Reactions of [14]Annulene and Dehydro[14]annulene with Organotricarbonylchromium Complexes: Crystal and Molecular Structures of Hexacarbonyl-*trans*-6a,12a-dihydro-octalenedichromium(0), Tricarbonyl-1,4-dihydrophenanthrenechromium(0), and Tricarbonylphenanthrenechromium(0)

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The crystal structures of the title compounds have been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Hexacarbonyl-*trans*-6a,12a-dihydro-octalenedichromium(0), (I), triclinic, space group $P\bar{1}$, $Z = 1$, $a = 11{\cdot}33(1)$, $b = 7{\cdot}10(1)$, $c = 9{\cdot}67(1)$ Å, $\alpha = 102{\cdot}1(1)$, $\beta = 135{\cdot}1(1)$, $\gamma = 100{\cdot}1(1)°$.

Tricarbonyl-1,4-dihydrophenanthrenechromium(0), (II), monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8{\cdot}649(3)$, $b = 12{\cdot}256(6)$, $c = 10{\cdot}915(4)$ Å, $\beta = 95{\cdot}4(1)°$. Tricarbonylphenanthrenechromium(0), (III), monoclinic, space group $P2_1/c$, $Z = 4$, $a = 8{\cdot}64(4)$, $b = 11{\cdot}69(4)$, $c = 13{\cdot}95(5)$ Å, $\beta = 101{\cdot}8°$. The structures were refined by least squares to R 0·103 [(I), 693 reflections], 0·084 [(II), 1456 reflections], and 0·050 [(III), 1898 reflections].

(I) has C_i symmetry with two $Cr(CO)_3$ moieties bound to the triene fragments of the dihydro-octalene ring. In (II) the $Cr(CO_3)$ is symmetrically bound to a benzene fragment of 1,4-dihydrophenanthrene. The results for (III) are compared with those obtained for an orthorhombic modification.

THE reaction of [14]annulene with trisamminetricarbonylchromium provides compound (I) in which the valence isomer, *trans*-6a,12a-dihydro-octalene, is co-ordinated to two tricarbonylchromium fragments. Monodehydro-[14]annulene reacts with trisacetonitriletricarbonylchromium to give (II) the tricarbonylchromium derivative of the valence isomer, 1,4-dihydrophenanthrene, and also tricarbonylphenanthrenechromium(0) (III). (III) was formed as the monoclinic polymorph which had been previously described by Deuschl and Hoppe;[1] the more accurate analysis reported here allows a detailed comparison with the structural results of Muir *et al.*[2] derived from an orthorhombic crystal modification.

EXPERIMENTAL

The available quantities of the three compounds did not allow recrystallisation procedures and diffraction data were accordingly limited in accuracy. Structural analyses were completed by heavy-atom methods, refinement of atomic parameters being achieved by full-matrix least-squares methods[3] minimising $\Sigma w\{|F_o| - |F_c|\}^2$. Atomic scattering

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[1] H. Deuschl and W. Hoppe, *Acta Cryst.*, 1964, **17**, 800.

[2] K. W. Muir, G. Ferguson, and G. A. Sim, *J. Chem. Soc.* (*B*), 1968, 467.

[3] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, '*X*-Ray System 1970,' Atlas Computer Laboratory.

factors used in the structure factor calculations were those for chromium, oxygen, and carbon[4] and for hydrogen.[5] No allowance was made for anomalous dispersion or for absorption effects, all integrated intensity data being obtained from Mo-K_α radiation. Four circle-diffractometer methods were used for intensity measurements on (I) and (II), while data for (III) were obtained from the linear diffractometer, PAILRED. All observed parameters are accompanied, in parentheses, by the estimated standard deviation of the observation.

Hexacarbonyl-trans-6a,12a-*dihydro-octalenedichromium*(0), (I)

Crystal Data.—$C_{20}H_{14}Cr_2O_6$, $M = 454{\cdot}1$, Triclinic, (Delaunay reduced cell), $a = 11{\cdot}33(1)$, $b = 7{\cdot}10(1)$, $c = 9{\cdot}67(1)$ Å, $\alpha = 102{\cdot}1(1)$, $\beta = 135{\cdot}5(1)$, $\gamma = 100{\cdot}1(1)^\circ$, $U = 469{\cdot}4(3)$ Å^3, $D_c = 1{\cdot}61$ g/cm^3, $Z = 1$, D_m (by flotation) 1·66 g/cm^{-3}, $F(000) = 454$. Space group (structure solution) $P\bar{1}$. Cell data were obtained from the least-squares refinement of the setting angles for 12 reflexions on a four-circle diffractometer. Zirconium-filtered Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 12·5 cm^{-1}.

TABLE 1

(I): Atomic co-ordinates ($\times 10^3$) and anisotropic thermal parameters ($U_{ij} \times 10^3$) *

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	280·8(4)	428·7(5)	51·9(5)	45(2)	43(2)	52(2)	25(2)	43(1)	27(1)
O(1)	237(2)	137(2)	210(3)	101(9)	76(11)	101(12)	59(8)	84(10)	64(10)
O(2)	280(2)	86(3)	−205(3)	105(10)	77(12)	108(15)	41(9)	92(12)	31(10)
O(3)	707(2)	565(3)	404(3)	73(9)	146(15)	81(12)	57(9)	67(10)	64(11)
C(1)	275(2)	657(3)	253(3)	27(8)	47(12)	61(14)	12(8)	36(10)	18(10)
C(2)	384(3)	771(3)	253(3)	63(10)	59(14)	66(15)	47(10)	51(11)	36(12)
C(3)	318(3)	748(4)	47(4)	77(14)	69(16)	95(20)	60(12)	71(16)	59(16)
C(4)	164(3)	580(3)	−173(3)	39(10)	55(14)	62(16)	23(10)	38(12)	32(12)
C(5)	17(3)	370(3)	−279(3)	49(10)	74(15)	54(16)	39(11)	34(12)	48(13)
C(6)	−40(2)	284(3)	−205(3)	33(8)	67(14)	44(13)	16(9)	28(10)	24(12)
C(7)	62(3)	594(4)	80(4)	42(4)	130(20)	69(20)	12(12)	38(15)	−42(15)
C(8)	260(3)	249(4)	152(3)	76(12)	66(16)	62(16)	55(12)	51(13)	38(14)
C(9)	278(3)	215(4)	−112(4)	61(12)	45(14)	81(18)	2(10)	57(13)	14(13)
C(10)	541(3)	517(3)	266(4)	55(12)	65(14)	90(18)	19(10)	66(14)	8(13)

* $T = \exp -2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)$.

Intensity data for reflexions with $2\theta \leqslant 46^\circ$ were collected on the Hilger–Watts four-circle diffractometer by use of a standard $\omega/2\theta$ scan routine with background measurements made at the extremities of each peak. Count rates did not exceed the linear range of the counter. The diffracted rays were collected by a circular aperture, diameter 3·5 mm, 260 mm from the crystal and then measured with a scintillation counter. Each background measurement was made for 150 s and the peak intensities were accumulated over 100 steps, each of 0·01°, with a count time of 3 s at each point, giving a total measuring time of 10 min for each reflexion. No systematic variations in the intensities of two reference reflexions were observed. The 693 reflexions with $F^2 \geqslant \sigma(F^2)$ were corrected for Lorentz and polarisation but not for absorption or extinction effects (crystal size 0·3 × 0·2 × 0·2 mm).

Refinement with unit weights for all observations and anisotropic thermal parameters for all atoms reduced the conventional residual to 0·103 and $\Sigma w\Delta^2/(N_o - N_v)$ (w is the weight attached to a reflexion, N_o the number of observations and N_v the number of variables) was 2·29.

An analysis of Δ^2 showed a marked dependence on F_o and new weights, w, were calculated from the expression $w = 1/(7{\cdot}010 - 0{\cdot}400F_o + 0{\cdot}0089F_o^2)$. Four further cycles of refinement resulted in R converging to 0·103 and $\Sigma w\Delta^2/(N_o - N_v)$ to 1·168. In the final cycle no parameter shifted $>0{\cdot}08\sigma$. A difference-Fourier synthesis using the final values of the refined parameters to calculate F_c showed no excursions of magnitude $>0{\cdot}8$ eÅ^{-3}. The calculated co-ordinates of the hydrogen atoms could not be correlated with positive areas of electron density and no hydrogen atom contributions were included in the structure-factor calculations. Observed and calculated structure factors for all three compounds are listed in Supplementary Publications No. SUP 20740 (5 pp., 1 microfiche).*

Final values of the atomic positional and thermal parameters together with their estimated standard deviations are listed in Table 1. The atomic labelling and intramolecular dimensions are shown in Figure 1 [see also Tables 2(*a*) and (*b*)]. A stereoscopic view giving a representation of the thermal motion is presented in Figure 2.

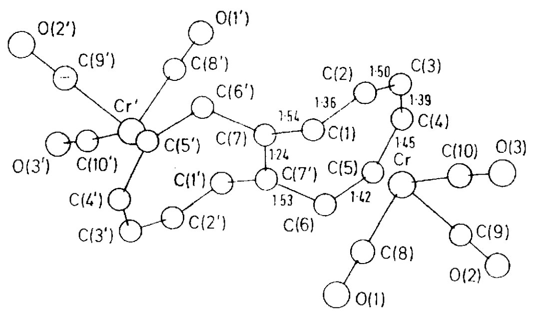

FIGURE 1 (I): Molecular stereochemistry, atom labelling, and C–C bond lengths (Å)

Tricarbonyl-1,4-*dihydrophenanthrenechromium*(0), (II)

Crystal Data.—$C_{17}H_{12}CrO_3$, $M = 317{\cdot}0$, Monoclinic, $a = 8{\cdot}649(3)$, $b = 12{\cdot}256(7)$, $c = 10{\cdot}915(4)$ Å, $\beta = 85{\cdot}4(1)^\circ$,

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full sized copies.)

[4] D. T. Cromer and J. A. Waber, *Acta Cryst.*, 1965, **18**, 104.

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1968, **42**, 3175.

$U = 1434{\cdot}1(2)$ Å^3, $D_c = 1{\cdot}46(1)$ g/cm^3, $Z = 4$, D_m (by flotation) $1{\cdot}47(2)$ g/cm^3, $F(000) = 317$. Space group $P2_1/n$ *from the* systematic absences: ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). Cell data were obtained from the least-squares refinement of the setting angles for 12 reflexions on a four-circle diffractometer. Mo-K_α radiation, μ(Mo-K_α) = 8·4 cm^{-1}.

Intensity data for reflexions with $2\theta \leqslant 44°$ were collected as for the preceding analysis. The scan range was varied with θ to take account of the wavelength dispersion and had a value at 0·65° for the (2,0,0) reflexion. The peak count for the (2,0,0) reflexion was accumulated over 65 steps with counts of 3 s at each step. Background counts of 96 s were taken at the extremities of the scan. The 1456 reflexions for which $F^2 \geqslant 2\sigma(F^2)$ were corrected for Lorentz and polarisation but not for extinction or absorption effects (crystal size 0·36 × 0·32 × 0·25 mm).

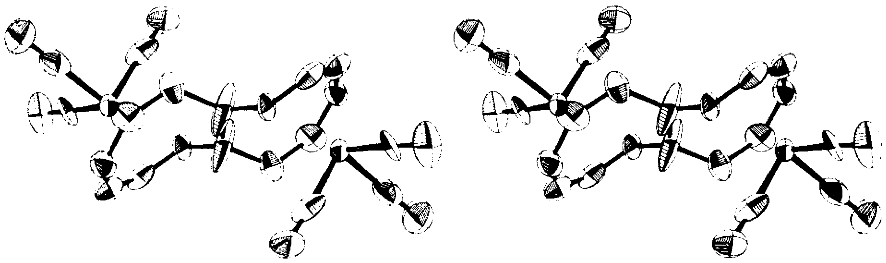

FIGURE 2 (I): Stereoscopic view of atomic thermal ellipsoids (50% probability)

TABLE 2

(I): Molecular geometry

(*a*) Intramolecular bond lengths (Å)

C(1)–C(2)	1·36(2)	Cr–C(1)	2·38(2)
C(2)–C(3)	1·50(3)	Cr–C(2)	2·23(2)
C(3)–C(4)	1·39(3)	Cr–C(3)	2·25(2)
C(4)–C(5)	1·45(3)	Cr–C(4)	2·25(2)
C(5)–C(6)	1·42(2)	Cr–C(5)	2·20(2)
C(6)–C(7′)	1·53(3)	Cr–C(6)	2·35(2)
C(7)–C(7′)	1·24 *	Cr–C(8)	1·88(2)
C(7)–C(1)	1·54(3)	Cr–C(9)	1·87(3)
C(8)–O(1)	1·16(2)	Cr–C(10)	1·79(2)
C(9)–O(2)	1·16(2)		
C(10)–C(3)	1·20(2)		

(*b*) Bond angles (deg.)

C(7)–C(1)–C(2)	123(2)	Cr–C(8)–O(1)	178(2)
C(1)–C(2)–C(3)	125(2)	Cr–C(9)–O(2)	177(2)
C(2)–C(3)–C(4)	131(2)	Cr–C(10)–O(3)	177(2)
C(3)–C(4)–C(5)	131(2)	C(8)–Cr–C(9)	91(3)
C(4)–C(5)–C(6)	132(2)	C(8)–Cr–C(10)	92(3)
C(5)–C(6)–C(7′)	127(2)	C(9)–Cr–C(10)	82(3)
C(6)–C(7′)–C(7)	131(2)		
C(1)–C(7)–C(6′)	108(2)		
C(1)–C(7)–C(7′)	120(3)		

(*c*) Plane C(1)—(6)

Equation $-0{\cdot}5669X + 0{\cdot}7854Y - 0{\cdot}2487Z = 1{\cdot}6804$ †

Deviations (Å): C(1) 0·09, C(2) −0·13, C(3) 0·04, C(4) 0·07, C(5) −0·06, C(6) 0·00, Cr −1·52

* See text. † X, Y, and Z are orthogonal co-ordinates in Å.

Refinement with unit-weights for all observations and anisotropic thermal parameters for all non-hydrogen atoms reduced the conventional residual to 0·102. A calculation of the least-squares plane through the central benzene ring, the one bonded to the chromium atom, revealed that the two carbon atoms C(2) and C(3) in one of the terminal rings were displaced significantly from the plane. This indicated the two CH_2 groups were located among the four atoms C(1)—(4). Atomic co-ordinates were calculated for the hydrogen atoms bonded to the known trigonal carbon atoms C(5)—(10). Further refinement of the non-hydrogen atom parameters resulted in R 0·089 (hydrogen atoms were included in the structure-factor calculations with isotropic thermal parameters of 10·0 Å^2). A difference-Fourier synthesis using reflexions with $\sin\theta \leqslant 0{\cdot}35$ showed two large positive peaks in the positions expected for two hydrogen atoms bonded to C(1). Idealised positions for these and for the hydrogen atom bonded to C(3) were calculated and included in the subsequent structure-factor calculations. Further refinement of the non-hydrogen atom parameters resulted in R 0·087 and a subsequent difference-Fourier synthesis clearly showed that two hydrogen atoms were bonded to C(4). The complex was now positively identified as containing 1,4-dihydrophenanthrene. Refinement of the heavy-atom parameters with the hydrogen atoms contributing to the structure-factor calculations with isotropic temperature factors of 10 Å^2 resulted in R 0·084. An analysis of Δ^2 showed no systematic dependence on F_o or $\sin\theta/\lambda$. In the final cycle no variable parameter shifted by $>0{\cdot}03\sigma$. A difference-Fourier synthesis calculated using the final values of the refined parameters showed no excursions of magnitude $>0{\cdot}6$ eÅ^{-3}.

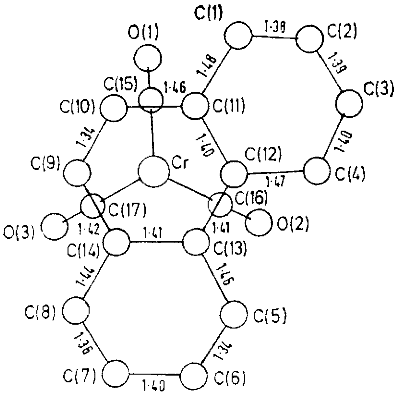

FIGURE 3 (II): Atom labelling and some intramolecular bond lengths (Å)

Final values of the atomic positional and thermal parameters are listed in Table 3. The atomic labelling and

TABLE 3

(II): Atomic co-ordinates (× 10^4) and vibrational parameters (× 10^3)

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	2246(2)	803(1)	1929(1)	65·7(9)	86(11)	58·6(9)	6·5(8)	1·5(7)	−14·5(8)
O(1)	−686(8)	1807(5)	1425(7)	71(4)	122(6)	114(6)	12(4)	−4(4)	−17(5)
O(2)	3290(9)	2137(6)	3832(7)	136(7)	129(7)	98(6)	21(6)	−26(5)	−51(5)
O(3)	596(12)	−210(7)	3723(9)	172(9)	151(9)	148(8)	−18(7)	69(7)	20(7)
C(1)	2630(19)	1842(14)	−735(12)	153(13)	209(18)	85(9)	98(14)	49(9)	23(12)
C(2)	3237(27)	2654(14)	−405(19)	222(22)	156(17)	158(18)	78(18)	1(15)	60(15)
C(3)	4624(22)	2696(11)	340(17)	190(17)	106(12)	177(17)	10(12)	54(17)	37(12)
C(4)	5248(13)	1958(10)	965(11)	92(8)	118(10)	128(10)	10(8)	48(7)	−20(9)
C(5)	6127(11)	463(8)	2632(10)	80(7)	109(10)	105(8)	10(7)	−14(6)	−12(7)
C(6)	6387(19)	−194(12)	3431(14)	187(16)	131(15)	147(13)	9(12)	−90(12)	−5(11)
C(7)	5432(21)	−936(11)	3390(15)	188(16)	129(14)	144(13)	9(12)	−40(12)	45(11)
C(8)	4249(16)	−1052(8)	2490(12)	136(11)	76(9)	115(10)	11(7)	7(8)	−13(7)
C(9)	2529(11)	−380(8)	796(10)	83(7)	101(9)	76(7)	4(6)	4(6)	−26(6)
C(10)	2117(10)	286(9)	35(9)	56(6)	155(12)	65(6)	−3(7)	4(5)	−40(7)
C(11)	3033(11)	1087(9)	82(9)	68(7)	139(11)	65(6)	26(7)	19(5)	5(7)
C(12)	4331(10)	1144(8)	950(9)	57(6)	96(8)	80(7)	2(6)	16(5)	−23(6)
C(13)	4766(10)	439(7)	1736(9)	59(6)	87(8)	82(7)	8(6)	−6(5)	−26(6)
C(14)	3863(10)	−332(7)	1662(9)	66(6)	88(8)	84(7)	11(6)	7(5)	−14(6)
C(15)	483(11)	1426(7)	1616(8)	65(6)	108(9)	73(6)	−9(6)	2(5)	−19(6)
C(16)	2907(10)	1611(7)	3097(9)	71(6)	100(8)	85(7)	19(6)	−3(5)	−11(7)
C(17)	1253(13)	203(8)	3028(10)	112(8)	91(9)	89(8)	−13(7)	28(7)	−21(7)

TABLE 4

(II): Molecular geometry

(*a*) Bond lengths (Å)

C(1)–C(2)	1·38(3)	Cr–C(9)	2·22(1)
C(2)–C(3)	1·39(3)	Cr–C(10)	2·21(1)
C(3)–C(4)	1·40(2)	Cr–C(11)	2·23(1)
C(4)–C(12)	1·47(2)	Cr–C(12)	2·24(1)
C(11)–C(12)	1·40(1)	Cr–C(13)	2·28(1)
C(1)–C(11)	1·48(2)	Cr–C(14)	2·26(1)
C(5)–C(6)	1·34(2)	Cr–C(15)	1·80(1)
C(6)–C(7)	1·40(3)	Cr–C(16)	1·83(1)
C(7)–C(8)	1·36(2)	Cr–C(17)	1·79(1)
C(8)–C(14)	1·44(2)	C(15)–O(1)	1·17(1)
C(13)–C(14)	1·41(2)	C(16)–O(2)	1·16(1)
C(5)–C(13)	1·46(1)	C(17)–O(3)	1·17(1)
C(9)–C(14)	1·42(1)		
C(9)–C(10)	1·34(2)		
C(10)–C(11)	1·46(2)		
C(12)–C(13)	1·41(2)		

(*b*) Bond angles (deg.)

C(11)–C(1)–C(2)	119(1)	C(4)–C(12)–C(13)	122(1)
C(1)–C(2)–C(3)	119(2)	C(11)–C(12)–C(13)	121(1)
C(2)–C(3)–C(4)	121(2)	C(5)–C(13)–C(12)	123(1)
C(3)–C(4)–C(12)	119(1)	C(5)–C(13)–C(14)	118(1)
C(13)–C(5)–C(6)	120(1)	C(12)–C(13)–C(14)	119(1)
C(5)–C(6)–C(7)	122(1)	C(8)–C(14)–C(9)	120(1)
C(6)–C(7)–C(8)	122(1)	C(8)–C(14)–C(9)	120(1)
C(7)–C(8)–C(14)	118(1)	C(9)–C(14)–C(13)	119(1)
C(14)–C(9)–C(10)	122(1)	C(15)–Cr–C(16)	88·9(5)
C(9)–C(10)–C(11)	120(1)	C(15)–Cr–C(17)	86·9(5)
C(1)–C(11)–C(10)	122(1)	C(17)–Cr–C(16)	90·9(5)
C(1)–C(11)–C(12)	119(1)	Cr–C(15)–O(1)	178(1)
C(10)–C(11)–C(12)	118(1)	Cr–C(16)–O(2)	178(1)
C(4)–C(12)–C(11)	117(1)	Cr–C(17)–O(3)	178(1)

(*c*) Equations * of molecular planes and atom deviations (Å) from them

Plane (i): C(9)—(14)

$$0{\cdot}6340X - 0{\cdot}3728Y - 0{\cdot}6775Z = 0{\cdot}9708$$

C(10) 0·00, C(11) 0·01, C(12) −0·01, C(13) 0·00, C(14) 0·01

Plane (ii): C(5)—(8), C(13), C(14)

$$0{\cdot}6532X - 0{\cdot}4135Y - 0{\cdot}6343Z = 1{\cdot}1383$$

C(5) 0·04, C(6) 0·00, C(7) −0·04, C(8) 0·04, C(13) −0·04, C(14) 0·00

* X, Y, Z are now co-ordinates (Å) referred to the orthogonal axes $X = ax \sin \beta$, $Y = by$, $Z = ax \cos \beta + CZ$.

intramolecular dimensions are shown in Figure 3 with a stereoscopic view of the thermal motion (50% probability) in Figure 4. Relevant molecular dimensions are collected in Tables 4.

Tricarbonylphenanthrenechromium(0), (III)

Crystal Data.—$C_{17}H_{10}CrO_3$, $M = 315{\cdot}0$, Monoclinic. Space group $P2_1/c$ from systematic absences: ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). Cell parameters were calculated from a least-squares analysis of high-angle reflexions on zero-level precession photographs (Mo-K_α). Crystal data from the present work are compared in Table 5 with those from the analysis of ref. 1. (Cell data for the latter have been converted from space group $P2_1/a$ to conform to the present work in space group $P2_1/c$.)

TABLE 5

Unit cell dimensions of (III)

	Present work	Ref. 1
a/Å	8·64(4)	8·63(2)
b/Å	11·69(4)	11·68(4)
c/Å	13·95(5)	14·06(4)
β/°	101·8	102·0
D_c/g cm^{-3}	1·514	1·506
D_m/g cm^{-3}	1·49(2)	1·508
U/Å^3	1377·9	1386·2
Z	4	4

Intensity data for the reflexions with $2\theta \leqslant 50°$ on the zero-level and with gradually decreasing $\theta_{\text{max.}}$ for upper levels were collected on a PAILRED diffractometer by use of silicon monochromated Mo-K_α radiation. 1898 Reflexions were measured which had $F^2 \geqslant 2\sigma(F^2)$. Data were corrected for Lorentz and polarisation effects but not for extinction or absorption [crystal size 0·4 × 0·2 × 0·2 mm, μ(Mo-K_α) = 8·4 cm^{-1}].

Initial non-hydrogen atom positions were taken from the earlier analysis.[1] Hydrogen atom co-ordinates were calculated and included in the structure-factor calculations with isotropic temperature factors of 6·0 Å^2. Refinement of the non-hydrogen atom parameters with anisotropic thermal

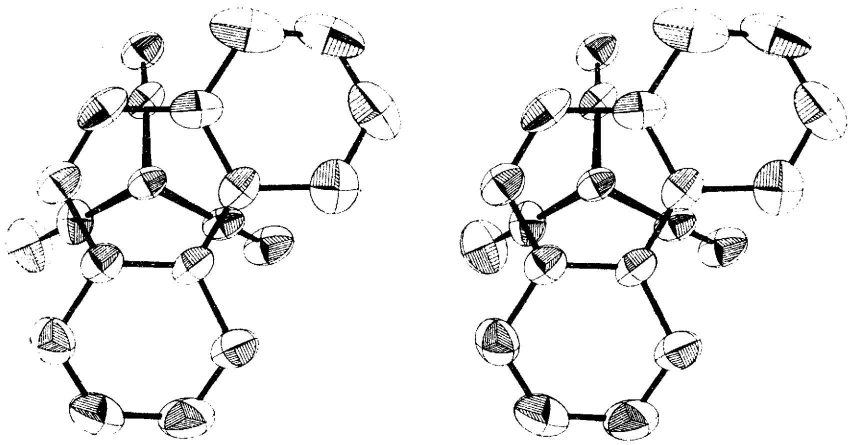

FIGURE 4 (II): Atomic thermal ellipsoids (50% probability)

parameters and with unit weights for all observations gave a final residual of 0·050. A final difference synthesis

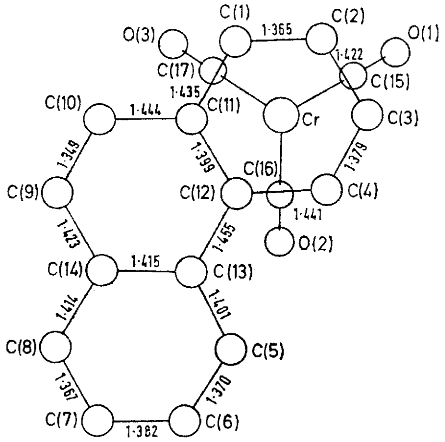

FIGURE 5 (III): Atom labelling and C–C bond lengths (Å) in the phenanthrene ligand

showed no excursions of magnitude $>0{\cdot}29$ eÅ^{-3}. No parameter shifted $>0{\cdot}7\sigma$ in the final cycle. Positional and thermal parameters are listed in Table 6. Atomic labelling and intramolecular dimensions are shown in Figure 5 (see also Table 7) with a stereoscopic view of the thermal motion shown in Figure 6.

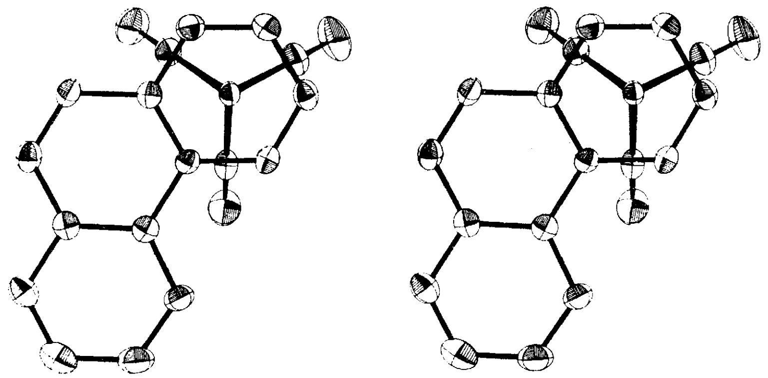

FIGURE 6 (III): Stereoscopic view of atomic thermal ellipsoids (50% probability)

DISCUSSION

The final structural results for (I) are essentially those described in our earlier report [6] which established the stoicheiometry of the complex and therefore that the bond length C(7)–C(7′) of 1·24 Å (Table 2) is subject to systematic error rather than being indicative of double bonding. C(7) is apparently disordered in the crystal. The root-mean-square components of its thermal motion are 0·13, 0·21, and 0·54 Å; if the centrically related atoms are assumed to vibrate independently, the vibration-corrected bond length becomes 1·48(4) Å.

The valence isomerisation of [14]annulene to a bicyclic hexaene is obviously dictated by the charge requirements of the tricarbonylchromium fragments (eighteen-electron rule). The chromium atom is not, however, bound symmetrically to six carbon atoms; the mean chromium–carbon distance of 2·23 Å [to C(2), C(3), C(4), and C(5)] is significantly less than that of 2·37 Å [to C(1) and C(6)]. A similar, if more pronounced, pattern is seen in 1,6-methanocyclodecapentaenetricarbonylchromium [7] where four metal–carbon bond

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[6] K. Stockel, F. Sondheimer, T. A. Clarke, M. Guss, and R. Mason, *J. Amer. Chem. Soc.*, 1971, **93**, 2571.

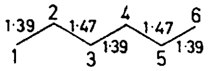
[7] P. E. Baikie and O. S. Mills, *Chem. Comm.*, 1966, 683.

TABLE 6

(III): Atomic co-ordinates (× 10^4), vibrational parameters (× 10^3) and their standard deviations

Atoms	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	1890·3(8)	2861·6(7)	4301·5(5)	33·9(4)	34·6(5)	35·5(4)	1·0(4)	−0·2(3)	−0·5(4)
O(1)	−736(6)	4211(5)	3112(4)	96(3)	107(5)	96(3)	53(3)	−24(3)	19(3)
O(2)	−102(5)	2477(5)	5784(3)	69(3)	128(5)	65(2)	−12(3)	28(2)	−13(3)
O(3)	3082(6)	5044(5)	5308(4)	99(4)	65(4)	96(3)	−15(3)	10(3)	−27(3)
C(1)	4097(5)	2706(5)	3743(3)	45(3)	43(4)	49(3)	−3(2)	10(2)	4(2)
C(2)	2854(6)	2496(5)	2985(3)	53(3)	51(4)	39(2)	−1(2)	10(2)	3(2)
C(3)	1745(6)	1626(5)	3082(3)	52(3)	42(4)	36(2)	3(2)	2(2)	−8(2)
C(4)	1897(5)	1017(5)	3943(3)	35(2)	40(3)	43(2)	−4(2)	4(2)	−8(2)
C(5)	2392(6)	−280(5)	5831(4)	43(3)	42(4)	59(3)	−5(2)	11(2)	4(2)
C(6)	2660(7)	−847(5)	6709(5)	60(3)	58(5)	80(4)	−3(3)	21(3)	22(3)
C(7)	3997(7)	−645(6)	7423(4)	79(4)	66(5)	53(3)	13(4)	20(3)	16(3)
C(8)	5088(6)	135(5)	7253(3)	54(3)	48(4)	43(3)	13(4)	7(2)	2(2)
C(9)	5954(5)	1604(5)	6213(3)	41(2)	38(4)	47(3)	2(2)	0(2)	−10(2)
C(10)	5711(5)	2241(5)	5390(3)	31(2)	36(3)	54(3)	−2(2)	1(2)	−3(2)
C(11)	4343(5)	2032(4)	4621(3)	32(2)	37(3)	40(2)	5(2)	8(2)	−2(2)
C(12)	3230(5)	1201(4)	4737(3)	36(2)	24(3)	38(2)	0(2)	7(2)	−5(2)
C(13)	3461(5)	551(4)	5646(3)	39(2)	33(3)	42(2)	4(2)	9(2)	−3(2)
C(14)	4833(5)	769(4)	6371(3)	41(2)	30(3)	41(2)	10(2)	6(3)	−6(2)
C(15)	271(7)	3697(6)	3574(4)	63(3)	66(5)	53(3)	12(3)	−3(3)	1(3)
C(16)	668(6)	2637(5)	5209(4)	43(3)	58(4)	51(3)	2(3)	0(2)	−10(3)
C(17)	2615(6)	4209(6)	4924(4)	61(3)	43(4)	54(3)	0(3)	2(2)	−3(3)

lengths average 2·20 Å and two average 2·56 Å. Both steric and simple electronic arguments would predict, albeit qualitatively, this trend. The averaged lengths for the chemically equivalent bonds in the co-ordinated triene fragment:



are sufficient to establish its weak (if any) Lewis acidity with respect to the tricarbonylchromium group.

TABLE 7

(III): Molecular geometry

(*a*) Bond lengths (Å); those headed M.F.S. are results of Muir *et al.*[2] (orthorhombic modification) and those headed L, of the free ligand [8]

		M.F.S.	L
C(1)–C(2)	1·365(6)	1·389	1·380
C(2)–C(3)	1·422(8)	1·385	1·404
C(3)–C(4)	1·379(7)	1·410	1·398
C(4)–C(12)	1·441(5)	1·439	1·403
C(11)–C(12)	1·399(7)	1·410	1·390
C(1)–C(11)	1·435(7)	1·440	1·466
C(5)–C(6)	1·370(8)	1·418	1·368
C(6)–C(7)	1·382(8)	1·401	1·391
C(7)–C(8)	1·367(9)	1·337	1·382
C(8)–C(14)	1·414(7)	1·415	1·448
C(13)–C(14)	1·415(6)	1·402	1·418
C(5)–C(13)	1·401(7)	1·402	1·406
C(9)–C(14)	1·423(7)	1·416	1·379
C(9)–C(10)	1·349(7)	1·333	1·372
C(10)–C(11)	1·444(5)	1·447	1·401
C(12)–C(13)	1·455(6)	1·462	1·448
Cr–C(1)	2·208(5)	2·212	
Cr–C(2)	2·207(5)	2·210	
Cr–C(3)	2·214(5)	2·206	
Cr–C(4)	2·213(5)	2·208	
Cr–C(11)	2·289(4)	2·289	
Cr–C(12)	2·278(5)	2·289	
Cr–C(15)	1·832(6)	1·828	
Cr–C(16)	1·826(6)	1·844	
Cr–C(17)	1·845(6)	1·857	
C(15)–O(1)	1·140(7)	1·165	
C(16)–O(2)	1·157(7)	1·145	
C(17)–O(3)	1·146(8)	1·136	

TABLE 7 (*Continued*)

(*b*) Bond angles (deg.)

C(11)–C(1)–C(2)	121·2(5)	C(4)–C(12)–C(13)	122·5(4)
C(1)–C(2)–C(3)	119·5(5)	C(11)–C(12)–C(13)	119·3(4)
C(2)–C(3)–C(4)	120·4(4)	C(5)–C(13)–C(12)	123·0(4)
C(3)–C(4)–C(12)	120·8(4)	C(5)–C(13)–C(14)	118·7(4)
C(13)–C(5)–C(6)	120·3(4)	C(12)–C(13)–C(14)	118·3(4)
C(5)–C(6)–C(7)	121·6(6)	C(8)–C(14)–C(9)	120·3(4)
C(6)–C(7)–C(8)	119·6(5)	C(8)–C(14)–C(13)	119·1(5)
C(7)–C(8)–C(14)	120·7(4)	C(9)–C(14)–C(13)	120·6(4)
C(14)–C(9)–C(10)	121·3(4)	C(15)–Cr–C(16)	88·6(3)
C(9)–C(10)–C(11)	119·9(5)	C(15)–Cr–C(17)	87·3(3)
C(1)–C(11)–C(10)	119·7(4)	C(17)–Cr–C(16)	89·1(3)
C(1)–C(11)–C(12)	119·7(4)	Cr–C(15)–O(1)	179·2(6)
C(10)–C(11)–C(12)	120·6(4)	Cr–C(16)–O(2)	179·0(6)
C(4)–C(12)–C(11)	118·3(4)	Cr–C(17)–O(3)	179·2(6)

(*c*) Equations of molecular planes * and deviations (Å) of atoms from them

Plane (i): C(1)—(14)

$$0{\cdot}6026X - 0{\cdot}6935Y - 0{\cdot}3948Z = -2{\cdot}6596$$

C(1) −0·064, C(2) −0·002, C(3) 0·057, C(4) 0·018, C(5) −0·015, C(6) −0·041, C(7) −0·016, C(8) 0·039, C(9) 0·039, C(10) −0·019, C(11) −0·014, C(12) −0·002, C(13) −0·002, C(14) 0·020

Plane (ii): C(1)—(4), C(11), C(12)

$$0{\cdot}6275X - 0{\cdot}6771Y - 0{\cdot}3843Z = -2{\cdot}5326$$

C(1) −0·024, C(2) 0·002, C(3) 0·021, C(4) −0·020, C(11) 0·024, C(12) −0·003

* X, Y, and Z are co-ordinates in Å referred to orthogonal axes where $X = ax \sin\beta$, $Y = by$, and $Z = ax \cos\beta + cz$.

For (III), our results follow closely on those described by Muir *et al.*[2] for the orthorhombic modification (there is little point in making a detailed comparison with the low-accuracy results of Deuschl and Hoppe[1]). The root-mean-square deviation between equivalent metal–carbon bond lengths is $0{\cdot}01_0$ Å while that between equivalent carbon–carbon bond lengths is $0{\cdot}02_1$ Å; this seems satisfactory although there are some differences [*e.g.*, C(5)–C(6)] which appear to be significant but are more likely to be a commentary on under-estimates in the estimated standard deviations. Compared with the free-ligand bond lengths, the root-mean-square difference between our results and those of Trotter[8] is $0{\cdot}02_3$ Å while that between those of ref. 2 and Trotter[8] is $0{\cdot}03_0$ Å.

The present results confirm the data of ref. 2 in that the tricarbonylchromium fragment is rather asymmetrically bound to the arene ring; the difference of *ca.* 0·05 Å between the Cr–C(11)[C(12)] bond lengths and those to C(1), C(2), C(3), and C(4) has been interpreted[2] as reflecting the differing free-valence of these atoms. This view seems reasonable and is reinforced by the similar pattern in tricarbonyl-9,10-dihydrophenanthrenechromium[9] and, to a less significant extent, by that in (II).

The 1,4-cyclohexadiene ring might have been expected, on steric grounds, to have directed the tricarbonylchromium group to bonding with the end ring. The observation of bonding to the centre ring carries the implication, therefore, that this mode is preferred for electronic reasons: the cyclohexadiene fragment concentrates electron density in the C(9)–C(10) and C(11)–C(12) bonds and presumably provides the middle ring with strong Lewis basicity.

These studies were initiated to obtain accurate structural parameters of [14]annulene and to determine the configuration of the ' stable ' and ' unstable ' isomers of monodehydro[14]annulene. The observation of the valence isomerisation of [14]annulene led us to hope that monodehydro[14]annulene would be isomerised to benz[10]annulene and that this would be stabilised through co-ordination. One may imagine, with retrospective wisdom, that the basicity of the central arene fragment in 1,4-dihydrophenanthrene is greater than that in benz[10]annulene in that there will be less bond fixation in the latter.

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[3/453 *Received, 28th February,* 1973]

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[8] J. Trotter, *Royal Inst. Chem. Lectures*, 1964, 2.

[9] K. W. Muir and G. Ferguson, *J. Chem. Soc.* (*B*), 1968, 476.