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AN UNUSUAL REACTION OF A π-COMPLEXED LITHIO-ARENE: THE CHARACTERIZATION AND STRUCTURE OF μ-(2,2'-DIFLUORO-5,5'-DIMETHYLBENZOPHENONE)BIS(TRICARBONYLCHROMIUM(0))

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Summary

(π-Lithioarene)tricarbonylchromium(0) complexes are suggested to be in equilibrium with carbene-bridged dimers at low temperature; the dimers can be trapped with acid chlorides or chloroformate esters yielding bis[(arene)tricarbonylchromium(0)]-carbinols or -ketones, respectively. Thus, the lithiation of (p-fluorotoluene)tricarbonylchromium(0) followed by addition of methyl chloroformate yields μ-(2,2'-difluoro-5,5'-dimethylbenzophenone)bis(tricarbonylchromium(0)); crystals of $C_{21}H_{12}Cr_2F_2O_7$ are monoclinic space group $P2_1/c$, with a = 7.170(2), b = 21.832(5), c = 13.428(2) Å, β = 98.91(2)°. The structure has been determined by the analysis of 1959 observed reflections recorded on a Syntex $P2_1$ automatic diffractometer and refined by full-matrix least-squares to R = 0.054, R_w = 0.045. The two $Cr(CO)_3$ tripods are oriented differently with respect to the bound arene rings. This shows that the orientation of the $Cr(CO)_3$ moiety is not governed primarily by the electronic properties of the ring substituents.

Introduction

We were intrigued by the recent report [1] that addition of (phenyllithium)-tricarbonylchromium(0), **1**, to a large excess of acetyl chloride gave the expected methyl ketone **2** only in low yield while the carbinol **3** was the most abundant product. This rather surprising result can be rationalized in two ways. One can invoke initial formation of ketone **2** followed by preferential attack on **2** by the lithio-complex **1**; however, preferential attack by **1** on the ketone **2** in the presence of a twenty-fold excess of the highly electrophilic acetyl chloride seems a rather improbable circumstance. The second, and perhaps more plausible, expla-

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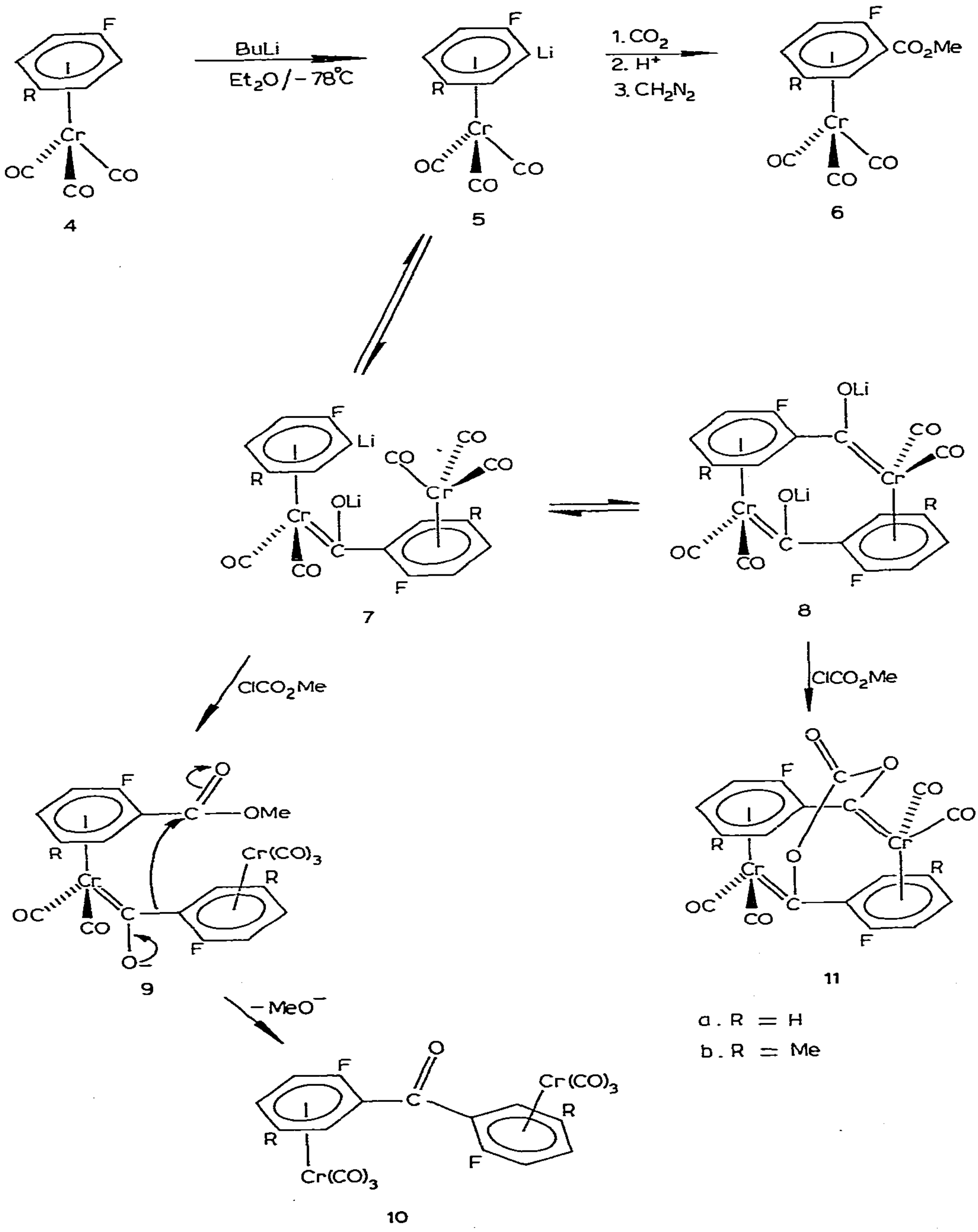
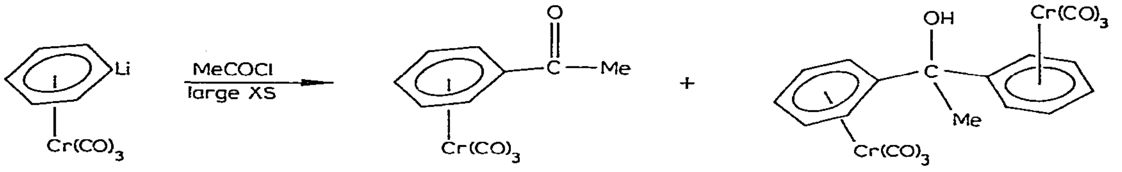


SCHEME 1

nation requires a pre-equilibrium in which the (phenyllithium)tricarbonylchromium(0) is already dimerised.

We now present experimental results using the lithio-derivative of (*p*-fluorotoluene)tricarbonylchromium(0) which give some support to this latter hypothesis.



1 2 3

Discussion

In connection with studies [2] concerning the mechanism of nucleophilic displacement of halogens in π-arene chromium tricarbonyl complexes, we had need of the methyl ester of (2-fluoro-5-methylbenzoic acid)tricarbonylchromium(0), **6b**. The closely analogous methyl ester of (*o*-fluorobenzoic acid)tricarbonylchromium(0), **6a**, is preparable either via direct reaction [3] of the arene with $Cr(CO)_6$ or by *ortho*-lithiation of (fluorobenzene)tricarbonylchromium(0), **4a**, to afford **5a** followed by carbonation and treatment with diazomethane [4]. Since the synthesis of the tri-substituted arene, 2-fluoro-5-methylbenzoic acid methyl ester, on an acceptable scale is non-trivial, Semmelhack's lithiation route [4] using the methyl arene derivative **4b** appeared to offer a reasonable alternative. However, we chose to capture the lithio-arene complex **5b** with methyl chloroformate in the expectation of producing the desired ester **6b** directly. (The introduction of the carbomethoxy functionality to fluoroarene chromium sandwich compounds, chromarenes, via, treatment of a π-complexed lithio-arene with methyl chloroformate proceeds in excellent yield [5].)

Lithiation of (*p*-fluorotoluene)tricarbonylchromium(0), **4b** with tert-butyllithium (three-fold excess) in ether at —78°C under nitrogen gave an orange-red solution which rapidly turned deep red on addition of excess methyl chloroformate at —78°C. Removal of solvent and chromatographic separation gave at least three air-stable products, none of which was the anticipated ester **6b** (scheme 1). The major product, a red crystalline solid, was shown by mass spectral analysis (see later) to have a molecular weight of 518. The surprisingly simple ^1H and ^{19}F NMR spectra of this product indicated the equivalence of two tri-substituted π-complexed rings and also showed the third substituent to have entered *ortho* to fluorine; thus a molecule of C_s or C_2 symmetry was indicated.

The assignment as the obvious structure, viz., the bis-$Cr(CO)_3$-complexed benzophenone, **10**, was rendered somewhat uncertain by the mass spectrum which, apart from the usual series of losses of 28 mass units, showed fragmentation of the parent ion with loss of CO_2, suggesting a carbonate. Of particular significance in the ^{13}C NMR spectrum was a peak at δ 265.5 ppm, typical of a carbene carbon [6]; the infrared spectrum (KBr) showed evidence for a cyclic carbonate with strong absorptions at 1855 (C═O) and 1232 cm^{-1} (C—O). However, upon repeated recrystallization of the material to obtain a sample suitable for X-ray crystallography, these extra peaks gradually disappeared. The final product was identified crystallographically as μ-(2,2′-difluoro-5,5′-dimethylbenzophenone)bis(tricarbonylchromium(0)).

The compound is shown in Fig. 1 and selected interatomic distances and angles are given in Table 1. The molecule looks like a tassled brassiere twisted about the centre carbonyl such that the dihedral angle between the two aro-

(Continued on p. 272)

TABLE 1

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (deg)

Cr(1)—C(1)	1.211(5)	Cr(1)—C(2)	2.198(4)	Cr(1)—C(3)	2.215(4)
Cr(1)—C(4)	2.179(4)	Cr(1)—C(5)	2.251(4)	Cr(1)—C(16)	2.196(5)
Cr(1)—C(11)	1.835(6)	Cr(1)—C(12)	1.843(5)	Cr(1)—C(13)	1.842(6)
Cr(2)—C(1a)	2.211(6)	Cr(2)—C(2a)	2.210(5)	Cr(2)—C(3a)	2.209(5)
Cr(2)—C(4a)	2.177(5)	Cr(2)—C(5a)	2.232(4)	Cr(2)—C(6a)	2.189(5)
Cr(2)—C(21)	1.842(6)	Cr(2)—C(22)	1.855(5)	Cr(2)—C(23)	1.865(3)
C(1)—C(2)	1.390(7)	C(2)—C(3)	1.403(6)	C(3)—C(4)	1.438(6)
C(4)—C(5)	1.404(7)	C(5)—C(6)	1.412(7)	C(6)—C(1)	1.417(7)
C(1)—H(1)	1.04(7)	C(2)—F(2)	1.355(3)	C(3)—C(31)	1.495(7)
C(4)—H(4)	1.00(7)	C(5)—C(51)	1.511(8)	C(6)—H(6)	1.04(7)
C(51)—H(511)	1.04(8)	C(51)—H(512)	1.01(7)	C(51)—H(513)	0.83(8)
C(1a)—C(2a)	1.403(6)	C(2a)—C(3a)	1.398(6)	C(3a)—C(4a)	1.419(6)
C(4a)—C(5a)	1.408(6)	C(5a)—C(6a)	1.427(7)	C(6a)—C(1a)	1.396(8)
C(1a)—C(6a)	1.408(6)	C(5a)—C(6a)	1.427(7)	C(6a)—C(1a)	1.396(8)
C(1a)—H(1a)	0.99(6)	C(2a)—F(2a)	1.354(5)	C(3a)—C(31)	1.510(6)
C(11)—O(11)	1.162(8)	C(12)—O(12)	1.157(6)	C(13)—O(13)	1.140(8)
C(21)—O(21)	1.146(8)	C(22)—O(22)	1.149(7)	C(23)—O(23)	1.141(6)
C(31)—O(31)	1.211(6)				
C(1)—Cr(1)—C(2)	36.7(2)	C(2)—Cr(1)—C(3)	37.1(1)	C(3)—Cr(1)—C(4)	38.2(2)
C(4)—Cr(1)—C(5)	36.9(2)	C(5)—Cr(1)—C(6)	37.0(2)	C(6)—Cr(1)—C(1)	37.5(2)
C(11)—Cr(1)—C(12)	87.4(3)	C(11)—Cr(1)—C(13)	88.9(3)	C(12)—Cr(1)—C(13)	89.2(3)
C(1)—Cr(1)—C(11)	105.1(2)	C(1)—Cr(1)—C(12)	166.1(2)	C(1)—Cr(1)—C(13)	97.0(2)
C(2)—Cr(1)—C(11)	140.3(2)	C(2)—Cr(1)—C(12)	132.0(2)	C(2)—Cr(1)—C(13)	87.0(2)
C(3)—Cr(1)—C(11)	165.9(2)	C(3)—Cr(1)—C(12)	98.8(2)	C(3)—Cr(1)—C(13)	103.8(2)
C(4)—Cr(1)—C(11)	130.5(2)	C(4)—Cr(1)—C(12)	87.2(2)	C(4)—Cr(1)—C(13)	140.2(2)

C(5)—Cr(1)—C(01)	98.7(2)	C(5)—Cr(1)—C(12)	105.4(2)	C(5)—Cr(1)—C(13)	163.8(2)
C(6)—Cr(1)—C(11)	87.2(3)	C(6)—Cr(1)—C(12)	140.1(2)	C(6)—Cr(1)—C(13)	130.2(3)
C(6)—C(1)—C(2)	117.6(5)	C(1)—C(2)—C(3)	124.0(4)	C(2)—C(3)—C(4)	116.4(4)
C(3)—C(4)—C(5)	121.7(4)	C(4)—C(5)—C(6)	118.4(4)	C(5)—C(6)—C(1)	121.5(5)
C(10)—C(2)—F(2)	117.8(4)	F(2)—C(2)—C(3)	118.1(4)	C(2)—C(3)—C(31)	125.0(4)
C(31)—C(3)—C(4)	118.5(4)	C(4)—C(5)—C(51)	121.4(5)	C(51)—C(5)—C(6)	120.1(5)
C(6)—C(1)—H(1)	122(4)	H(1)—C(1)—C(2)	120(4)	C(10)—C(2)—F(2)	117.8(4)
F(2)—C(2)—C(3)	118.1(4)	C(2)—C(3)—C(31)	125.0(4)	C(31)—C(3)—C(4)	118.5(4)
C(3)—C(4)—H(4)	120(4)	H(4)—C(4)—C(5)	119(4)	C(4)—C(5)—C(51)	121.4(5)
C(51)—C(5)—C(6)	120.1(5)	C(5)—C(6)—H(6)	120(4)	H(6)—C(6)—C(1)	118(4)
C(5)—C(51)—H(511)	114(4)	C(5)—C(51)—H(512)	103(4)	C(5)—C(51)—H(513)	112(4)
H(511)—C(51)—H(512)	118(6)	H(511)—C(51)—H(513)	108(6)	H(512)—C(51)—H(513)	102(7)
Cr(1)—C(11)—O(11)	178.1(5)	Cr(1)—C(12)—O(12)	179.8(5)	Cr(1)—C(13)—O(13)	179.4(6)
C(3)—C(31)—C(3a)	118.9(4)	C(3)—C(31)—O(31)	120.7(4)	O(31)—C(31)—C(3a)	120.5(4)
C(1a)—Cr(2)—C(2a)	37.0(2)	C(2a)—Cr(2)—C(3a)	36.9(2)	C(3a)—Cr(2)—C(4a)	37.7(2)
C(4a)—Cr(2)—C(5a)	37.2(2)	(C5a)—Cr(2)—C(6a)	37.7(2)	C(6a)—Cr(2)—C(1a)	37.0(2)
C(21)—Cr(2)—C(23)	89.6(2)	C(21)—Cr(2)—C(22)	88.7(3)	C(22)—Cr(2)—C(23)	88.6(2)
C(1a)—Cr(2)—C(21)	110.7(2)	C(1a)—Cr(2)—C(23)	93.0(2)	C(1a)—Cr(2)—C(22)	160.6(2)
C(2a)—Cr(2)—C(21)	147.6(2)	C(2a)—Cr(2)—C(23)	89.9(2)	C(2a)—Cr(2)—C(22)	123.7(2)
C(3a)—Cr(2)—C(21)	158.1(2)	C(3a)—Cr(2)—C(23)	112.2(2)	C(3a)—Cr(2)—C(22)	93.9(2)
C(4a)—Cr(2)—C(21)	120.7(2)	C(4a)—Cr(2)—C(23)	149.5(2)	C(4a)—Cr(2)—C(22)	89.0(2)
C(5a)—Cr(2)—C(21)	91.2(2)	C(5a)—Cr(2)—C(23)	159.5(2)	C(5a)—Cr(2)—C(22)	112.0(2)
C(6a)—Cr(2)—C(21)	87.0(2)	C(6a)—Cr(2)—C(23)	122.0(2)	C(6a)—Cr(2)—C(22)	149.1(2)
C(6a)—C(1a)—C(2a)	117.9(4)	C(1a)—C(2a)—C(3a)	123.0(3)	C(2a)—C(3a)—C(4a)	117.5(4)
C(3a)—C(4a)—C(5a)	122.0(4)	C(4a)—C(5a)—C(6a)	117.3(4)	C(5a)—C(6a)—C(1a)	122.2(4)
C(1a)—C(2a)—F(2a)	118.3(4)	F(2a)—C(2a)—C(3a)	118.7(4)	C(2a)—C(3a)—C(31)	123.5(4)
C(31)—C(3a)—C(4a)	119.0(4)	C(4a)—C(5a)—C(51a)	122.0(4)	C(51a)—C(5a)—C(6a)	120.7(5)
Cr(2)—C(21)—O(21)	177.3(5)	Cr(2)—C(23)—O(23)	179.4(5)	Cr(2)—C(22)—O(22)	178.9(5)

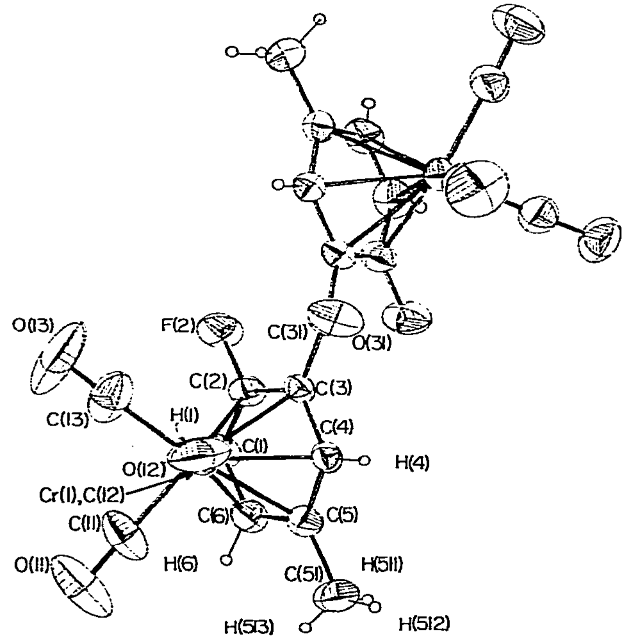


Fig. 1. The molecule of μ-(2,2'-difluoro-5,5'-dimethylbenzophenone)bis(tricarbonylchromium(0)). The atoms in the top half of the molecule, and numbered in Table 5 with a postscript a, are related to those in the lower half by a C_2 rotation. Other equivalences are Cr(1) = Cr(2) and C(1*i*) and O(1*i*) = C(2*i*) and O(2*i*).

matic rings is 71.9(4)° and such that the fluorine atoms are close to each other, rather than H(4) and H(4a). As can be seen, the molecule has close to C_2 symmetry although the twist relative to the C(3)C(3a)C(31)O(31) plane is different (i = 1—6, C(i) 36.7(4)°, C(ia) 45.6(4)°). The twist angle is considerably larger than was reported for benzophenone (56°) [7,8]. This twist was postulated to be caused by the steric repulsion of the hydrogen atoms *ortho* to the carbonyl group. We assume that the bigger fluorine atoms cause the larger twist angle observed here, since the F(2)—F(2a) distance of 3.263(4) Å is close to the average non-bonded value of 3.3 Å observed in F_2 [9].

Within the rings, carbon—carbon distances do differ significantly. Thus C(1)—C(2) (1.390(7) Å) differs from C(3)—C(4) (1.438(6) Å) by 5.2σ but there are no systematic differences. Sets of three alternate bonds have averages of 1.413 and 1.408 Å for C(i) and 1.416 and 1.401 Å for C(ia), close to values observed previously [10—20] and the distribution of "long" and "short" distances is different in the two rings.

Cr—C(carbonyl) (range 2.177(5)—2.232(4), avg. 2.205(5) Å, and C—O (range 1.140(8)—1.162(8), avg. 1.149(8) Å) are similar to those observed in other arenetricarbonylchromium(0) compounds [12—20].

Chromium—carbon(ring) distances are significantly different. This is caused by the opening up of the ring C(1)—C(2)—C(3) angles (also in C(ia)) by the fluorine atom attached to C(2) and at the corresponding *meta*-positions (range 121.5(5)—124.0(4), avg. 122.4(5)°) and a corresponding decrease in the angles at the *ortho* and *para* positions (range 116.4(4)—118.4(4), avg. 117.5(4)°), an effect observed in fluorobenzene [21]. This will bring C(*i*), C(*ia*) $i = 2, 4, 6$ closer to chromium (range 2.177(5)—2.210(5), avg. 2.191(5) Å) than $i = 1, 3, 5$ (range 2.209(5)—2.251(4), avg. 2.222(5) Å). There is a complication because the least squares planes calculations (Table 2) show the rings are folded slightly but significantly, about the C(2)C(5) and C(2a)C(5a) axes such that the ring looks like an open book with the spine (C(2)C(5), C(2a)C(5a)) away from the chromium atom. The displacement of the exocyclic atoms from the ring shows no consistent pattern. Thus the methyl group (C(51), C(51a)) is bent away from the chromium atom whereas the carbonyl group (C(31)) is bent towards chromium. The fluorine atoms are bent away from chromium, but considering that C(2) and C(2a) are already above the mean plane, then the fluorine atoms are bent back slightly towards the chromium atom. The errors in the hydrogen atom positions are too great to allow any conclusions.

The orientation of the tricarbonyl group with respect to the arene ring is illustrated in Fig. 2. Two positions, eclipsed and staggered are normally observed, the former being found for symmetric arenes [12—15], and the latter where electron-withdrawing or donating groups are disposed such that centres of alternate positive and negative charge occur on the ring [16—18]. Our molecule is a masterpiece of indecision. In 2A, the tripod is nearly eclipsed (CO, Cr(1), centre of ring, C(*i*) ($i = 2, 4, 6$) torsional angles ~7°), such that the octahedral Cr(1) to ring "bonds" are to C(1), C(3), C(5), formally centres of negative charge, (even though the Cr(1)—C(*i*) ($i = 1, 3, 5$) distances are longer than those for $i = 2, 4, 6$ (see above)), as would be expected theoretically [16]. In 2B, the

TABLE 2

LEAST SQUARES PLANES AND INTERPLANAR ANGLES

Plane	Atoms	Distance from plane (Å)
1	C(1)C(2)C(3)C(4)C(5)C(6) Cr(1)*H(1)*F(2)*C(31)* H(4)*C(51)*H(6)*	C(1) 0.013(5), C(2) —0.020(4), C(3) 0.000(4) C(4) 0.027(4), C(5) —0.032(4), C(6) 0.020(5) Cr(1) 1.701(1), H(1) 0.05(7), F(2) —0.009(3), C(31) 0.073(4), H(4) 0.12(7), C(51)—0.078(7) H(6) 0.17(7)
2	C(1a)C(2a)C(3a)C(4a) C(5a)C(6a) Cr(2)*H(1a)*F(2a)*C(31)* H(4a*)C(51a*)H(6a)*	C(1a) —0.014(4), C(2a) 0.019(4), C(3a) —0.005(4) C(4a)—0.016(4), C(5a) 0.024(4), C(5a) —0.011(4) Cr(2) —1.697(1), H(1a) —0.00(7), F(2a) 0.022(2) C(31) —0.048(4), H(4a) —0.02(7), C(51) 0.069(7) H(6a) 0.08(7)
3	C(3)C(3a)C(31)O(31)*	O(31) 0.028(4)

Dihedral angles

Planes 1, 2	71.9(4)°	Planes 1, 3	36.7(4)°	Planes 2, 3	45.6(4)°

Torsional angles

C(11)Cr(1)C(6)	7.6(4)°	C(21)Cr(2)CE(2)C(6a)	22.0(4)°
C(12)Cr(1)CE(1)C(4)	7.1(4)°	C(22)Cr(2)CE(2)C(2a)	21.7(4)°
C(13)Cr(1)CE(1)C(2)	7.4(4)°	C(23)Cr(2)CE(2)C(4a)	20.2(4)°

CE(1) and CE(2) are the centres of the rings C(*i*) and C(*i*a) ($i = 1—6$) respectively and are obtained by averaging the coordinates of the six carbon atoms.

* Atoms given no weight in determining the plane.

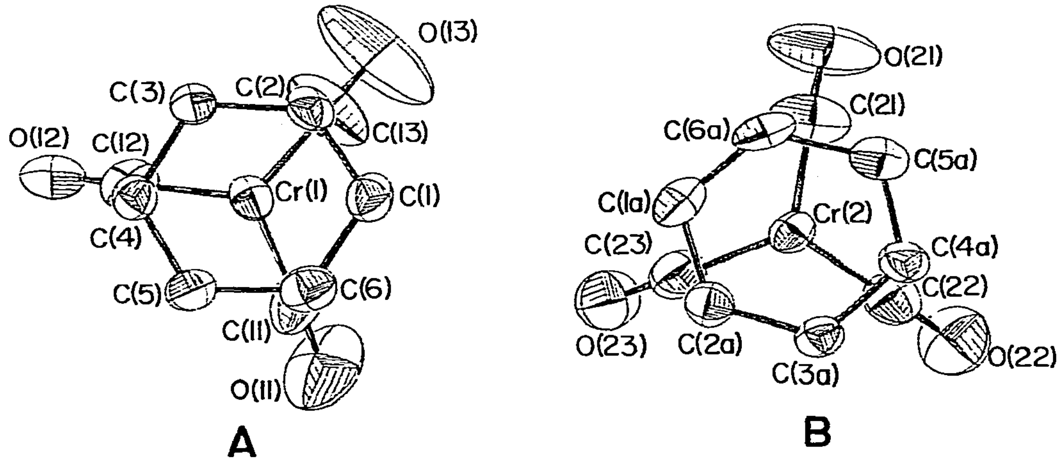


Fig. 2. Fragments of the molecule projected down the centre of the ring—chromium axis and showing the orientation of the $M(CO)_3$ fragment. A, ring C(*i*) (*i* = 1—6)—Cr(1); B, ring C(*i*a) (*i* = 1—6)—Cr(2).

tripod is nearly in the staggered position (CO, Cr(2), centre of ring, C(*i*a) (*i* = 2, 4, 6) torsional angles ~21° vs. ideal 30°) and the deviation of 9° puts the carbonyl groups nearer C(2a), C(4a), C(6a), formally centres of positive charge. Clearly steric factors, whether intra or intermolecular must be at least as important as formal charge in determining conformation in this case. Other angular and distance parameters agree well with those determined previously for similar systems [12—20].

The packing of the molecules in the unit cell is shown in Fig. 3. The packing is very complex but the molecules can be considered as forming a type of double layer centred about $y = 1/4$ $(3/4)$. In the *c* direction molecules related by the *c* glide are arranged in a herring-bone pattern so that the $Cr(2)(CO)_3$ tripod and the associated ring lie close to $x = 0$, $y = 1/4$ and are oriented so that the car-

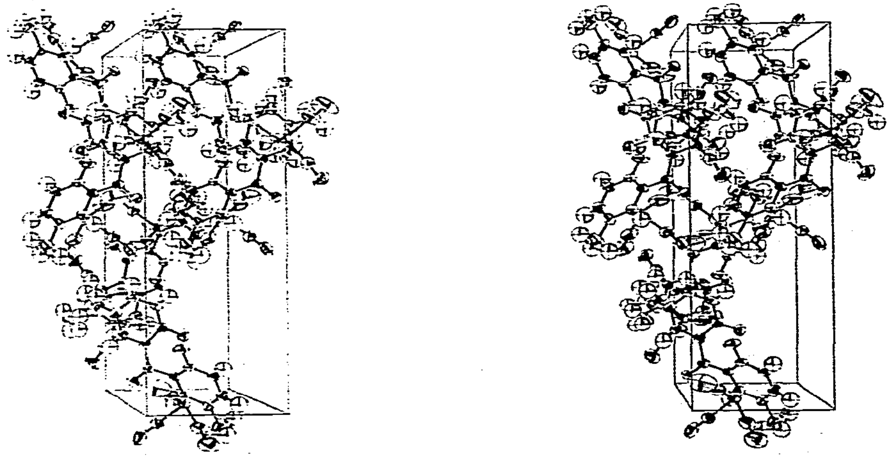


Fig. 3. The packing within the unit cell. The *a* and *b* axes are parallel to the bottom and side of the page, respectively, and the view is down c^*.

bonyl groups of one molecule point at the ring of the next molecule related by the *c* glide. On the other hand, the $Cr(1)(CO)_3$ tripod and associated ring are alternately close to $y = 0$ and $y = 1/2$. Within the layer on the *b* and *c* directions, the molecular packing appears to be determined by the need to interlock the external groups on the rings and the tricarbonyl tripod. Thus, the C(51a) methyl group of a molecule related to the reference molecule A by the *c* glide sits between C(21)O(21) and C(22)O(22) of A. Between C(22)O(22) and C(23)O(23) of A lies F(2) of A, and between C(23)O(23) and C(21)O(21) of A lies the C(51) methyl group of a molecule related by an *a* translation followed by a 2_1 operation.

The $Cr(1)(CO)_3$ tripod is involved in packing between layers in the *b* direction. Molecules related by an inversion centre are arranged such that pairs of $Cr(1)(CO)_3$ tripods interlock. In addition H(6) of a molecule related by the *a* translation lies between C(12)O(12) and C(13)O(13); the C(51a) methyl group and H(4a) of a molecule related by 2_1 lie between C(12)O(12) and C(11)O(11), also O(11) of a molecule related by an *a* translation followed by inversion lies between C(11)O(11) and C(13)O(13). All interactions appear to be Van der Waals.

Mass spectrometry under both electron impact (EI) and chemical ionization (CI) conditions aided in the structural assignments of the compounds. These data are presented in Table 3. Of the three fractions that were separated chromatographically, the first to elute was a very minor component which contained no chromium and was not further investigated. The second and major fraction, immediately after its isolation, gave an electron impact spectrum which was shown by computer subtraction techniques to be a mixture spectrum of **10** and

TABLE 3

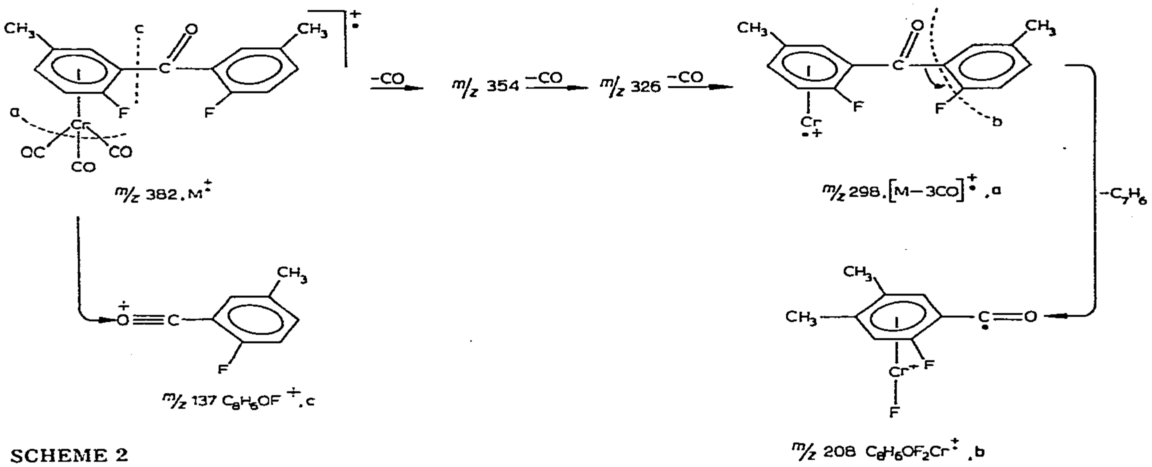
PARTIAL MASS SPECTRA OF COMPOUNDS 10 AND 12

	m/z (rel. ab., %)	
	Compound 10	Compound 12
A. Electron impact ionization		
M^+	518(0.4)	382(2)
$[M-CO]^+$	490(0)	354(0.5)
$[M-2\,CO]^+$	462(17)	326(41)
$[M-3\,CO]^{+\,a}$	434(42)	298(91)
$[M-4\,CO]^+$	406(40)	
$[M-5\,CO]^+$	378(56)	
$[M-6\,CO]^+$	350(49)	
		263(25)
$[M-6\,CO-C_6H_7]^+$	260(100)	
$C_8H_6OF_2Cr^{+\,b}$	208(37)	208(100)
	165(46)	165(54)
$C_8H_6OF^{+\,c}$	137(24)	137(45)
B. Chemical ionization (methane)		
$[M+H]^+$	518(80)	383(40)
$[M+H-CO-HCO]^+$	462(14)	326(39)
$[M+H-3\,CO]^+$	435(100)	299(100)
$[M+H-2\,CO-HCO]^+$	434(97)	298(19)

a, *b* and *c* refer to ion structures proposed in Scheme 2.

an isomeric substance with essentially the same spectrum but showing an additional loss of CO_2 from the molecular ion. This suggests a carbonate and supports structure **11**. Using the single crystal upon which the X-ray crystallographic data had been obtained, the EI and CI mass spectra were in accord with structure **10**, viz., a molecular weight of 518 and successive losses of six carbonyl groups (see Table 3); this pure sample did not show loss of CO_2 from the molecular ion.

The third fraction was identified only on the basis of its mass spectrum, which indicated a molecular weight of 382. In addition to three successive losses of 28 mass units that support the presence of three carbonyls, fragment ions at *m/z* 208 and 137 in the electron impact spectrum are consistent with structure **12** according to the fragmentation mechanism proposed in Scheme 2.



SCHEME 2

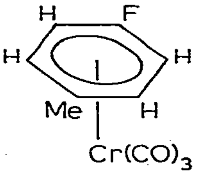
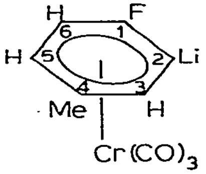
Of course **12** is readily visualized as arising from photolytic decomposition of **10**. Such a loss of a $Cr(CO)_3$ is well-precedented, and indeed has been used synthetically when $Cr(CO)_3$ was temporarily π-complexed to an arene to modify its normal chemistry [22].

It is thus apparent that the major product is the bis-[$Cr(CO)_3$]-complexed benzophenone **10** which, initially at least, contains an isomeric molecule incorporating carbene and carbonate moieties. Furthermore, some decomposition of **10** occurs with loss of a $Cr(CO)_3$ group giving rise to the mono-complexed benzophenone **12**.

In an attempt to elucidate further the course of this reaction, it was followed by ^{13}C NMR spectroscopy at low temperature. When (*p*-fluorotoluene)tricarbonylchromium(0), **4b**, and a three-fold excess of tert-butyllithium in ether/toluene-d_8 were sealed at −196°C and allowed to warm to −80°C, the arene was essentially unchanged but, at −50°C more than 70% of the arene had been lithiated within a few minutes. The spectral data for **4b** and **5b** are presented in Table 4 and show several features of interest. The ^{13}C shifts of the ring carbons follow the pattern previously noted [23] for non-complexed lithioarenes, viz., a marked deshielding of the ring-carbon actually lithiated and smaller high frequency shifts for its neighbours. There are minor changes in $^{n}J(CF)$ values but

TABLE 4

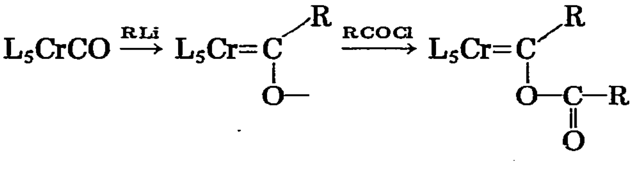
^{13}C NMR CHEMICAL SHIFTS [a] FOR ARENE- AND LITHIO-ARENE COMPLEXES OF $Cr(CO)_3$

		
C(1)	144.8 (J = 263.3) [b]	153.2 (J = 232.5)
C(2)	80.7 (J = 19.6)	111.8 (J = 36.6)
C(3)	94.7 (J = 4.0)	107.7 (J <0.5)
C(4)	103.4 (J = 0)	111.1 (J = 0)
C(5)	94.7 (J = 4.0)	97.3 (J <0.5)
C(6)	80.7 (J = 19.6)	83.2 (J = 41.5)
CH_3	19.2	19.3
CO	232.7	239.4

[a] Data obtained at —50°C in 50/50 toluene-d_8/ether. [b] Carbon—fluorine coupling constants in Hz.

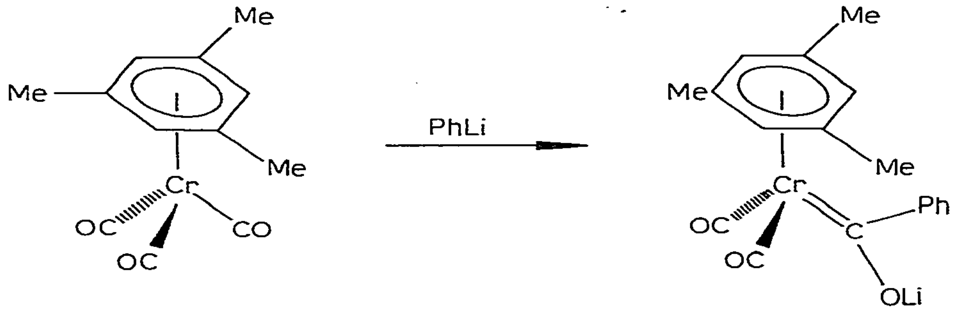
the decrease in J(CF) with increasing n value still holds. The chemical shift of the carbonyl carbon upon metallation is entirely consistent with previous investigations in which development of a positive [24] or negative [25] charge at the benzylic carbon resulted in shielding and deshielding respectively of the carbonyl carbon.

Concomitant with the gradual appearance of the lithioarene, **5b**, there developed two other peaks, at δ 256.7 and 234.3 ppm in the ratio 1 : 2, while no new ring-carbon resonances appeared. An obvious conclusion here is that nucleophilic attack on a carbonyl carbon has occurred giving rise to a carbene centre and a dicarbonyl grouping. One might visualize attack by the tert-butyl anion (although this has been discounted previously [26]) leading ultimately to an acyloxycarbene complex of the type previously isolated by Fischer [27] and by Connor [28].



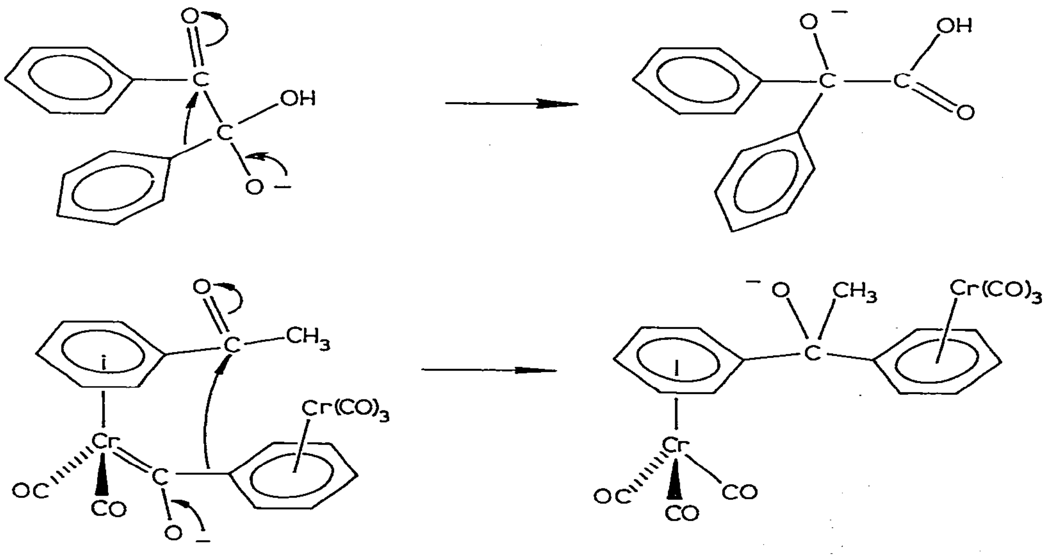
$$L_5CrCO \xrightarrow{RLi} L_5Cr{=}C\begin{smallmatrix}R\\ O^-\end{smallmatrix} \xrightarrow{RCOCl} L_5Cr{=}C\begin{smallmatrix}R\\ O{-}C(=O){-}R\end{smallmatrix}$$

However, we find no NMR or mass spectroscopic evidence for such tert-butylcarbene complexes which should be moderately stable. We instead raise the possibility of nucleophilic attack by the only other type of anion present, i.e., the complexed lithio-arene itself leading to carbene-bridged dimers such as **7** and **8**. Precedent for such a process is provided by Fischer's report [29] of the formation of carbene complexes by addition of an aryllithium to an arenetricarbonylchromium:



One might cavil at the relevance of the previous discussion to the mechanism of the benzophenone formation since a more prosaic mechanism can be invoked in which anion **5b** exclusively attacks the initially formed ester **6** rather than the large excess of methyl chloroformate. However, this would require that the intermediate ketone be extremely susceptible to nucleophilic attack — much more so than the chloroformate ester. Furthermore, such a mechanism must be viewed in the light of the closely related data of Rausch [1] who showed that, contrary to expectations, addition of (lithiobenzene)tricarbonylchromium, **1**, to a twenty-fold excess of acetyl chloride gave the acetophenone complex **2** as the minor product.

We suggest that an alternative mechanism (as in Scheme 1) is also possible in which the carbene-bridged dimer **7** can capture methyl chloroformate giving **9** which can now yield the major product **10** directly via intramolecular phenyl migration; the migratory aptitude of a π-complexed phenyl ring has been well studied [30]. Indeed, the migration proposed closely parallels the benzilic acid



SCHEME 3

rearrangement (Scheme 3) and the analogy of a carbene-chromium moiety to a carbonyl group is nicely shown by Fischer's recent work on mixed anhydrides [31]. In a similar fashion, the di-bridged intermediate **8** can be seen to lead immediately to the bridged carbonate ester **11**; such a process is closely analogous to the formation of cyclic carbonate esters by reaction of glycols with chloroformate esters — a reaction of more than 50 years vintage [32]!

We have shown that, at low temperatures, the lithioarene complex **5** is initially formed and that there is ^{13}C NMR and mass spectroscopic evidence for a dicarbonyl-chromium carbene system such as in **7** or **8**. Quenching of this cold solution with a three-fold excess of methyl chloroformate gave the NMR spectra (^{1}H, ^{13}C and ^{19}F) attributable to the doubly-complexed benzophenone **10** as well as a new carbene peak at δ 265.5 ppm. After removal of solvent, the mass spectrum showed a parent peak at m/z 518 as well as a $P - 44$ peak. However, after several hours, both the $P - 44$ mass spectral peak and the δ 265.5 ppm ^{13}C NMR peak had almost disappeared.

In summary, it is suggested that there may be an equilibrium between the monomeric lithioarene complex **5** and its dimers **7** and **8**. In cases where the electrophile has only a single leaving group (Me_3SiCl, CH_3OSO_2F, etc.) the presence of dimers will not be detected since they do not lead to new products. However, when the electrophile has more than one potential leaving group or site of nucleophilic attack then a kinetically favored intramolecular process may compete with the monomer—dimer equilibrium. Nevertheless, we appreciate that these mechanistic arguments can only be verified by an X-ray crystallographic structural characterisation of thermally unstable molecules such as **11** and attempts to obtain such data are continuing.

Experimental section

NMR data were obtained on a Bruker WH90 spectrometer operating in the FT mode at 90, 84.66 and 22.62 MHz for ^{1}H, ^{19}F and ^{13}C nuclei, respectively. The low temperature ^{13}C data were obtained on a Bruker WM 250 spectrometer operating at 62.86 MHz. Mass spectrometry was performed on a VG micromass 7070 spectrometer equipped with a VG2035 data system. Samples were introduced via the direct insertion probe with the ion source temperature at 200° C. Chemical ionization spectra were run with methane as reagent gas, 1000 μA emission, and 150 eV electron energy. For electron impact, the electron energy was 70 eV. Microanalysis results were from Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

(*p*-Fluorotoluene)tricarbonylchromium (1.5 g; 6.1 mmol) was dissolved in ether (80 ml) and treated with a three-fold excess of tert-butyllithium at —78°C under a nitrogen atmosphere. The now orange-red solution rapidly turned deep red on addition of a five-fold excess of methyl chloroformate. The solution was stirred at —78°C during 1 h and was then allowed to warm to room temperature and the solvent removed in vacuo. The crude reaction product was taken up in benzene and flushed through a short-column of silica gel to remove any polar impurities. This material was chromatographed on a Merck silica gel 60 prepacked column by elution with 10% ethyl acetate in hexane and then by 25% ethyl acetate in hexane. The second and major fraction (isolated yield 0.95 g, 60%) was a red crystalline solid, m.p. 185°C. Anal. Found: C, 48.53; H, 2.57. $C_{21}H_{12}Cr_2F_2O_7$ calcd.: C, 48.65; H, 2.32%. The ^{1}H NMR spectrum shows a narrow multiplet at δ 5.6 ppm (1H); ^{19}F spectrum shows a doublet (8.85 Hz) of triplets (5.80 Hz) at 139.8 ppm to high field of $CFCl_3$. The proton-decoupled ^{13}C spectrum shows π-complexed arene resonances at δ 144.4 ($^1J(CF) = 264.5$ Hz), 76.9 ($^2J(CF) = 22.1$ Hz), 90.7 ($^2J(CF) = 11.8$ Hz), 94.9 ($^3J(CF) = 2.9$ Hz), 96.4 ($^3J(CF) = \sim 1$ Hz), 101.1 ppm ($^4J(CF) = 0$), and singlet absorptions at δ 19.0 (CH_3), 163.9, 230.4 and 265.5 ppm. The mass spectroscopic data are listed in Table 3. The third fraction (30 mg) was identified mass spectroscopically as 12 and the data are presented in Table 3.

Collection of the X-ray data

A roughly cubic crystal was chosen for X-ray studies after examination under a polarizing microscope for homogeneity. Precession photographs showed the crystal was monoclinic and unit cell parameters were obtained from least squares fit of χ, ϕ and 2θ for 15 reflections in the range $19.2 < 2\theta < 25.6°$ recorded on a Syntex $P2_1$ diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). Crystal data and other numbers related to data collection are summarized in Table 5. The density was obtained by flotation in

TABLE 5

CRYSTAL DATA

Compound	$[(C_6H_3F(CH_3))_2CO](Cr(CO)_3)_2$
f.w.	518.31
Crystal size (mm)	A rough cube 0.15 × 0.15 × 0.15
Systematic absences	$h0l$, $l \neq 2n$, $0k0$, $k \neq 2n$
Space group	$P2_1/c$ (no. 14)
Unit cell (Å and deg)	$a = 7.170(2)$, $b = 21.832(5)$, $c = 13.438(2)$ $\beta = 98.91(2)$
Volume (Å^3)	2078.0(8)
Z	4
ρ calc. (g cm^{-3})	1.66
ρ obs (g cm^{-3})	1.69(1)
Linear absorption coefficient (cm^{-1})	11.41
Max 2θ, reflections collected	55°, h, k, $\pm l$
Standard reflections, e.s.d. (%)	2, 0, 2, 4.38; 2, 6, 4, 2.60;
Temperature (°C)	22
No. of indenepdent reflections	4144
No. with $I > 3\sigma(I)$	1959
$3\sigma(I) > I > \sigma(I)$ where $F_c > F_0$	575
$3\sigma(I) > I > \sigma(I)$ where $F_c < F_0$	845
$I < \sigma(I)$, rejected	765
Final R_1, R_2 [a]	0.054; 0.045
Final shift in e.s.d., max. avg.	0.19, 0.07
g (secondary extinction)	4.69×10^{-8}
Final difference map	
Highest peak (e(Å^3)), location	0.39; 0.050, 0.75; 0.025
lowest valley (e(Å^3)), location	−0.59; 0.125, 0.825, 0.900
weighting	$w = \{(\sigma_F)^2 + (0.02F_0)^2\}^{-1}$
Error in an observation of unit weight 0.991	

[a] $R_1 = \Sigma \frac{(|F_0| - |F_0|)}{\Sigma |F_0|}$; $R_2 = \left\{\frac{\Sigma\omega(|F_0| - |F_c|)^2}{\Sigma\omega F_0{}^2}\right\}^{1/2}$

TABLE 6

ATOMIC POSITIONAL PARAMETERS AND TEMPERATURE FACTORS (Å^2)^a

	x^a	y^a	z^a	U_{eq} (×10^3)
Cr(1)	3337(1)	157.1(3)	1943.3(5)	32.0(5)
Cr(2)	27(1)	2185.7	4911.4(5)	31.1(4)
C(1)	5547(7)	781(2)	2058(3)	43(3)
C(2)	4002(7)	1101(2)	2446(3)	37(3)
C(3)	3157(6)	807(2)	3191(3)	29(3)
C(4)	4005(7)	241(2)	3576(3)	35(3)
C(5)	5647(6)	11(2)	3260(3)	40(3)
C(6)	6354(7)	316(2)	2469(4)	45(3)
C(51)	6591(10)	−566(3)	3708(5)	66(4)
F(2)	3211(4)	1627(1)	2045(2)	58(2)
C(1a)	2162(8)	2726(2)	4268(3)	46(4)
C(2a)	2496(6)	2102(2)	4120(3)	38(3)
C(3a)	1094(6)	1699(2)	3673(3)	33(3)
C(4a)	−719(7)	1947(2)	3327(3)	36(3)
C(5a)	−1109(7)	2576(2)	3404(4)	40(3)
C(6a)	366(8)	2954(2)	3909(3)	44(3)
C(51a)	−3010(9)	2843(3)	2999(5)	61(4)
F(2a)	4236(4)	1876(1)	4472(2)	58(2)
C(11)	4058(9)	−421(2)	1087(4)	65(4)
O(11)	4543(8)	−796(2)	569(4)	113(4)
C(12)	1426(7)	−369(2)	2152(4)	46(3)
O(12)	230(5)	−702(2)	2284(3)	73(3)
C(13)	1756(10)	492(3)	869(5)	80(4)
O(13)	774(10)	703(2)	210(4)	149(5)
C(21)	−1503(9)	2692(4)	5529(4)	63(4)
O(21)	−2500(8)	3009(2)	5877(3)	104(4)
C(23)	1589(8)	2083(2)	6136(4)	48(3)
O(23)	2539(6)	2021(2)	6893(3)	69(3)
C(22)	−1394(8)	1520(2)	5237(4)	48(3)
O(22)	−2269(6)	1106(2)	5422(3)	80(3)
C(31)	1406(7)	1020(2)	3562(3)	36(3)
O(31)	236(5)	655(1)	3750(3)	55(3)
H(1)	605(9)	110(3)	148(5)	21(13)
H(4)	339(10)	−1(3)	407(5)	9(12)
H(6)	741(9)	11(3)	212(5)	26(14)
H(511)	574(10)	−84(3)	409(5)	57(19)
H(512)	781(10)	−41(3)	410(5)	60(22)
H(513)	698(11)	−78(3)	328(5)	79(23)
H(1a)	325(10)	297(3)	460(5)	35(16)
H(4a)	−167(10)	166(3)	301(5)	−7(10)
H(6a)	25(10)	335(3)	394(5)	12(12)
H(511a)	−287(10)	306(3)	231(6)	57(19)
H(512a)	−330(10)	313(3)	343(5)	67(23)
H(513a)	−395(10)	252(3)	278(5)	81(25)

	Anisotropic temperature factors (×10^3)^b					
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(1)	44.9(5)	25.4(4)	26.5(4)	−2.5(4)	6.0(3)	−2.0(3)
Cr(2)	38.7(4)	27.6(4)	28.0(4)	−5.4(3)	5.6(3)	1.3(3)
C(1)	48(3)	33(3)	50(3)	−7(2)	20(3)	−1(2)
C(2)	47(3)	21(2)	43(3)	−2(2)	8(2)	1(2)
C(3)	35(3)	26(2)	28(2)	0(2)	6(2)	−5(2)
C(4)	43(3)	36(3)	27(2)	1(2)	10(2)	−1(2)
C(5)	38(3)	45(3)	38(3)	9(2)	10(2)	2(2)
C(6)	45(3)	48(3)	43(3)	4(2)	9(2)	−6(2)
C(51)	63(4)	67(4)	71(4)	32(3)	19(4)	18(3)
F(2)	85(2)	29(1)	64(2)	7(1)	23(2)	10(1)

TABLE 6 (continued)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1a)	57(4)	33(3)	50(3)	—12(3)	6(3)	—7(2)
C(2a)	35(3)	41(3)	40(3)	1(2)	8(2)	—5(2)
C(3a)	36(3)	29(2)	35(3)	1(2)	10(2)	—5(2)
C(4a)	39(3)	36(3)	33(3)	8(2)	3(2)	—4(2)
C(6a)	50(3)	42(3)	30(3)	10(2)	9(2)	4(2)
C(6a)	66(4)	21(2)	48(3)	0(2)	15(3)	1(2)
C(51a)	65(4)	64(4)	53(4)	29(3)	1(3)	3(3)
F(2a)	37(2)	57(2)	79(2)	1(1)	1(2)	—16(2)
C(11)	89(5)	56(4)	57(4)	—23(3)	40(3)	—19(3)
O(11)	153(5)	89(4)	107(4)	—29(3)	73(4)	—54(3)
C(12)	46(3)	45(3)	47(5)	—5(3)	9(2)	—13(2)
O(12)	59(3)	72(3)	93(3)	31(3)	25(2)	26(2)
C(13)	123(6)	44(4)	69(4)	—8(4)	—28(4)	8(3)
O(13)	215(7)	96(4)	118(4)	—15(4)	—108(5)	39(3)
C(21)	90(5)	61(4)	41(3)	27(3)	22(3)	7(3)
O(21)	150(5)	97(4)	73(3)	73(3)	48(3)	7(3)
C(23)	61(4)	39(3)	45(3)	0(3)	0(3)	—4(3)
O(23)	88(3)	66(3)	49(2)	4(2)	—18(2)	—4(2)
C(22)	50(3)	52(3)	44(3)	2(3)	6(3)	8(2)
O(22)	74(3)	74(3)	96(3)	—20(2)	26(3)	24(2)
C(31)	41(3)	30(2)	38(3)	—1(2)	5(2)	—9(2)
O(31)	50(2)	36(2)	84(3)	—9(2)	27(2)	—9(2)

[a] Cr(1)—C(31) × 10^4, H(1)—H(513a) × 10^3. $U_{eq} = 1/3(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$. [b] Anisotropic temperature factors were obtained from the expression for the temperature effect $\exp[-2\pi^2(U_{11}h^2b^2 + ... + 2U_{12}hkb_1b_2 + ...)]$ where b_i are the reciprocal lattice vectors.

aqueous zinc bromide solution. Intensity data were also recorded in the Syntex $P2_1$ diffractometer using a coupled θ(crystal)—2θ(counter) scan. Corrections were made for Lorentz-polarization effects but not for absorption. This will introduce a maximum error in F_0 of 2.5%.

Solution of the structure

The chromium atoms were found from a three-dimensional Patterson synthesis and a series of full-matrix least-squares refinements followed by three-dimensional electron density difference syntheses revealed all the atoms. At this stage, the temperature factors of all atoms except hydrogen were made anisotropic. Tests were made at each stage to show the use of the increased parameters were significant [33]. Further refinements using full-matrix least-squares and minimizing $\Sigma\omega(|F_0| - |F_c|)^2$ was terminated when the maximum shift/error was about 0.2. Corrections were made for secondary extinction using the method of Larson [34]. Throughout the refinement, the scattering curves were taken from ref. [35] and anomalous dispersion corrections from ref. [36] were applied to the curve for chromium. The atom parameters are listed in Table 6 [*,**].

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[*] Tables of structure factors have been deposited. See NAPS document no. 03905 for 19 pages of supplementary materials. Order from NAPS c/o Microfiche Publications, P.O. Bos 3513, Grand Central Station, New York, NY 10017. Remit in advance in U.S. funds only $7.75 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada, add postage of $4.50 for the first 20 pages and $1.00 for each 10 pages of material thereafter. $1.50 for microfiche postage.

[**] All calculations were carried out on CDC-6400 and CYBER 170/730 computers. Preliminary data treatment used programs from the XRAY 76 package [37]. The structure was solved using programs from the SHELX package [38]. Final refinement and difference syntheses used the full matrix least squares program CUDLS and the Fourier program SYMFOU written internally by J.S. Stephens and J.S. Rutherford, respectively. Diagrams were prepared using ORTEP II [39].

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