane mixture.

II: m.p. 128.5–130°C. Found: C, 56.37; H, 3.75. $\text{C}_{17}\text{H}_{14}\text{CrO}_4\text{Si}$ calc.: C, 56.34; H, 3.89%.

III: m.p. 129–130°C. Found: C, 56.23; H, 3.82. $\text{C}_{17}\text{H}_{14}\text{CrO}_4\text{Si}$ calcd.: C, 56.34; H, 3.89%.

Bis(tricarbonylchromium)-trans- μ -[1-4a(10a)- η -5-8a(4b)- η -10,10-dimethyl-10-sila-9-oxa-9,10-dihydrophenanthrene] (V)

A mixture of 0.36 g (1 mmol) of II, 0.46 g (2 mmol) of $(\text{CO})_3\text{Cr}(\text{NH}_3)_3$ and 20 ml of dioxane was boiled for 4 h, cooled to 20°C and filtered. The residue after evaporation in vacuo was extracted repeatedly with heptane. The residue from extraction was chromatographed by a heptane/acetone (1/4) mixture on Al_2O_3 and boiled in heptane under inert atmosphere before use. After evaporation of the eluate, 0.14 g of complex V were isolated. Orange crystals of V were obtained by crystallization from a acetone/hexane mixture at -20°C, m.p. 200°C. Found: C, 48.43; H, 2.79. $\text{C}_{20}\text{H}_{14}\text{Cr}_2\text{O}_7\text{Si}$ calcd.: C, 48.35; H, 2.83%. Mass-spectrum m/e (relative intensity): 498 $[\text{M}]^+$ (10); 414 $[\text{M}-3\text{CO}]^+$ (40); 386 $[\text{M}-4\text{CO}]^+$ (25); 358 $[\text{M}-5\text{CO}]^+$ (40); 278 $[\text{M}-6\text{CO}-\text{Cr}]^+$ (100).

X-Ray crystallographic study

Unit cell parameters and intensities of diffraction reflections were measured with an automated X-ray diffractometer Nicolett R3m (T 20°C, λ Mo- K_α , graphite monochromator, $2\theta/\theta$ scan, absorption corrections were neglected because of the small dimensions of the crystals).

Crystals of II are monoclinic, a 17.146(1), b 7.502(2), c 12.722(3) Å, β 93.38(2)°, d_{calcd} 1.47 g cm⁻³, μ 8.2 cm⁻¹, $Z = 4$, space group $P2_1/c$.

Crystals of III are monoclinic, a 10.162(2), b 18.107(4), c 9.911(2) Å, β 114.40(1)°, d_{calcd} 1.45 g cm⁻³, μ 8.1 cm⁻¹, $Z = 4$, space group $P2_1/a$.

Crystals of V are triclinic, a 7.377(4), b 10.007(6), c 13.655(5) Å, α 95.43(4), β 93.67(4), γ 94.03(4)°, d_{calcd} 1.66 g cm⁻³, μ 12.4 cm⁻¹, $Z = 2$, space group $P\bar{1}$.

A total of 1272 (II), 1834 (III), 1756 (V) reflections was obtained; 1243, 1299 and 1744 respectively with $I > 2\sigma(I)$ being considered "observed" and used in the solution by the heavy atom method and the full-matrix least-squares anisotropic refinement of the structures. All calculations were carried out with a Nova-3 computer using XTL and SHELXTL program packages.

The final R - and R_w -values are 0.029 and 0.034 for II, 0.027 and 0.036 for III, respectively. After the isotropic refinement of V abnormally large values of an overall temperature parameter ($B_{\text{iso}} \approx 13 \text{ \AA}^2$) and unrealistic geometrical parameters of the O-Si-C fragment were found, the discrepancy factor being $R = 0.123$. The subsequent anisotropic refinement diminished the R -value to only 0.086.

In the structures of II and III difference syntheses revealed all hydrogen atoms, which were included in refinement-fixed isotropic temperature parameters ($B = 5.0 \text{ \AA}^2$).

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