Synthesis, Structure, and Haptotropic Rearrangement of Benzocyclo-octatetraenetricarbonylchromium(0) Complexes *

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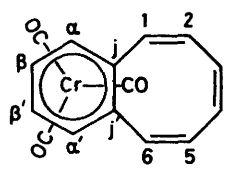
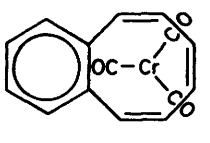
The two tricarbonylchromium isomers of benzocyclo-octatetraene complexed at the benzo ring (1) and at the eight-membered ring (2) have been synthesized. Their structure in solution was determined from a ^{1}H and ^{13}C n.m.r. study. In addition, crystal structures of (1) and (2) have been determined by *X*-ray analysis. Rate constants and activation parameters have been measued for the migration of tricarbonylchromium from the eight- to the six-membered ring of benzocyclo-octatetraene in decalin and di-n-butyl ether.

This paper deals with synthesis, *X*-ray structure, and reactivity of two bicyclic $Cr(CO)_3$ complexes (1) and (2). Interest in $Cr(CO)_3$ polycyclic complexes has arisen because in many instances they show behaviour not observable in their monocyclic counterparts. For example, they can be readily reduced to stable dianions,[2] they profoundly influence the aromatic or antiaromatic character of the ligand (*e.g.* in systems like biphenylene,[3] benzo- and dibenzo-cycloheptatrienyl anion,[4,5] and dibenzotropylium cation[6]), and they undergo migration of the metal unit from one ring to the other, known as haptotropic rearrangement.[3-7] No complete explanation exists thus far but attempts are being made to correlate the reactivity of bicyclic complexes with structural characteristics of their ground states. In particular, haptotropic rearrangements have been the object of a recent theoretical study by Albright *et al.*[8] establishing, on the basis of extended Hückel MO calculations, the favoured intramolecular pathways for metal migration; in addition, an electron-counting method was proposed stating which of the possible pathways are allowed and which forbidden. The ability of the tricarbonylchromium group to migrate from one ring to another as well as the reactivity in some indenyl complexes of molybdenum have also been related to the slippage of the metal away from the centre of the ring.[9] Finally, an electron counting method was also used to predict the *endo–exo* conformation of the $Cr(CO)_3$ unit within the complex.[10]



(1)



(2)

Table 1. ^{1}H N.m.r. parameters[a] for free and complexed benzocyclo-octatetraene

	BCOT	(1)	(2)
H_i		Chemical shifts,[b] δ_i	
α = α′	6.951	5.430	6.776
β = β′	7.197	5.626	6.912
1 = 6	6.528	6.304	5.274
2 = 5	6.006	6.115	5.453
3 = 4	5.854	5.998	6.501
i, j		Coupling constants, J_{ij}/Hz	
α,β = α′,β′	7.86 ± 0.04	6.60 ± 0.02	7.72 ± 0.02
α,β′ = α′,β	1.25 ± 0.04	1.16 ± 0.02	1.23 ± 0.02
α,α′	0.83 ± 0.05	0.28 ± 0.02	0.63 ± 0.04
β,β′	7.29 ± 0.06	6.32 ± 0.03	7.34 ± 0.04
1,α = 6,α′	−0.4[c]	−0.35 ± 0.02	0.4[c]
1,α′ = 6,α	0.4[c]	0.35 ± 0.02	0.0[c]
1,2 = 5,6	11.72 ± 0.01	11.70 ± 0.04	10.99 ± 0.05
1,3 = 4,6	−0.94 ± 0.04	−0.79 ± 0.08	−2.73 ± 0.09
1,4 = 3,6	0.75 ± 0.03	0.61 ± 0.08	0.22 ± 0.08
1,5 = 2,6	−0.24 ± 0.01	−0.16 ± 0.04	−0.15 ± 0.05
1,6	0.02 ± 0.02	0.09 ± 0.04	0.15 ± 0.08
2,3 = 4,5	3.80 ± 0.02	4.26 ± 0.05	8.07 ± 0.08
2,4 = 3,5	−0.73 ± 0.02	−0.68 ± 0.05	0.14 ± 0.07
2,5	1.51 ± 0.02	0.98 ± 0.06	−0.80 ± 0.09
3,4	11.88 ± 0.01	11.98 ± 0.05	9.86 ± 0.09

[a] *T* 298 K, solvent $[^{2}H_6]$acetone, internal standard Me_4Si. [b] The uncertainties in δ are ⩽0.001 p.p.m. [c] These values have not been refined by iteration.

Results and Discussion

The two isomers (1) and (2) were synthesized by treating benzocyclo-octatetraene (BCOT) with hexacarbonylchromium and triamminetricarbonylchromium, respectively. Heating BCOT with $Cr(CO)_6$ in di-n-butyl ether–tetrahydrofuran (THF) (9:1 v/v) at 120 °C afforded first (after *ca.* 1 h) a transient red complex. After 2 h a yellow complex appeared along with the red one. Prolonged heating (22 h) yielded only the yellow compound identified as isomer (1). When BCOT was refluxed in THF with $(NH_3)_3Cr(CO)_3$ for 5 h a red complex was formed which after purification on silica gel and crystallization from hexane was identified as isomer (2). Thus, isomer (2) is thermodynamically less stable than (1). The ^{1}H n.m.r. spectral parameters of the free ligand, BCOT, and of the two complexed isomers (1) and (2) are listed in Table 1. The ^{13}C n.m.r. chemical shifts and the $^{1}J_{C-H}$ coupling constants for the three molecules

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* For preliminary results see ref. 1.

Table 2. ^{13}C N.m.r. chemical shifts[a] δ (p.p.m.), and $^{1}J_{CH}$/Hz (in parentheses) for free and complexed benzocyclo-octatetraene

C_i	BCOT	(1)	(2)
α,α′	130.51	95.33	131.09
	(157.7 ± 0.5)	(174.3 ± 0.5)	(158.8 ± 0.5)
β,β′	127.76	93.90	127.66
	(160.7 ± 0.5)	(176.3 ± 0.5)	(161.0 ± 0.5)
j, *j*′	138.98	109.38	139.41
1,6	134.45	130.40	92.96
	(157.7 ± 0.5)	(162.5 ± 1.0)	(160.0 ± 0.5)
2,5	131.93	133.76	104.05
	(159.6 ± 1.0)	(157.0 ± 0.5)	(169 ± 2)
3,4	131.68	130.69	104.16
	(159.9 ± 1.0)	(157.0 ± 1.0)	(169 ± 2)
C≡O		234.38	232.72[b]

[a] *T* 298 K; solvent [$^2H_6$]acetone; internal standard Me_4Si. [b] At 313 K.

Table 3. Selected geometrical parameters for (**1**)

Bond lengths (Å)			
Cr–C(α)	2.176(4)	C(α)–C(*j*)	1.39(1)
Cr–C(β)	2.189(4)	C(α)–C(β)	1.39(1)
Cr–C(β′)	2.195(5)	C(β)–C(β′)	1.37(1)
Cr–C(α′)	2.178(4)	C(β′)–C(α′)	1.39(1)
Cr–C(*j*′)	2.220(3)	C(α′)–C(*j*′)	1.41(1)
Cr–C(*j*)	2.208(3)	C(*j*′)–C(*j*)	1.42(1)
Cr–C	1.828(4)	C(*j*′)–C(6)	1.46(1)
Cr–C′	1.819(4)	C(6)–C(5)	1.33(1)
Cr–C″	1.829(4)	C(5)–C(4)	1.45(1)
C–O	1.15(1)	C(4)–C(3)	1.31(1)
C′–O′	1.14(1)	C(3)–C(2)	1.46(1)
C″–O″	1.15(1)	C(2)–C(1)	1.31(1)
		C(1)–C(*j*)	1.48(1)

Bond angles (°)			
C″–Cr–C′	89.6(2)	C(*j*′)–C(α′)–C(β′)	121.2(4)
C″–Cr–C	89.3(2)	C(*j*)–C(*j*′)–C(α′)	118.0(3)
C–Cr–C′	87.9(2)	C(*j*)–C(*j*′)–C(6)	125.4(3)
Cr–C–O	178.6(4)	C(α′)–C(*j*′)–C(6)	116.4(3)
Cr–C′–O′	178.5(4)	C(*j*′)–C(6)–C(5)	127.8(4)
Cr–C″–O″	177.9(4)	C(6)–C(5)–C(4)	127.7(4)
C(α)–C(*j*)–C(*j*′)	119.1(4)	C(5)–C(4)–C(3)	127.6(4)
C(α)–C(*j*)–C(1)	117.5(4)	C(4)–C(3)–C(2)	126.8(4)
C(*j*′)–C(*j*)–C(1)	123.2(3)	C(3)–C(2)–C(1)	128.8(4)
C(β)–C(α)–C(*j*)	121.8(4)	C(2)–C(1)–C(*j*)	127.6(4)
C(β′)–C(β)–C(α)	119.4(5)		
C(α′)–C(β′)–C(β)	120.4(5)		

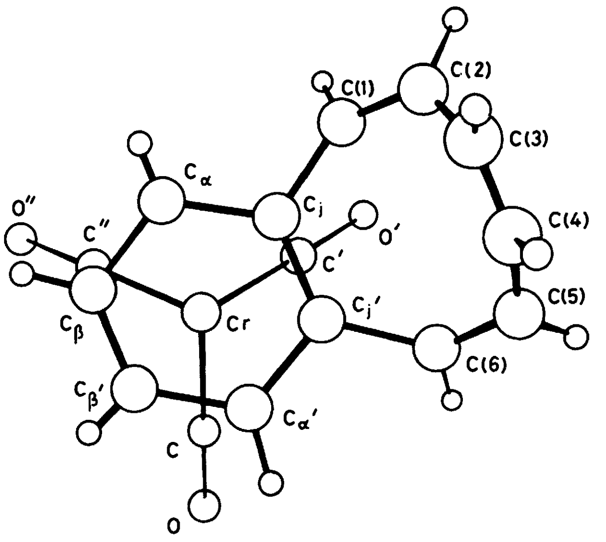


Figure 1. Molecular structure of isomer (**1**) as viewed orthogonally to the co-ordination plane

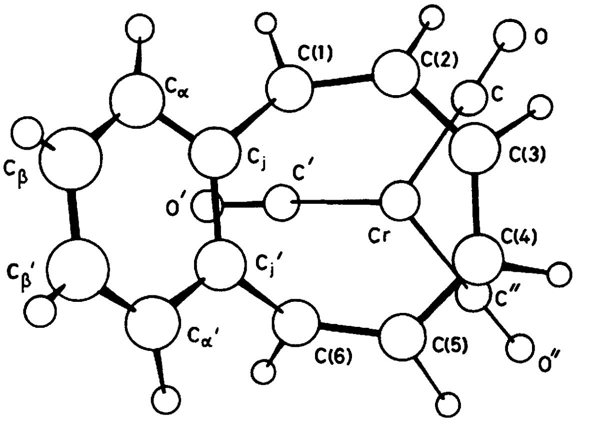


Figure 2. Molecular structure of isomer (**2**) as viewed orthogonally to the co-ordination plane

are given in Table 2. The spectra were run at 298 K; at this temperature the carbonyl signals of (**2**) are very broad because of the well known fluxional phenomenon observed in cyclo-olefin–M(CO)$_3$,[11] and the chemical shift of Table 2 was obtained at 313 K, a temperature at which the carbonyl resonances appear as a sharp singlet.

The molecular structures of (**1**) and (**2**), as viewed orthogonally to the co-ordination plane of the ligand, are shown in Figures 1 and 2. Selected geometrical parameters are reported in Table 3 and in Table 4 for (**1**) and (**2**), respectively. The relevant molecular features of the two complexes are discussed below.

Complex (**1**).—Complexation of BCOT at the benzo moiety causes the well known large upfield shift in the signal of the aromatic protons and a moderate decrease of the vicinal $^3J_{H-H}$ coupling constant (Table 1).[12] Moreover, hydrogen-bearing carbon atoms and the junction carbon atoms of the aromatic ring exhibit an upfield shift of *ca.* 35 and 29 p.p.m. respectively, along with an increase in the $^1J_{C-H}$ coupling constant (*ca.* 16 Hz). These effects are commonly observed when aromatic substrates are complexed with tricarbonylchromium.[13]

The effects of complexation on the unco-ordinated moiety of the molecule are small and difficult to interpret. It may be worth mentioning that while the ^{1}H and ^{13}C chemical shifts of C-1 and -6 show an upfield effect (−4.05 and −0.22 p.p.m., respectively), C-2—5 show a smaller effect in the opposite direction. The upfield shift observed could be attributed to the fact that the pivot atoms C-1 and -6 show more sp^3 character in the complex than in the ligand. [This effect is more relevant in isomer (**2**); see below.]

The conformation of BCOT in complex (**1**) as determined by *X*-ray analysis is almost identical to the tub conformation of the free ligand;[14] in fact, carbon–carbon bond lengths and bond angles show no significant variation both in the benzo and in the COT moiety (Table 3), and no C–C bond length alternation is observed in the benzo ring: in addition the dihedral angle between the planes φ and ψ as defined in Table 5 (which gives the equations of the corresponding least-square planes with the deviations from them) is 138°, *i.e.* almost identical to that in the ligand, 137°.[14] The chromium atom is at practically the same distance from the six benzene carbons and the conformation of

Table 4. Selected geometrical parameters for (**2**)

Bond lengths and non-bonded distances (Å)

Cr–C(1)	2.312(5)	C(*j*)–C(1)	1.47(1)
Cr–C(2)	2.181(6)	C(1)–C(2)	1.38(1)
Cr–C(3)	2.211(6)	C(2)–C(3)	1.40(1)
Cr–C(4)	2.211(6)	C(3)–C(4)	1.38(1)
Cr–C(5)	2.176(6)	C(4)–C(5)	1.42(1)
Cr–C(6)	2.313(5)	C(5)–C(6)	1.37(1)
Cr–C(*j*)	3.150(6)	C(6)–C(*j*′)	1.48(1)
Cr–C(*j*′)	3.151(6)	C(*j*)–C(*j*′)	1.38(1)
Cr–C	1.855(4)	C(*j*)–C(α)	1.39(1)
Cr–C′	1.853(5)	C(α)–C(β)	1.37(1)
Cr–C″	1.851(5)	C(β)–C(β′)	1.36(1)
C–O	1.15(1)	C(β′)–C(α′)	1.37(1)
C′–O′	1.13(1)	C(α′)–C(*j*′)	1.39(1)
C″–O″	1.15(1)		

Bond angles (°)

C″–Cr–C′	93.2(2)	C(6)–C(*j*′)–C(*j*)	120.6(4)
C′–Cr–C	92.7(2)	C(6)–C(*j*′)–C(α′)	119.9(5)
C″–Cr–C	81.6(2)	C(α′)–C(*j*′)–C(*j*)	119.5(5)
Cr–C–O	176.2(5)	C(β′)–C(α′)–C(*j*′)	120.1(5)
Cr–C′–O′	177.2(5)	C(β)–C(β′)–C(α′)	120.4(6)
Cr–C″–O″	177.5(5)	C(α)–C(β)–C(β′)	120.5(5)
C(*j*)–C(1)–C(2)	126.7(5)	C(*j*)–C(α)–C(β)	120.0(5)
C(1)–C(2)–C(3)	128.6(6)	C(*j*′)–C(*j*)–C(α)	119.5(5)
C(2)–C(3)–C(4)	131.1(6)	C(α)–C(*j*)–C(1)	119.9(5)
C(3)–C(4)–C(5)	131.5(6)	C(α)–C(*j*)–C(*j*′)	119.5(5)
C(4)–C(5)–C(6)	131.0(6)		
C(5)–C(6)–C(*j*′)	125.8(5)		

$Cr(CO)_3$ with respect to the cyclo-octatetraene ring is an *endo* conformation, *viz.*, the symmetry-unique carbonyl group points to the interior of the unco-ordinated moiety of the molecule.[10] The $Cr(CO)_3$ group, however, is significantly rotated (*ca.* 20°) from a 'staggered' conformation (Figure 1).

Complex (**2**).—The trend $\delta_1 < \delta_2 < \delta_3$ observed for the chemical shifts of the olefinic protons in complex (**2**) (Table 1) is the same as that found for other cyclohexadienyl- and cycloheptadienyl-$M(CO)_3$ complexes (M = Cr, Mn, Fe), for which a bent structure was inferred;[15] for the isoelectronic benzocycloheptatrienyl-$Cr(CO)_3$ anion, in particular, a bent 5-hapto structure was proved on the basis of detailed n.m.r. analysis.[4] By comparison with the free ligand, loss of double-bond fixation is clearly indicated by a net increase in the vicinal coupling constant, $^3J_{2,3}$, from 3.80 in the free ligand to 8.07 Hz in the complex and by a decrease of $^3J_{3,4}$ from 11.88 to 9.86 Hz. Therefore, delocalization of electrons over the six carbon atoms seems fairly extensive.

More detailed information can be drawn from the ^{13}C n.m.r. results. Co-ordination of the cyclo-octatetraene moiety causes an upfield shift of all six C-1—6 involved in complexation; the effect, however, is much greater for C-1 and -6 than for the other four atoms. This different effect on the two sets of atoms is also shown by the change in the $^1J_{C-H}$ coupling constants on complexation, *viz.* the increase for C-1 and -6 is quite small (*ca.* 2 Hz) while a larger effect (*ca.* 9 Hz) is observed for C-2—5. We interpret the effect of $Cr(CO)_3$ on ^{13}C parameters in terms of a reduced interaction of chromium with C-1 and -6 due to an increase in sp^3 character of these pivot carbons with respect to their configuration in the ligand. Thus, structural changes in the hexatriene unit on addition of tricarbonylchromium consist not only in the planarization of the six carbons but also in a tendency towards tetrahedralization at the terminal C-1 and -6. The result is a preference by the metal for the butadiene residue.

Table 5. Equations of the least-square planes with distances (Å) of the atoms from planes given in brackets

(**1**) Plane φ C(α′), C(β′), C(β), C(α), C(*j*), C(*j*′), C(6), C(1)
$0.7722x + 0.0349y - 0.6344z = -1.5063$
[C(α′) 0.011; C(β′) 0.011; C(β) 0.015; C(α) −0.010; C(*j*) −0.041; C(*j*′) −0.040; C(6) 0.018; C(1) 0.036]

Plane ψ C(6), C(5), C(1), C(2)
$0.8729x + 0.4676y - 0.1394z = 2.4112$
[C(6) 0.002; C(5) −0.002; C(1) 0.002; C(2) −0.002]

(**2**) Plane φ C(α′), C(β′), C(β), C(α), C(*j*), C(*j*′), C(6), C(1)
$-0.3900x + 0.8648y + 0.3163z = 0.2402$
[C(α′) −0.041; C(β′) −0.026; C(β) 0.021; C(α) 0.041; C(*j*) 0.014; C(*j*′) 0.001; C(6) 0.048; C(1) −0.058]

Plane ψ C(1), C(2), C(3), C(4), C(5), C(6)
$-0.1249x + 0.2225y + 0.9669z = 1.8043$
[C(1) 0.054; C(2) −0.097; C(3) 0.062; C(4) 0.055; C(5) −0.080; C(6) 0.023]

X-Ray structural studies of (**2**) confirm the interpretation of the n.m.r. results. The most significant features of isomer (**2**) are the following.

(a) The metal unit is co-ordinated with six of the eight carbon atoms of the cyclo-octatetraene ring as indicated by the Cr–C distances (Table 4): the longer distance (3.150 Å) of chromium from C-*j* and -*j*′ excludes any bonding with the ring junction carbon atoms. On the other hand, the six bound carbon atoms are not at the same distance from the metal, namely Cr–C-2, Cr–C-3, Cr–C-4, and Cr–C-5 are significantly shorter (0.1 Å) than Cr–C-1 and Cr–C-6. Thus, the $Cr(CO)_3$ group is shifted away from the ring fusion bond towards the butadiene residue.

In planar aromatic complexes like naphthalene-, phenanthrene-, and triphenylene-$Cr(CO)_3$, the shifting of the chromium atom away from the centre of the aromatic ring has been related to the tendency of the metal unit to migrate from one ring to the other;[10] in naphthalene-$Cr(CO)_3$, for example, the calculated activation energy for migration through a least-motion pathway is extremely high and symmetry forbidden.[8] This high potential barrier could shift the metal group towards an η^4-co-ordination mode in the opposite direction. Other interpretations have been offered, based on the lower effectiveness of the ring junction carbon atoms to interact with chromium with respect to the carbons bonded to hydrogen;[16] alternatively, the slippage may arise from retention of maximal aromaticity in the uncomplexed ring. As far as complex (**2**) is concerned, which differs from the above both in number of π-electrons and configuration, the slippage may be explained in terms of decreased bonding of chromium to C-1 and -6 due to the increased tetrahedralization of these two atoms which, in turn, can be explained by the conformation of the COT ring assumed in complex (**2**).

The orientation of tricarbonylchromium with respect to the benzene ring is shown in Figure 2. The metal group adopts an '*endo*' conformation, and the molecule has a pseudo plane of symmetry orthogonal to the co-ordination plane and containing the symmetry-unique carbonyl group. As far as we are aware, the only other known bicyclic-$Cr(CO)_3$ complex which adopts an *endo* conformation is biphenylene-$Cr(CO)_3$.[10] The conformation preference in bicyclic-ML_n complexes has been rationalized on the basis of molecular orbital calculations by Albright *et al.*[10] and the '*endo*' conformation adopted by complexes (**1**) and (**2**), a 4*n* system, is in accord with a π-electron counting method proposed by the authors.

(b) The set of the six co-ordinated carbon atoms on one side, and the benzene ring together with C-1 and -6 on the other side, are contained in two planes φ and ψ (Table 5), forming a

Table 6. Rate constants and activation parameters for isomerization (2) ⟶ (1)

Solvent decalin[a]

T/K	$10^3\ k_{obs}$/s^{-1}	$10^3\ k_{is}$/s^{-1}	$10^3\ k_{dec}$/s^{-1}	% Isomerization
428 ± 0.5	1.09 ± 0.07	0.88 ± 0.06	0.21 ± 0.01	81.1
438 ± 0.5	2.70 ± 0.22	2.20 ± 0.18	0.50 ± 0.04	81.5
448 ± 0.5	4.59 ± 0.08	3.72 ± 0.06	0.87 ± 0.02	81.0
453 ± 0.5	8.26 ± 0.24	6.66 ± 0.20	1.59 ± 0.05	80.6

$\Delta H^‡$(is) 28.8 ± 1.8 kcal mol^{-1}, $\Delta S^‡$(is) −6.0 ± 4.0 cal mol^{-1} K^{-1}
$\Delta H^‡$(dec) 28.8 ± 1.7 kcal mol^{-1}, $\Delta S^‡$(dec) −8.8 ± 3.9 cal mol^{-1} K^{-1}

Solvent di-n-butyl ether[a]

T/K	$10^3\ k_{obs}$/s^{-1}	$10^3\ k_{is}$/s^{-1}	$10^3\ k_{dec}$/s^{-1}	% Isomerization
433 ± 0.5	4.14 ± 0.09	2.95 ± 0.06	1.19 ± 0.03	71.3
443 ± 0.5	8.85 ± 0.52	6.65 ± 0.39	2.20 ± 0.13	75.2
454 ± 0.5	21.7 ± 0.65	16.7 ± 0.50	5.03 ± 0.15	76.8

$\Delta H^‡$(is) 31.4 ± 1.0 kcal mol^{-1}, $\Delta S^‡$(is) 1.6 ± 2.2 cal mol^{-1} K^{-1}
$\Delta H^‡$(dec) 26.0 ± 1.4 kcal mol^{-1}, $\Delta S^‡$(dec) −12.8 ± 3.1 cal mol^{-1} K^{-1}

[a] The concentration of the reagent (1) is 4 × 10^{-3}M in all experiments; the vials are sealed under argon.

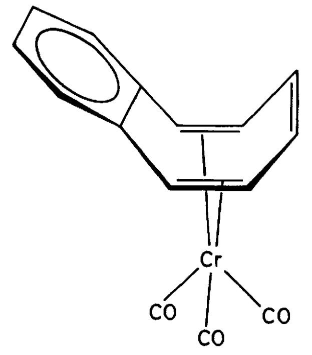
dihedral angle of *ca.* 123°. In tetramethylcyclo-octatetraene-$Cr(CO)_3$ the corresponding dihedral angle is 119°.[17] Thus, when the co-ordination with the metal constrains the cyclo-octatetraene moiety to assume a half-tub conformation the dihedral angle between the two planes of the molecule is *ca.* 120°. As we have shown before, the dihedral angle in free BCOT and in (**1**) is *ca.* 140°. This decrease in dihedral angle is probably the cause for the rehybridization of the pivot atoms C-1 and -6 which is responsible for their weaker bonding to the metal.

(c) Taking the C–C bond lengths in the C-1—6 chain of free BCOT as a reference, *viz.* 1.32, 1.45, 1.31, 1.44, 1.33 Å,[14] the actual pattern in complex (**2**), 1.38, 1.40, 1.38, 1.42, 1.37 Å, shows a net increase in π-electron delocalization as shown above for the molecule in solution by the variation in the $^3J_{HH}$ coupling constants.

Isomerization (**2**) ⟶ (**1**). As described above, (**1**) is thermodynamically more stable than (**2**). In fact, isomer (**2**) when dissolved in decalin or di-n-butyl ether and heated to 150—180 °C underwent isomerization to isomer (**1**) along with some decomplexation. Prolonged heating of (**1**) at the same temperatures caused only decomplexation and no conversion into (**2**). The rate of migration of the $Cr(CO)_3$ group from the eight- to the six-membered ring was measured in decalin and di-n-butyl ether at various temperatures. The kinetics were followed by monitoring the decrease of reagent (**2**) as well as the increase of product (**1**) by h.p.l.c. analysis which also showed the presence of the free ligand, BCOT, along with another unidentified, uncomplexed product. Rates and activation parameters are given in Table 6, where the first-order rate constants for isomerization, k_{is}, and for decomplexation, $k_{dec.}$, were calculated by taking into account the yield of isomerization. Both processes followed first-order kinetics within the interval of concentration, 5 × 10^{-4}—5 × 10^{-3}M; the yield of isomerization in decalin was slightly higher than in di-n-butyl ether and, in the latter, isomerization increases with temperature. These results reflect the difference in $\Delta H^‡$ for the two reactions in the two solvents used.

The order of reaction along with the low values of the entropy of activation in both solvents are consistent with an intramolecular mechanism for rearrangement. Further support in favour of an intramolecular mechanism comes from competitive experiments carried out in the presence of ligands with great complexation ability;[18] thus, when the isomerization (**2**) ⟶ (**1**) was carried out in the presence of a large excess of hexamethylbenzene, no cross-products could be identified. The solvent effect on the isomerization process, as measured by k_{is} (di-n-butyl ether)/k_{is} (decalin) *ca.* 2.3, is very low and is in accord with the formation of a non-polar transition state. Conversely, decomplexation is more sensitive to solvent effects as shown by the relatively high negative entropy of activation in the more co-ordinating di-n-butyl ether.

Mechanistically, isomerization and decomplexation should follow different pathways. However, one could visualize a plausible first step common to both, namely the formation of an η^4-intermediate (**3**) in which the chromium co-ordinates C-1, -2 and -5, -6 of the COT moiety and leaves unco-ordinated the double bond between C-3 and -4. This double bond lies out of the plane of the other four carbons, forcing the intermediate to adopt the less strained tub-shaped conformation. An η^4-$Cr(CO)_3$ intermediate was postulated in the arene-exchange reaction of arene-$Cr(CO)_3$ complexes.[9a] It was calculated that the formation of a planar η^4-intermediate requires *ca.* 10 kcal mol^{-1} and an additional 15 kcal mol^{-1} would be required to bend the unco-ordinated double bond unit 25° away from the metal. In the η^4-complex postulated as a potential intermediate in our system the change in conformation from planar to the more stable puckered form may not require additional energy. The driving force for the formation of the η^4-intermediate is likely to be relief of strain in the ligand not requiring participation of the metal. Evidence for our hypothesis comes from the behaviour of the well known η^4-$Cr(CO)_4$-1,5-dibenzo-cyclo-octatetraene complex which on heating isomerizes to η^6-$Cr(CO)_3$-dibenzocyclo-octatetraene.[19]



(**3**)

From the considerations above it is clear that the formation of the η^4-intermediate is not rate-determining for either isomerization or decomplexation ($\Delta H^‡$ *ca.* 30 kcal mol^{-1} is substantially higher than that required for the η^4-complex). The experimentally determined activation parameters are consistent with a rate-determining step in which, once formed, this η^4-complex experiences further slippage of the metal to give two kinds of η^2-intermediates (or transition states), one involving C-*j*, -*j'* and the other C-1, -2 or -5, -6. The first one will result in isomerization and the second in decomplexation. According to Albright *et al.*[8] isomerization across the C–C ring fusion bond is a 'partially allowed' least-motion pathway for this 12π-electron system and would not require assistance by the solvent. In turn, decomplexation should require such assistance; this is reflected in the significantly larger negative value of $\Delta S^‡$ (−12 cal mol^{-1} K^{-1}) for decomplexation as compared with +1.6 ± 2 cal mol^{-1} K^{-1} for isomerization when both processes are performed in di-n-butyl ether.

Another available intramolecular pathway for isomerization involves the formation of an η^3-allyl-type intermediate involving the C-1, -*j*, and -α (non-least-motion path); this is the only allowed route for $4q + 2$ π-electron systems, *e.g.* naphthalene-$Cr(CO)_3$. Recently, it has been reported [7f] that the enthalpy of activation for the haptotropic rearrangement in dimethoxy- and dimethyl-naphthalene-$Cr(CO)_3$ in benzene is *ca.* 30 kcal mol^{-1}, a value very close to that obtained for our system. Therefore, because of the similarity between the activation enthalpies it is not possible to rule out the hypothesis of a non-least-motion path for the haptotropic shift in benzocyclo-octatetraene-$Cr(CO)_3$. In conclusion, both the least-motion and the non-least-motion pathways seem to be available for the migration of $Cr(CO)_3$ and it appears that it is not possible to distinguish between the two on the basis of only the $\Delta H^{\ddagger}$ values.

Experimental

General.—All reactions were carried out under pure, dry argon. M.p.s are uncorrected. Mycroanalyses were carried out by Mr. L. Turiaco, Università di Padova. I.r., u.v., and mass spectra were recorded on a Beckman IR-9, a Perkin-Elmer 572, and a VG 16 Micromass instrument, respectively. ^1H and ^{13}C n.m.r. spectra were run with a Bruker WP 80 SY spectrometer. The proton spectral parameters were obtained by computer simulation on a Bruker Aspect-2000 computer using the Bruker PANIC program. The ^{13}C line assignments were based on selective proton-decoupling experiments.

H.p.l.c. analyses were made on a Perkin-Elmer Series 3 liquid chromatograph equipped with a 5″ Merck Lichrocart Si60 5μ silica column; the peak detection was performed by a Perkin-Elmer LC75 variable-wavelength u.v. detector equipped with a Perkin-Elmer LC75 Autocontrol unit, the peak areas being measured by means of a Varian CDS-111 integrator.

Benzocyclo-octatetraene (BCOT).—A 10^{-2}M solution of benzocyclo[2.2.2]octatriene [20] in dry, nitrogen-saturated THF was irradiated for 7 h with a low-pressure, 17 W mercury lamp in a quartz reactor. Higher concentrations caused formation of tars. The reaction was monitored by g.l.c. (20% SE-30 on Chromosorb P) until conversion was 99%. The solvent was then removed at reduced pressure and the residue purified by column chromatography (silica; pentane as eluant). The yield was quantitative, m.p. 49 °C (from pentane) (lit.,[21] 49.5—50 °C) (Found: C, 93.7; H, 6.6. Calc. for $C_{12}H_{10}$: C, 93.5; H, 6.5%); $\lambda_{max.}$(cyclohexane) 230 and 275 nm (ε 18 650 and 800 dm^3 mol^{-1} cm^{-1}). For the ^1H and ^{13}C n.m.r. data, see Tables 1 and 2.

Synthesis of Complex (**1**).—A 1M solution of BCOT (0.5 g) in anhydrous, oxygen-free Bu_2O–THF (9:1 v/v) was treated at 120 °C (oil-bath) with excess (2 g) of freshly sublimed $Cr(CO)_6$. The solution quickly became red, the ligand BCOT and traces of one red complex (R_F 0.45) being detected by t.l.c. (silica plate; 15% diethyl ether in pentane as eluant). After 2 h, a yellow complex (R_F 0.30) was detected by t.l.c. along with the red one. Upon refluxing overnight the red compound disappeared; the orange solution was filtered twice on a 2″ silica column under argon pressure, the solvents pumped off, and the residue purified by column chromatography (silica; 10% diethyl ether in pentane as eluant) yielding (**1**) (0.23 g, 24%), m.p. 92—93 °C (from cyclohexane) (Found: C, 62.0; H, 3.5. $C_{15}H_{10}CrO_3$ requires C, 62.1; H, 3.5%); $\nu_{max.}$(KBr disk) 1 965vs and 1 889vs cm^{-1} ($C\equiv O$); $\lambda_{max.}$(cyclohexane) 240sh, 280sh, 305, and 340 nm (ε 22 200, 8 700, 7 100, and 6 700 dm^3 mol^{-1} cm^{-1}); *m/z* 290 (M^+, 19.7%), 262 (M^+ – CO, 1.6), 234 (M^+ – 2CO, 13.1), 206 (M^+ – 3CO, 95.1), 154 [M^+ – $Cr(CO)_3$, 2.9], and 52 (Cr^+, 100). For the n.m.r. data, see Tables 1 and 2.

Synthesis of Complex (**2**).—A 1M solution of BCOT (0.5 g) in anhydrous, oxygen-free THF was refluxed with excess of $(NH_3)_3Cr(CO)_3$ (1.2 g).[22] After 5 h, t.l.c. showed the presence of some unchanged BCOT, of a red compound, and of traces of (**1**). The solution was worked-up as above, and the residue extracted several times with hot cyclohexane. On cooling, dark red crystals of (**2**) were obtained (0.35 g, 37%), m.p. 130 °C (decomp.) (Found: C, 60.2; H, 3.4. $C_{15}H_{10}CrO_3$ requires C, 62.1; H, 3.5%); $\nu_{max.}$(KBr disk) 1 973vs, 1 923vs, and 1 901vs cm^{-1} ($C\equiv O$); $\lambda_{max.}$(cyclohexane) 250, 335, and 410 nm (ε 9 200, 10 800, and 2 100 dm^3 mol^{-1} cm^{-1}); *m/z* 290 (M^+, 13.8%), 262 (M^+ – CO, 7.9), 234 (M^+ – 2CO, 23.8), 206 (M^+ – 3CO, 100), 154 [M^+ – $Cr(CO)_3$, 20.0], and 52 (Cr^+, 95.9). For the n.m.r. data, see Table 1.

Kinetics.—Oxygen- and moisture-free 4×10^{-4}—4×10^{-3}M solutions of (**2**) were prepared in decalin or di-n-butyl ether and sealed in vials under argon. The vials were then immersed in an oil-bath maintained at the appropriate temperature, and the thermolysis of (**2**) was monitored by h.p.l.c. (0.2% propan-2-ol in n-hexane as eluant; flow 1.5 ml min^{-1}).

Crystal Data.—(**1**), $C_{12}H_{10}Cr(CO)_3$, $M = 290.24$. Monoclinic, $a = 11.453(6)$, $b = 11.468(6)$, $c = 10.322(5)$ Å, $\beta = 110.16(7)°$, $V = 1\,272.7$ Å^3 (by least-squares refinement on diffractometer angles for 20 automatically centred reflexions, $\lambda = 0.7107$ Å), space group $P2_1/n$, $Z = 4$, $D_x = 1.514$ g cm^{-3}. Yellow. Crystal dimensions: 0.15 × 0.25 × 0.20 mm, μ(Mo-K_α) = 8.1 cm^{-1}. (**2**), $C_{12}H_{10}Cr(CO)_3$, $M = 290.24$. Monoclinic, $a = 12.834(6)$, $b = 10.317(6)$, $c = 9.718(6)$ Å, $\beta =$

Table 7. Final positional parameters with standard deviations in parentheses (× 10^4) for (**1**)

Atom	*x*	*y*	*z*
Cr	2 209(1)	917(1)	3 429(1)
O	4 191(4)	−859(4)	3 811(4)
O′	2 110(4)	1 110(5)	531(4)
O″	4 132(4)	2 786(3)	4 222(5)
C	3 424(5)	−180(4)	3 677(5)
C′	2 130(5)	1 037(5)	1 644(5)
C″	3 406(4)	2 050(5)	3 914(5)
C(1)	1 316(5)	3 294(4)	4 619(6)
C(2)	1 139(5)	3 894(5)	5 610(6)
C(3)	791(5)	3 477(5)	6 763(6)
C(4)	1 358(5)	2 672(5)	7 659(5)
C(5)	2 455(5)	2 017(5)	7 724(5)
C(6)	2 645(4)	1 403(4)	6 724(5)
C(*j*′)	1 761(4)	1 170(3)	5 339(4)
C(α′)	1 601(5)	−12(4)	4 925(5)
C(β′)	320(6)	−328(5)	3 616(6)
C(β)	220(5)	507(6)	2 672(6)
C(α)	381(4)	1 681(5)	3 047(5)
C(*j*)	1 134(4)	2 030(4)	4 358(4)
H(1)	1 500	3 678	3 988
H(2)	1 244	4 763	5 600
H(3)	191	3 935	6 980
H(4)	1 057	2 517	8 253
H(5)	2 994	2 041	8 464
H(6)	3 423	1 004	6 927
H(α′)	2 025	−706	5 541
H(β′)	704	−986	3 229
H(β)	−249	378	1 797
H(α)	36	2 193	2 487

Table 8. Final positional parameters with standard deviations in parentheses (× 10^4) for (**2**)

Atom	*x*	*y*	*z*
Cr	5 809(1)	3 235(1)	2 291(1)
O	7 186(5)	4 237(6)	418(6)
O′	6 669(4)	548(5)	2 271(6)
O″	4 295(4)	2 924(6)	−544(5)
C	6 677(6)	3 383(7)	1 169(7)
C′	6 336(5)	1 568(6)	2 243(7)
C″	4 859(6)	3 063(8)	549(7)
C(1)	6 981(5)	3 202(8)	4 491(7)
C(2)	6 791(7)	4 437(8)	3 939(8)
C(3)	5 806(8)	5 073(8)	3 461(8)
C(4)	4 776(8)	4 604(8)	3 116(8)
C(5)	4 366(7)	3 319(10)	3 085(8)
C(6)	4 831(5)	2 198(7)	3 688(8)
C(*j*′)	5 474(5)	2 060(6)	5 150(6)
C(α′)	5 058(6)	1 400(7)	6 144(8)
C(β′)	5 634(8)	1 318(8)	7 519(9)
C(β)	6 616(7)	1 873(8)	7 915(8)
C(α)	7 051(6)	2 513(7)	6 946(8)
C(*j*)	6 485(5)	2 597(6)	5 546(6)
H(1)	7 620	2 839	4 444
H(2)	7 349	5 065	3 650
H(3)	5 689	6 036	3 076
H(4)	4 213	5 111	2 499
H(5)	3 764	3 428	2 537
H(6)	4 396	1 447	3 132
H(α′)	4 398	1 091	5 778
H(β′)	5 438	936	8 025
H(β)	7 024	1 846	8 702
H(α)	7 707	2 983	7 182

103.41(8)°, $V = 1\,251.7$ Å^3 (by least-squares refinement on diffractometer angles for 20 automatically centred reflexions, $\lambda = 0.7107$ Å), space group $P2_1/a$, $Z = 4$, $D_x = 1.539$ g cm^{-3}. Dark red. Crystal dimensions: 0.20 × 0.20 × 0.30 mm, μ(Mo-K_α) = 8.1 cm^{-1}.

Data Collection and Processing.—Philips PW 100 Computer-controlled four-circle diffractometer; θ–2θ scan method, 2θ range: 0—45°; speed: 2.50—2.35 deg min^{-1}; graphite-monochromated Mo-K_α radiations; 2 369 reflexions measured for (**1**) and 2 341 for (**2**) of which 1 866 > 3σ(*I*) for (**1**) and 1 647 for (**2**); decay <2% both for (**1**) and (**2**).

Structure Analysis and Refinement.—The structures were solved by the heavy-atom method. The positions of all non-hydrogen atoms were revealed by subsequent Fourier synthesis and refined anisotropically. The hydrogen atoms were located from the final difference Fourier synthesis; they were included in the calculations but not refined. Blocked-cascade least-square refinements were used; they converge to the conventional *R* index of 0.039 (R_w 0.037) for (**1**) and of 0.043 (R_w 0.040) for (**2**). The weighting scheme used in the final calculations was of the form $W^{-1} = a_j|F_0|^j$. The a_j parameters were calculated using the program PESO.[23] Scattering factors for the atoms were taken from Cromer and Waber;[24] the scattering factor for Cr was corrected for the real and imaginary parts of anomalous dispersion using Cromer's values.[25] All computations were carried out on a CDC CYBER 76 computer using the programs of ref. 26. The positional parameters of the atoms are listed in Tables 7 and 8; the atom-numbering scheme being shown in Figures 1 and 2. The thermal parameters and the lists of observed and calculated structure factors are available from the authors on request.

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