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CHROMIUM ASSISTED 1,5-SIGMATROPIC REARRANGEMENT OF HEXAETHYLIDENECYCLOHEXANE TO 1,3,5-TRIETHENYL-2,4,6-TRIETHYLBENZENE

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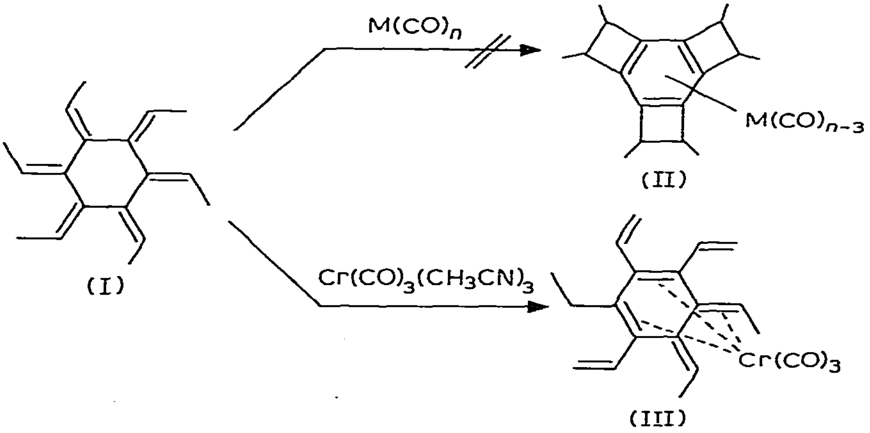
Summary

Hexaethylidenecyclohexane (I) in dioxane reacts with chromium tricarbonyl-triacetonitrile with double 1,5-sigmatropic hydrogen migration to give the chromium tricarbonyl complex III, the structure of which has been determined by NMR and X-ray analysis. Heating solutions of III results in a further rearrangement to form the chromium tricarbonyl complex of 1,3,5-triethyl-2,4,6-trivinylbenzene (V). The latter releases the ligand IV on prolonged heating in an atmosphere of carbon monoxide.

Introduction

While perfluorobenzo-1,2:3,4:5,6-tricyclobutene has been obtained in moderate yield [1], all attempts to produce the benzotricyclobutene by pyrolysis have led to the formation of the more stable radialenes [2]. More recently a non-pyrolytic synthesis of this strained molecule in 0.5% yield from a preformed tetracyclic reagent was described [3].



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We hoped that by starting from the stable and easily accessible hexaethylidenecyclohexane I [4] and using complexation with an appropriate metal carbonyl to facilitate the valence isomerisation to the benzotricyclobutane derivative II.

Results and discussion

We found that stirring equimolar quantities of I and chromium tricarbonyl-triacetonitrile complex in dioxane at room temperature for 30 h led to the formation of an orange-red solution from which on removal of the solvent a crystalline orange-red solid could be obtained as the sole product. After recrystallization from hexane at −78°C it melted at 135–135.5°C.

The molecular ion appears at *m/e* 376, in agreement with the formula $C_{18}H_{24}Cr(CO)_3$. Its 400 MHz NMR spectrum (Fig. 1) showed a total of 16 groups of multiplets: six signals for two vinyl groups, six for two ethyl groups with inequivalent methylene protons, and four which can be assigned to two ethylidine groups. The arrangement of these groups around a six-membered ring was determined by Nuclear-Overhauser-Difference-Spectroscopy [5]. It was shown that the vinylic protons at C(30) are in the neighbourhood of protons 20b, 40a, and 41. In this way the immediate neighbouring substituents of the vinyl group were determined to be two ethyl groups at C(2) and C(4). The substituents neighbouring the ethyl groups at C(4) and C(2) were found to be a vinyl and an ethylidene group, respectively. By this method structure III was deduced. Furthermore, the chemical

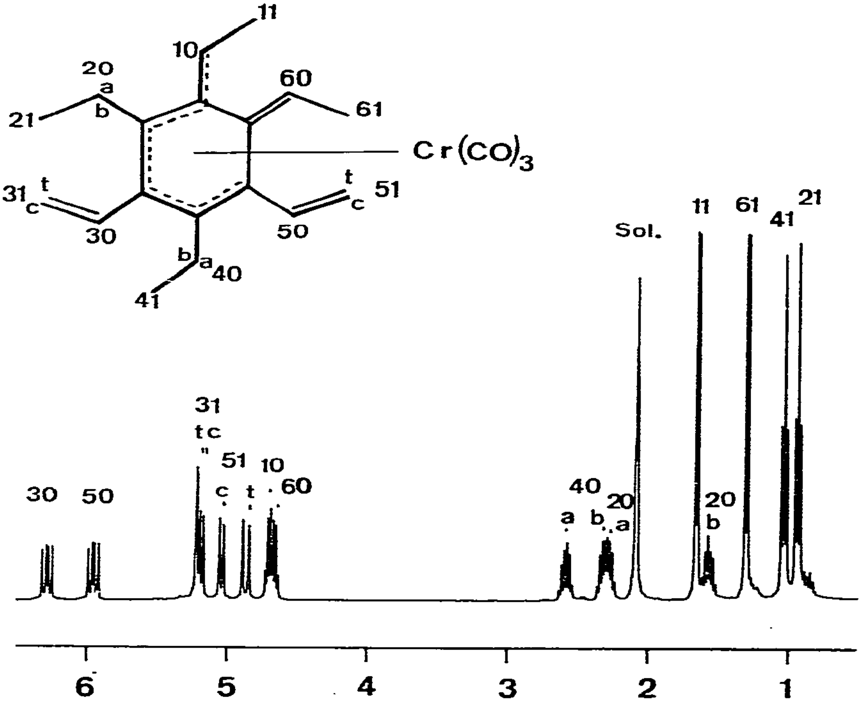


Fig. 1. ¹H NMR spectrum (400 MHz) of III.

shifts and the coupling constants of the vinyl groups show that they are not complexed to the metal. Also due to the vicinal arrangement of the two ethylidene groups, to maintain the 18 electron configuration for the chromium atoms, almost five of the carbon atoms of the six-membered ring are complexed with the metal. This is also in agreement with the ^{13}C NMR data, which show a singlet at δ 127.69 ppm due to the uncomplexed ring carbon C(6) and five singlets between δ 115.91 and 71.43 ppm which arise from the complexed ring carbon atoms C(1)–C(5); in addition the doublet at δ 99.27 ppm can be assigned to C(10) (for the complete ^{13}C NMR data, cf. experimental section). No structural dynamics could be detected by ^{1}H NMR between −60 and +60°C.

X-Ray structure analysis

The above structural assignment was confirmed by X-ray determination of the structure which is shown in Fig. 2. Complexation of the exocyclic double bond to the metal results in an appreciable distortion of the ring skeleton. Carbon–carbon double bonds can still be recognised at C(30)–C(31), C(50)–C(51), C(6)–C(60), C(4)–C(5), C(2)–C(3), and C(1)–C(10) (Table 1), though the last three are significantly lengthened as a result of their interaction with the chromium atom. These three olefinic bonds can be regarded as occupying three vacant coordination sites of the approximately octahedrally coordinated chromium atom, whereby it should be noted that the terminal carbon atoms of the triene, C(5) and C(10), are at a relatively large distance from the metal (> 2.4 Å). Although the planarity of the C(1)–C(5) part of the ring is retained (plane 1) (maximum deviation from this plane 0.07 Å), a total delocalization of the system does not appear to occur since the intervening C–C single bonds C(1)–C(2) and C(3)–C(4) are significantly longer. Similar interaction of the π-system with the vinyl group at C(5) also seems unlikely for the same reason, although this also lies in the plane. The second vinyl group at C(3) is twisted out of this plane by an angle of 65.2° along C(3)–C(30). The plane defined by atoms C(6), C(60), C(1), and C(5) lies at 52.2° to plane 1.

The η^6-stabilization of the *o*-quinodimethane system is unexpected, although a number of η^4-iron tricarbonyl complexes of *o*-quinodimethane are known [6].

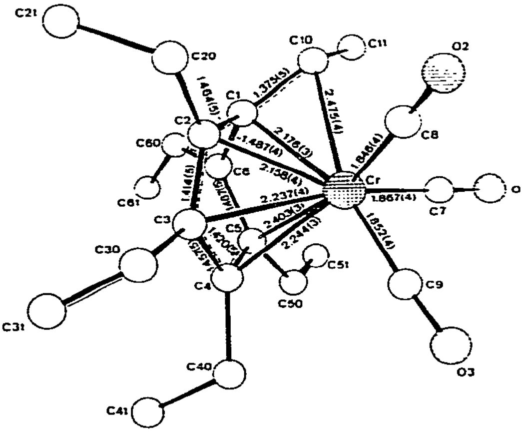


Fig. 2. The molecular structure of III, showing the arbitrary numbering scheme.

TABLE 1

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN III

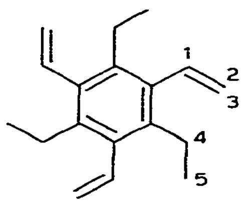
(a) Distances			
Cr–C(1)	2.176(3)	C(2)–C(3)	1.414(5)
Cr–C(2)	2.158(4)	C(2)–C(20)	1.516(5)
Cr–C(3)	2.237(4)	C(3)–C(4)	1.457(5)
Cr–C(4)	2.244(3)	C(3)–C(30)	1.485(5)
Cr–C(5)	2.403(3)	C(4)–C(5)	1.420(5)
Cr–C(7)	1.867(4)	C(4)–C(40)	1.516(5)
Cr–C(8)	1.846(4)	C(5)–C(6)	1.487(5)
Cr–C(9)	1.852(4)	C(5)–C(50)	1.472(5)
Cr–C(10)	2.475(4)	C(10)–C(11)	1.493(6)
O(1)–C(7)	1.148(5)	C(20)–C(21)	1.502(6)
O(2)–C(8)	1.154(5)	C(30)–C(31)	1.243(7)
O(3)–C(9)	1.153(5)	C(40)–C(41)	1.535(6)
C(1)–C(2)	1.464(5)	C(50)–C(51)	1.321(6)
C(1)–C(6)	1.487(4)	C(6)–C(60)	1.335(5)
C(1)–C(10)	1.375(5)	C(60)–C(61)	1.492(6)
(b) Angles			
C(2)–C(1)–C(6)	115.1(3)	C(3)–C(4)–C(5)	119.6(3)
C(2)–C(1)–C(10)	121.0(3)	C(3)–C(4)–C(40)	120.2(3)
C(6)–C(1)–C(10)	121.5(3)	C(5)–C(4)–C(40)	120.1(3)
C(1)–C(10)–C(11)	125.5(3)	C(4)–C(40)–C(41)	111.2(3)
C(1)–C(2)–C(3)	116.5(3)	C(4)–C(5)–C(6)	115.6(3)
C(1)–C(2)–C(20)	120.6(3)	C(4)–C(5)–C(50)	122.5(3)
C(3)–C(2)–C(20)	122.8(3)	C(6)–C(5)–C(50)	121.4(3)
C(2)–C(20)–C(21)	111.7(3)	C(5)–C(50)–C(51)	126.3(4)
C(2)–C(3)–C(4)	118.9(3)	C(1)–C(6)–C(5)	105.6(3)
C(2)–C(3)–C(30)	120.0(3)	C(1)–C(6)–C(60)	123.5(3)
C(4)–C(3)–C(30)	120.9(3)	C(5)–C(6)–C(60)	130.9(3)
C(3)–C(30)–C(31)	129.9(5)	C(6)–C(60)–C(61)	128.2(3)
C(7)–Cr–C(8)	98.4(2)	Cr–C(7)–O(1)	178.0(3)
C(7)–Cr–C(9)	88.6(2)	Cr–C(8)–O(2)	176.7(4)
C(8)–Cr–C(9)	82.3(2)	Cr–C(9)–O(3)	176.4(3)

Reaction of complex III

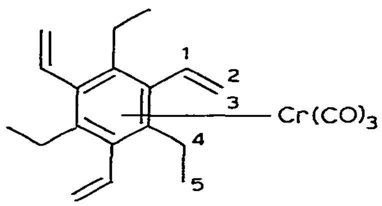
When the above reaction was carried out in refluxing dioxane, or alternatively, purified III heated in dioxane, the rearrangement process continued and the products isolated were the hitherto unknown 1,3,5-triethenyl-2,4,6-triethylbenzene (IV) and its π-arylchromium tricarbonyl complex (V).

A dioxane solution of III at room temperature was stable to exposure of carbon monoxide. However, its addition at 80°C changed the colour of the solution from orange-red to pale yellow and IV was released quantitatively. Both III and V are relatively air stable, but prolonged exposure of both compounds results in the formation of IV.

The facile 1,5-sigmatropic rearrangement of the ethylidene groups under these mild conditions in the presence of chromium is surprising in view of the observation that I is stable in refluxing dioxane and flash pyrolysis at elevated temperatures giving only a very poor yield of IV [7].



(IV)



(V)

Experimental

Procedure:

III. Hexaethylidenecyclohexane (I), 0.7 g (2.9 mmol) and 1.2 g (4.6 mmol) of chromium tricarbonyl-triacetonitrile in 60 ml of dry dioxane were stirred at room temperature and under argon for 48 h. The reaction vessel was evacuated periodically to remove the acetonitrile formed. The orange-red slurry was filtered, the filtrate evaporated to dryness and subjected to high vacuum sublimation at 60–70°C. The sublimate was a small amount of unreacted I. The residue was recrystallized from pentane at −78°C to give 0.9 g (83% yield) of an orange-red crystalline solid, m.p. 135–135.5°C. Anal. Found: C, 67.10; H, 6.37; Cr, 13.73. $C_{21}H_{24}CrO_3$ calcd.: C, 67.01; H, 6.43; Cr, 13.81%. Mass spectrum *m/e* 376 (M^+, 8); 348 (1); 320 (10); 292 (50); 52 (100).

^{13}C NMR of III (THF-d_8, 310 K, reference: solvent δ 25.40 ppm, 100.6 MHz) (for the numbering of the carbon atoms cf. Fig. 2) CO resonances at δ 237.16 (s), 235.44 (s) and 234.82 (s) ppm; uncomplexed C(6) at δ 127.59 (s) ppm, five complexed ring atoms at δ 115.91 (s), 113.62 (s), 109.61 (s), 88.10 (s), and 71.43 (s) ppm; C(10) at δ 99.27 (d) ppm and C(60) at δ 122.38 (d) ppm. Vinyl carbon atoms at δ 133.20 (d), 131.76 (d), and 123.82 (t), 115.65 (t) ppm. C(20) and C(40) are degenerated at δ 24.90 (t) ppm; methyl groups at δ 17.47 (q), 16.43, 16.31 (q) and 15.33 (q) ppm. The 400 MHz ^1H NMR data are shown in Table 2.

IV + V. 0.5 g (2.1 mmol) of I and 0.7 g chromium tricarbonyl-triacetonitrile in 50 ml of dry dioxane were stirred and heated at 80–90°C under argon for 12 h. The reaction vessel was, as above, evacuated periodically. The orange slurry was filtered and the filtrate evaporated to dryness. The products were separated by preparative TLC using silica gel and hexane/benzene (1/1). The front running colourless fraction gave a white crystalline solid (0.2 g, 40% yield) IV, m.p. 55–56°C. Anal. Found: C, 89.81; H, 10.13. $C_{18}H_{24}$ calcd.: C, 89.94; H, 10.06%. ^1H NMR ($CDCl_3$, 80 MHz): δ(H(5)) 0.97 (t, 9H); δ(H(4)) 2.62 (q, 6H); vinyl (δ(H(1)) 6.80m δ(H(2)) 5.45, δ(H(3)) 5.48, (Σ9H) $J_{2,3}$ 2.2 Hz, $J_{1,3}$ 18 Hz, $J_{1,2}$ 11.5 Hz; mass-spectrum: *m/e* 240 (M^+, 90); 225 (100); 211 (70).

The yellow fraction ($R_f = 0.5$) gave 0.3 g (40% yield) of a yellow crystalline solid V which was further purified by high vacuum sublimation at 60–70°C, m.p. 110–111°C. Anal. Found: C, 67.20; H, 6.09; Cr, 13.88. $C_{21}H_{24}CrO_3$ calcd.: C, 67.01; H, 6.43; Cr, 13.81%. ^1H NMR (C_6D_6, 80 MHz) δ(H(5)) 0.83 (t, 9H); δ(H(4)) 2.47 (q, 6H); vinyl δ(H(1)) 6.24, δ(H(2)) 5.18, δ(H(3)) 5.33, (Σ9H); $J_{2,3}$ 2.0 Hz, $J_{1,2}$ 11.0 Hz; $J_{1,3}$ 17.5 Hz; mass spectrum: *m/e* 376 (M^+, 10); 320 (15); 292 (100); 52 (70). Infrared (Nujol): ν(C=O) 1960sh, 1935s, 1890sh, 1860s, 1830sh cm^{-1}.

IV. A solution of 0.25 g (0.66 mmol) of III in 5 ml of dioxane in an atmosphere of

TABLE 2

400 MHz ^1H NMR DATA FOR COMPOUND III

Dissolved in toluene-d_8 and the solvent signal at δ 2.08 ppm was used as internal reference.

Proton	Chemical shift (ppm) at		Coupling constants (Hz)		NOE	
	213 K	333 K			H irradiated	H affected
10	4.61	4.72	$J_{10,11}$	6.9		
11	1.61	1.67			11	10, 60, 51t, 51c
20a	2.22	2.29	$J_{20a,b}$	13.5	20a	20b, 21, 10, 30
20b	1.47	1.59	$J_{20,21}$	7.4		
21	0.93	0.93			21	20a, 20b
30	6.12	6.32	$J_{30,31c}$	10.6	30	31c, 20b, 40b
31c	5.12	5.24	$J_{30,31t}$	16.8		
31t	5.13	5.20	$J_{31c,t}$	1.8		
40a	2.56	2.60	$J_{40a,b}$	14.1	40a	40b, 30, 41, 50
40b	2.25	2.33	$J_{40,41}$	7.3		
41	0.99	1.04			41	40a, 40b, 50, 30
50	5.80	5.99	$J_{50,51c}$	11.0	50	50c, 40a, 40b
51c	5.07	5.03	$J_{50,51t}$	17.1	51c	51t, 50
51t	4.87	4.87	$J_{51c,t}$	1.6	51t	51c, 11, 61
60	4.52	4.68	$J_{60,61}$	6.4	61	60, 51t
61	1.24	1.31				

carbon monoxide was heated for 5 h at 80–90°C. The colour of the solution turned from orange-red to pale yellow. The solvent and the volatiles including $Cr(CO)_6$ were removed at room temperature under vacuum. The residue 0.15 g (95% yield) was a white crystalline solid, which melted at 55–56°C and had IR and ^1H NMR spectra identical to those of IV.

The crystal structure determination of III

Reflections were collected from a single crystal of III mounted on a Nonius-CAD4 diffractometer using graphite monochromated Mo-K_α X-radiation. Intensities were measured by a coupled 0–20 technique with scan speeds varying from 1.3–10.0° min^{-1} depending on the standard deviation to intensity ratio of a preliminary 10° min^{-1} scan. The intensity of the reflection and its standard deviation were calculated from INT-2 (BGL + BGR) and (INT + 4(BGL + BGR))$^{1/2}$ respectively, where INT, BGL and BGR are the peak intensity, the left and right backgrounds, and the time spent measuring the background was half that taken to measure the peak. A Zr filter was inserted in front of the detector if the peak count was greater than 50,000 counts sec^{-1}. The intensities of the three monitor reflections remeasured after every 90 minutes of X-ray exposure showed no significant variation during the course of data collection. Intensities were corrected for Lorentz and polarisation effects, but not for those of absorption (μ 5.92 cm^{-1}). Pertinent crystal data are given in Table 3; the cell parameters were obtaining by a least-squares fit to the θ values of 75 automatically centred reflections ($9 < \theta < 20°$).

The structure was solved by Patterson (Cr) and Fourier methods (C and O).

TABLE 3

CRYSTALLOGRAPHIC DATA FOR III

$C_{21}H_{24}O_3Cr$
Crystal system, monoclinic
Space group $P2_1/n$
(non-standard setting of $P2_1/c$.14)
a 8.971(1) Å
b 19.526(3) Å
c 11.158(1) Å
β 98.940(8)°
V 1930.8 Å^3
Monochromated (graphite) Mo-K_α
X-radiation λ 0.71069 Å
Reflections measured [$\pm h.k.k$] 4351
μ(Mo-K_α) 5.92 cm^{-1}
Number of variables (P) 226
Observed reflections (N) 2511
$R = 0.045$
$R_w = 0.047$ ($\omega = 1/\sigma^2(F)$)
$(\Sigma\omega(|F_0|-|F_c|)^2)^{1/2}/N - P = 2.1$

M 376.4 a.m.u.
$F_{000} = 792$ e
$Z = 4$
D_c 1.295 g cm^{-3}
T 18°C
Take off angle: θ 6.15°
θ limits: $1 < \theta < 27°$
$\theta - 2\theta$ scan technique (48 steps)
Horizontal detector aperture:
$5.0 + 1.25 \tan\theta$ mm
Vertical aperture: 4 mm
(Ω)-scan range: $0.8 + 0.35 \tan\theta°$

Refinement was by full-matrix least-squares, and Cr, C, and O were allowed anisotropic thermal motion. Hydrogen atom positions were calculated (C–H 0.95 Å) and held constant during refinement (U_H 0.05 Å^2). Refinement of the structure with 2511 observed reflections $I > 2.0\sigma(I)$, where $\sigma(I) = (\sigma(I)_{\text{Poisson}} + (kI)^2)^{1/2}$, $k = 0.02$) resulted in a final $R = 0.045$, $R_w = 0.047$ ($\omega = I/\sigma^2(F)$) at a data/variable ratio of 11.1. The quantity minimised was $\Sigma\omega(F_0 - F_c)^2$. In the final refinement cycle the mean shift to error ratio was 0.05, and the final difference Fourier synthesis was essentially featureless except for several peaks [$\leqslant 0.4$ eÅ^{-3}] in the vicinity of the chromium atom. Neutral atom scattering factors for all nonhydrogen atoms were those of Cromer and Waber [6] while the best spherical scattering factors were used for hydrogen [7]. The real and imaginary components of the anomalous scattering factors for Cr were included in the structure factor calculation [8]. Final atomic

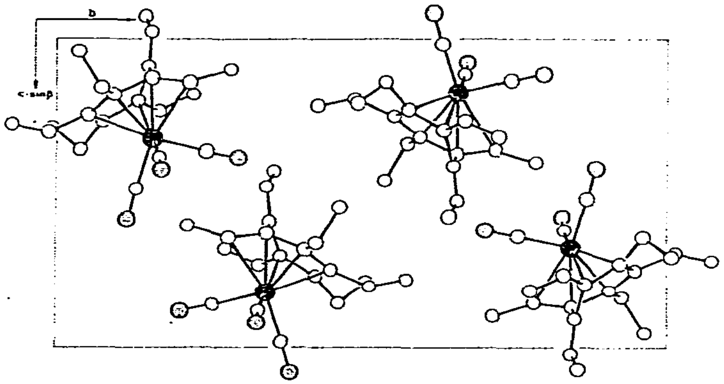


Fig. 3. The contents of one unit cell of III viewed down the shortest axis (a) away from the origin.

TABLE 4

FINAL ATOMIC COORDINATES FOR III AND THEIR STANDARD DEVIATIONS IN PARENTHESES (× 10^4)

Atom	x	y	z	Atom	x	y	z
Cr	1102(1)	1572(1)	3239(1)	H(10)	−1091	2174	1811
O(1)	2423(3)	2973(1)	3826(2)	H(111)	1349	2935	1401
O(2)	−1819(3)	1718(1)	4205(2)	H(112)	338	2843	151
O(3)	2117(3)	1160(1)	5830(2)	H(113)	−289	3215	1196
C(1)	463(3)	1550(1)	1277(2)	H(201)	−2317	1148	1618
C(2)	−58(3)	930(1)	1819(3)	H(202)	−1927	454	2269
C(3)	1065(4)	511(1)	2479(3)	H(211)	−1968	645	−254
C(4)	2619(3)	755(1)	2690(2)	H(212)	−1578	−47	396
C(5)	3032(3)	1328(1)	2030(3)	H(213)	−3204	242	278
C(6)	1979(3)	1498(1)	905(2)	H(30)	37	−96	3681
C(7)	1917(4)	2438(2)	3624(3)	H(311)	577	−1130	3190
C(8)	−698(4)	1682(2)	3822(3)	H(312)	1499	−836	2133
C(9)	1769(4)	1308(2)	4826(3)	H(401)	3304	111	4127
C(10)	−197(3)	2174(1)	1420(3)	H(402)	4415	715	4070
C(11)	338(4)	2847(2)	1015(3)	H(411)	4167	−408	2409
C(20)	−1715(4)	738(2)	1608(3)	H(412)	5278	195	2353
C(21)	−2146(4)	362(2)	431(4)	H(413)	5534	−313	3433
C(30)	638(5)	−135(2)	3034(3)	H(50)	5213	1470	2967
C(31)	940(6)	−737(2)	2804(5)	H(511)	5908	2431	2058
C(40)	3801(4)	383(1)	3573(3)	H(512)	4261	2455	1172
C(41)	4784(4)	−79(2)	2903(4)	H(60)	1367	1703	−820
C(50)	4500(3)	1673(2)	2335(3)	H(611)	4431	1732	−346
C(51)	4936(4)	2230(2)	1816(4)	H(612)	3975	972	−588
C(60)	2216(4)	1557(1)	−241(3)	H(613)	3521	1519	−1587
C(61)	3644(5)	1437(2)	−738(3)				

positional parameters appear in Table 4. These together with a table of the final atomic thermal parameters and a list of observed and calculated structure amplitudes have been deposited *. III crystallises as independent molecules, separated by distances greater than 3.0 Å. Figure 3 gives the contents of the unit cell.

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* Information may be obtained from Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen, B.R.D. on submission of the title of the article, the name of the authors and the literature reference.

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