

was filtered and brought to dryness at  $<10^\circ$ . The residue was treated with methylamine in about 30 ml THF left overnight, and all volatile material removed. The product was chromatographed on 150 g silica (0.08 mm) with acetone, recrystallized from ethyl acetate, m.p.  $96\text{--}98^\circ$ , and sublimed under high vacuum, m.p.  $101^\circ$  uncorr., lit.:  $104\text{--}105^\circ$  [1]. The elemental analysis was satisfactory and the NMR. spectrum agreed with the data in the literature [4].

The IR. spectra were measured with a *Perkin-Elmer* Grating instrument (slit  $3\text{ cm}^{-1}$ , scan rate  $400\text{ cm}^{-1} \cdot \text{min}^{-1}$ ). The tetrachloromethane solutions were thermostatted in infrasil quartz cuvettes (*Hellma*) by means of brass cuvette-holders of our design which were connected to a circulating water bath. The temperature, monitored with a thermistor inside the cuvettes, was measured by a *Knauer* Temperatur-Messgerät, and the readings compared with a calibrated thermometer. The spectrophotometer was connected to a precision recorder (*Houston Instr.*) so that accurate voltage readings could be made, especially those of temperature dependence which was measured on a fivefold expanded scale. Tetrachloromethane of spectrophotometric quality (*Fluka AG*) was treated with dried potassium carbonate AR. and cycled over phosphorus pentoxide as described earlier [8]. The solutions were made by weight directly in the cuvettes.

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## 196. Synthesis and Structure of Tris(2'-[2-phenyl-1,3-dioxolano])-chromium(III)

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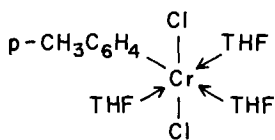
(15. VII. 74)

*Summary.* Tris(2'-[2-phenyl-1,3-dioxolano])chromium(III) **3** has been synthesised and has been shown to have the *cis* (or *fac*) configuration **3a** by X-ray analysis: the Cr–C bond length is 2.037 (10) Å.

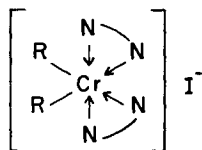
We have reported on the structures of the octahedral  $\sigma$ -bonded mono- and bis-(organo)chromium(III) compounds **1** and **2a, b, c** [1–4]: now we wish to report on the structure of the  $\sigma$ -bonded tris(organo)chromium(III) compound **3**.

The compound **3**, which possesses masked aldehydo-groups in the aryl rings bonded to chromium, was synthesised by the usual *Grignard* route [5]. It is formulated as the unsolvated tris(aryl)Cr(III) compound  $\text{C}_{27}\text{H}_{27}\text{O}_6\text{Cr}$ , M.W. = 499.5 on the basis of its analysis, its magnetic moment ( $3.74\text{ BM}$ )<sup>1)</sup>, its reaction with  $\text{HgCl}_2$  to give three

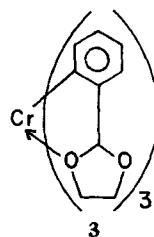
<sup>1)</sup> We thank Drs. S. and G. Olivé of MRSA, Zurich, for this measurement.



**1** THF = Tetrahydrofuran

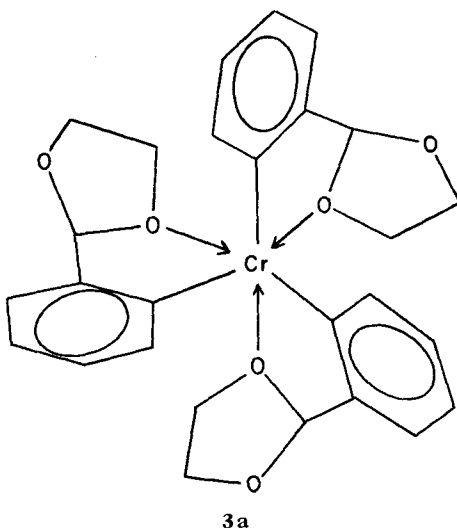


**2a** R = C<sub>6</sub>H<sub>5</sub>  
**b** R = 2-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
**c** R = (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>  
 NN = 2,2'-bipyridyl



equivalents of 2-(2'-chloromercuriphenyl)1,3-dioxolane, and its reaction with acetyl acetone to give Cr(acac)<sub>3</sub> and 2-phenyl-1,3-dioxolane.

The red-orange crystals of **3**, obtained from pyridine solution, are orthorhombic space group Pna2<sub>1</sub> with  $a = 21.804$ ,  $b = 8.651$ ,  $c = 12.702$  Å.  $D_c = 1.376$  ( $Z = 4$ )  $D_m = 1.396$  g · cm<sup>-3</sup>,  $\mu(\text{Mo K}\alpha) = 546$  m<sup>-1</sup>. Intensities were measured on a linear diffractometer equipped with a graphite monochromator: 1812 significant independent reflections with  $\vartheta \leq 25^\circ$  (Mo K $\alpha$  radiation) were obtained. The structure was solved by *Patterson & Fourier* methods and refined by least squares with anisotropic temperature factors for Cr, O, and C to a final R-factor of 0.068.



As far as the bond lengths and angles are concerned the molecule has, to a good approximation, the symmetry 3 ( $C_3$ ) and is therefore in the *cis* (or *fac*) configuration **3a** in which each of the carbon atoms bonded to chromium is *trans* to an oxygen atom. The Cr-C and Cr-X ( $X = \text{N}, \text{O}$ ) bond lengths in **1**, **2a** to **c**, and **3** are compared in the Table and it can be seen that these lengths vary qualitatively with the inverse of the electronegativity of the *trans* ligand. This variation parallels the *trans* effect series developed for d<sup>8</sup> square planar Pt(II) complexes [6]. The dioxolane rings each

Table

Compound	X	Cr–C	Cr–X( <i>trans</i> to C)	Cr–X( <i>trans</i> to X)	Ref.
<b>1</b>	O	2.014(10)	2.214(7)	2.045(8)	[1]
<b>2a</b>	N	2.087(4)	2.147(4)	2.087(4)	[2]
<b>2b</b>	N	2.101(12)	2.156(10)	2.071(10)	[3]
<b>2c</b>	N	2.106(9)	2.156(7)	2.103(7)	[4]
<b>3a</b>	O	2.037(10)	2.157(8)	–	–

have an envelope form, but different conformations so that these rings are not related by  $C_3$  symmetry: the atoms lying out of the planes are O(1), O(4) and C(25). The differences in the conformations of these rings may be attributed to packing forces operating on a flexible ring.

Compound **3** is remarkably inert towards certain substrates (*e.g.*  $O_2$ ,  $H_2O$ , methanol, ketones, nitriles, and ethylene oxide) though it does form a 1:1 solvate on crystallizing from pure, dry, oxygen-free acetone. The bulky bidentate ligands of **3** will tend to render the chromium centre inaccessible thereby inhibiting reaction with the various substrates enumerated above. The carbon atoms bonded to chromium are more accessible and may therefore participate in chemical reactions (*e.g.* with

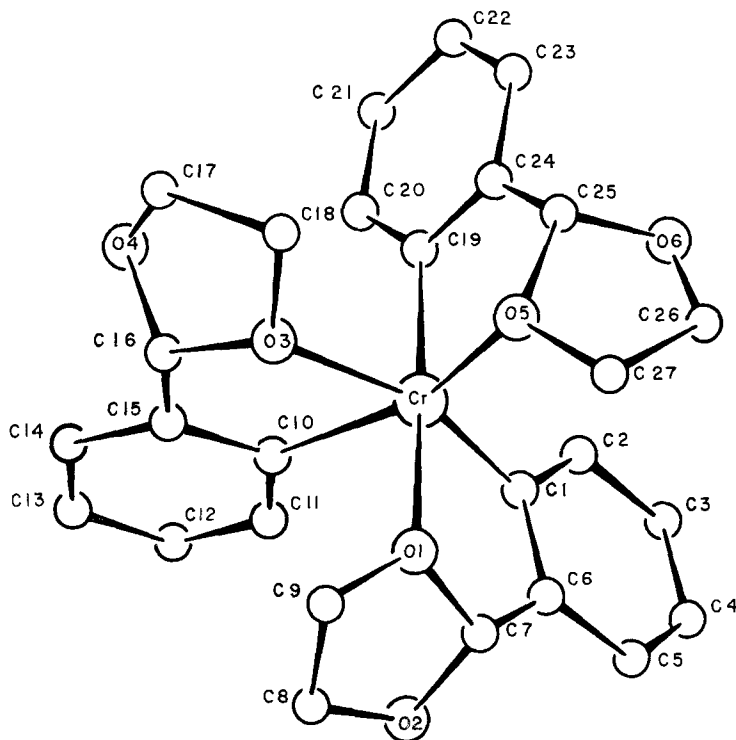


Fig. The molecule projected onto the plane of O(1), O(3) O(5) with the labelling of the atoms. Hydrogen atoms have been omitted for clarity.

HgCl<sub>2</sub>). The dioxolane rings at the top of the molecule are exposed to attack and their oxygen atoms should be available for hydrogen bonding.

The greater reactivity of Ph<sub>3</sub>Cr(THF)<sub>3</sub> as compared with **3** may imply that the former has the *trans* (or *mer*) configuration with a labile THF *trans* to Ph and labile Ph groups *trans* to one another.

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## 197. Photoaddition of Oxa-enones to 2-Chlorodifluoromethyl-3-chloro-3,3-difluoro-propene

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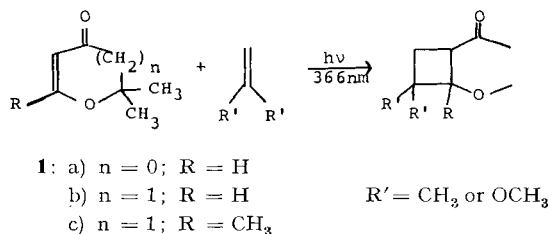
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(5. VIII. 74)

*Summary.* Electronic effects determine the regioselectivity in the photoaddition of oxa-enones to olefins.

Oxa-enones (**1**) have been shown to photoadd to polarized olefins such as isobutylene or 1,1-dimethoxyethylene in a regioselective manner [1]. This regioselectivity was ascribed to an electronic control – inverted charge distribution in the C–C double bond of the excited oxa-enone molecule – rather than to steric arguments alone (*scheme 1*).

*Scheme 1*



Both factors, however, would have been expected to exert a parallel regiocontrol in the reactions investigated previously. In order to assess the importance of electronic *vs* steric control, 2-chlorodifluoromethyl-3-chloro-3,3-difluoro-propene (**2**) has

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