The phase transition reflects a concerted change in the hydrogen-bond network between the ions. As shown in Fig. 2, no major structural readjustment occurs but each individual ion undergoes a rotational change, the most dramatic effect associated with the N(1) dimethylammonium ion which effectively rotates about the b axis by about 60°. As a consequence several modifications are made to the N—H···Cl contacts in the system. At room temperature three simple hydrogen bonds and one asymmetric bifurcated hydrogen bond are found. These involve all four amine H atoms of the two independent [NH$_2$(CH$_3$)$_2$] ions of the asymmetric unit as well as all four Cl atoms of the [CoCl$_4$]. As shown in Fig. 1, Cl(3) has contact with two H atoms H(11) and H(21) at distances of 2.48 (3) and 2.41 (4) Å respectively. In addition H(12) is bonded to Cl(4) of the ion at $(x - \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2})$ and H(22) is asymmetrically bifurcated to Cl(2) and Cl(1) of another [CoCl$_4$] ion at $(-x, 1 - y, 1 - z)$ with distances of 2.42 (4) and 2.89 (4) Å. Upon cooling below the transition temperature one of the dimethylammonium ions rotates substantially about the b axis, so that the two hydrogen bonds it formed previously are broken and replaced by the new contacts H(12)···Cl(2) and H(11)···Cl(4) $(x - 1, y, z)$. The crosslinking of the hydrogen-bond network in the bc plane is lost with the result that isolated stacks of ions are formed along the a axis. The bonding from the second ammonium ion is perturbed much less; the bond from H(21) to Cl(3) is retained, whereas H(22) takes up a more symmetrically bifurcated

position between Cl(2) and Cl(1) of the adjacent ion at $(-x, 1 - y, 1 - z)$ with distances of 2.74 (4) and 2.72 (4) Å respectively.

The low-temperature form of the cobalt compound is isostructural with the room-temperature form of the previously reported mercury analogue (Ben Salah, Bats, Fuess & Daoud, 1982). A unit cell for the cadmium analogue [NH$_2$(CH$_3$)$_2$][CdCl$_4$] of $Pnma$, $a = 18.05$, $b = 15.68$ and $c = 11.36$ Å has been reported (Daoud, 1976), implying that other hydrogen-bond networks may be possible in this family.

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Disorder in the Structure of (η⁶-Benzo[*b*]thiophene)tricarbonylchromium(0)

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Abstract. [Cr(C$_8$H$_6$S)(CO)$_3$], $M_r = 270.23$, monoclinic, $P2_1/n$, $a = 6.619$ (3), $b = 11.708$ (4), $c = 13.995$ (5) Å, $\beta = 100.15$ (3)°, $V = 1067.58$ Å^3, $Z = 4$, $D_x = 1.681$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 12.181$ cm^{-1}, $F(000) = 544$, $T = 298$ K, $R = 0.041$ for 1725 reflections with $I > 2\sigma(I)$. The structure shows that the Cr(CO)$_3$ tripod is complexed to the benzene part of the benzothiophene moiety with

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a staggered conformation. An interesting feature is the disorder in the structure resulting from the existence of two isomeric molecules. The thiophene plane makes an angle of 3° with the benzene plane and is tilted away from the metal atom in both isomers.

Introduction. Arene chromium tricarbonyl complexes play a useful role in organic synthesis because of their ability to impose regio and stereo control in organic reactions (Davies, 1982). Such complexes of various aromatic and heteroaromatic ligands have been prepared, but very few of them involve sulfur heterocycles. Of these few, chromium tricarbonyl complexes of thiophene (Segard, Pommier, Roques & Guiochon, 1974) and benzo[*b*]thiophene (Fischer, Goodwin, Krieter, Simmons, Sonogashira & Wild, 1968; Davidson, Patel & Preston, 1987) have been prepared but their chemical reactions have not been explored in detail. In the course of our attempt to synthesize benzo[*b*]thiophene derivatives with substituents in the benzene ring, we undertook the synthesis of the chromium tricarbonyl complex of this ligand. This is because the standard substitution reactions on the uncomplexed ligand lead to preferential substitution in the thiophene ring and the only means hitherto available for synthesizing benzo[*b*]thiophene with substituents in any of the positions between 4 to 7 requires either expensive starting materials or some round-about procedure (Datta & De, 1989, and references therein).

It is important to establish the conformation of the Cr(CO)₃ 'tripod' in an arene chromium tricarbonyl complex, since this guides the regio chemistry of the substitution reactions. It is now accepted (Solladie-Cavallo & Wipff, 1980) that nucleophiles enter the positions of the aromatic ring which are 'eclipsed', while the 'staggered' positions are susceptible to electrophilic attack. The present X-ray crystallographic study of the benzo[*b*]thiophene chromium tricarbonyl complex was undertaken to gain a precise knowledge of the conformation.

Table 1. *Atomic coordinates* ($\times 10^4$) *for the non-hydrogen atoms and equivalent isotropic displacement parameters* ($\text{Å}^2 \times 10^3$) *with e.s.d.'s in parentheses*

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Cr	11117 (1)	1993 (1)	1206 (1)	37 (1)
CS(1)*	7966 (3)	4565 (2)	947 (2)	73 (1)
CS(2)*	7577 (3)	3404 (3)	-670 (2)	97 (1)
O(1)	14178 (4)	172 (3)	1887 (3)	74 (1)
O(2)	14137 (4)	3632 (3)	2286 (3)	74 (1)
O(3)	13031 (5)	2247 (4)	-555 (2)	88 (2)
C(1)	7573 (7)	4503 (5)	-123 (5)	93 (3)
C(3)	8059 (5)	2532 (4)	272 (3)	48 (1)
C(4)	8243 (6)	1322 (4)	309 (3)	62 (2)
C(5)	8558 (6)	784 (4)	1206 (4)	65 (2)
C(6)	8825 (6)	1407 (4)	2074 (3)	59 (1)
C(7)	8759 (5)	2587 (4)	2056 (3)	49 (1)
C(8)	8309 (5)	3163 (3)	1152 (3)	44 (1)
C(9)	12982 (6)	871 (3)	1640 (3)	49 (1)
C(10)	12961 (6)	3020 (3)	1865 (3)	47 (1)
C(11)	12313 (6)	2149 (3)	124 (3)	53 (1)

* CS = ½C + ½S.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Cr—C(3)	2.296 (3)	Cr—C(4)	2.229 (4)
Cr—C(5)	2.208 (4)	Cr—C(6)	2.213 (4)
Cr—C(7)	2.234 (4)	Cr—C(8)	2.300 (4)
Cr—C(9)	1.831 (4)	Cr—C(10)	1.841 (4)
Cr—C(11)	1.838 (4)	CS(1)—C(1)	1.476 (7)
CS(1)—C(8)	1.675 (4)	CS(2)—C(1)	1.497 (7)
CS(2)—C(3)	1.654 (5)	O(1)—C(9)	1.149 (5)
O(2)—C(10)	1.143 (5)	O(3)—C(11)	1.140 (6)
C(3)—C(4)	1.422 (6)	C(3)—C(8)	1.420 (5)
C(4)—C(5)	1.386 (7)	C(5)—C(6)	1.403 (7)
C(6)—C(7)	1.382 (6)	C(7)—C(8)	1.418 (5)

C(3)—Cr—C(4)	36.6 (2)	C(4)—Cr—C(5)	36.4 (2)
C(5)—Cr—C(6)	37.0 (2)	C(6)—Cr—C(7)	36.2 (2)
C(3)—Cr—C(8)	36.0 (1)	C(7)—Cr—C(8)	36.4 (1)
C(9)—Cr—C(10)	87.4 (2)	C(9)—Cr—C(11)	88.9 (2)
C(10)—Cr—C(11)	90.2 (2)	C(1)—CS(1)—C(8)	96.9 (3)
C(1)—CS(2)—C(3)	98.1 (3)	CS(1)—C(1)—CS(2)	123.0 (4)
CS(1)—C(1)—H(1)	118.5 (3)	CS(2)—C(1)—H(1)	118.5 (3)
CS(2)—C(3)—C(4)	130.4 (3)	CS(2)—C(3)—C(8)	110.3 (3)
C(4)—C(3)—C(8)	119.4 (4)	C(3)—C(4)—H(4)	120.4 (2)
C(3)—C(4)—C(5)	119.0 (4)	H(4)—C(4)—C(5)	120.6 (3)
C(4)—C(5)—H(5)	119.2 (3)	C(4)—C(5)—C(6)	121.5 (4)
H(5)—C(5)—C(6)	119.2 (3)	C(5)—C(6)—H(6)	119.7 (3)
C(5)—C(6)—C(7)	120.4 (4)	H(6)—C(6)—C(7)	119.9 (2)
C(6)—C(7)—H(7)	120.4 (2)	C(6)—C(7)—C(8)	119.5 (4)
H(7)—C(7)—C(8)	120.0 (2)	CS(1)—C(8)—C(3)	111.7 (3)
CS(1)—C(8)—C(7)	128.3 (3)	C(3)—C(8)—C(7)	120.0 (3)
Cr—C(9)—O(1)	177.9 (4)	Cr—C(10)—O(2)	178.1 (3)
Cr—C(11)—O(3)	179.1 (3)		

Two atoms in the thiophene moiety, adjacent to the benzene ring, appeared with equal heights in the electron density map, though one should correspond to a sulfur and the other to a carbon. Moreover, the distances from these two atoms to the respective nearest neighbours in the benzene ring were found to be nearly equal. This led us to postulate a static disorder resulting from the presence of two types of benzothiophene moieties occurring randomly in equal number: the sulfur and carbon positions in type I being interchanged to produce type II. Consequently $(\frac{1}{2}C + \frac{1}{2}S)$ was placed at each of the disordered positions. Five hydrogen atoms were placed in their calculated positions with isotropic temperature factor $U = 0.08$ Å^2. The position of the sixth hydrogen atom which is bonded to the disordered carbon was not determined. To obtain a realistic weighting scheme, $\sigma(I)$ values in the data file were multiplied by a factor of 2.5 and then, with $w = [\sigma^2(F) + 0.009F^2]^{-1}$, refinement converged $[(\Delta/\sigma)_{max} = 0.409]$ at $R = 0.041$ and $wR = 0.047$ with $S = 1.43$. Refinement of C/S ratio on the disordered site was not attempted. Final difference Fourier map showed maximum and minimum peak heights of 0.3 and -0.3 e Å^{-3} respectively. The *SHELXTL-Plus* program package (Sheldrick, 1988) used.

Discussion. The refined positional parameters of the non-hydrogen atoms are presented in Table 1. Bond distances and angles are given in Table 2.*

The interesting feature is the disorder in the crystal structure resulting from the existence of two isomeric molecules with interchangable carbon and sulfur positions, occurring at random but with equal prob-

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54479 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
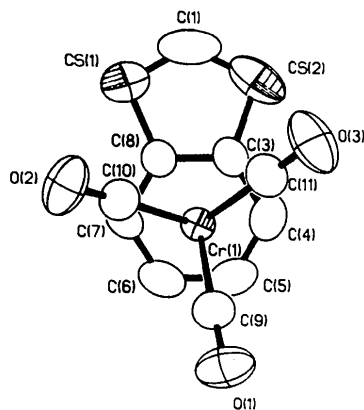
ability in the structure. Prochiral unsaturated hydrocarbon ligands, on complexation with metal carbonyls, form chiral organotransition metal complexes, with the metal carbonyl moiety attached to one face of the ligand (Davies, 1982). In the present case, there is an equal probability of the $Cr(CO)_3$ 'tripod' attaching itself to either of the two sides of the arene ligand. This is corroborated by the fact that though the thiophene moiety suffers from disorder, no disorder is observed in the metal tripod.

The view of the molecule (Fig. 1) clearly shows that the $Cr(CO)_3$ tripod is selectively complexed with the benzene of the benzothiophene moiety and has a staggered conformation with respect to it. Although the benzothiophene moiety is expected to be planar, it is observed that when complexed with the $Cr(CO)_3$ complex, the thiophene plane always tilts away from the $Cr(CO)_3$ making an angle of $\sim 3°$ with the benzene plane. This is possibly due to a repulsive interaction between the 'tripod' and the π-electron system of the thiophene ring. This bending may be expected to cause some hindrance to the delocalization of electrons in the molecule which might eventually influence its reactivity.

The C—C bonds in the benzene ring have expected values but, of these, the three bonds common with and adjacent to the thiophene part appear to be slightly more elongated than the remaining three. The distances of the disordered atom positions from the neighbouring carbons are intermediate to those of the expected C—S and C—C bond distances.

Fig. 1. A view of the molecule projected onto the benzene plane showing the staggered conformation of the $Cr(CO)_3$ tripod.

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