Organometallic Chemistry

Synthesis, structure, and rearrangements of new tricarbonylchromium complexes of substituted heptalenes

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Reactions of 1,2,5,6,8,10-hexamethylheptalene (**1**) and its bond isomer, 1,4,5,6,8,10-hexamethylheptalene (**2**), with tricarbonylchromium complexes $L_3Cr(CO)_3$ ($L = NH_3$ and Py) have been investigated. Thermodynamically less stable complex **1** exhibits higher reactivity with respect to $Py_3Cr(CO)_3/BF_3 \cdot Et_2O$ under the conditions of Öfele's reaction than complex **2**. At 10—30 °C, the $Cr(CO)_3$ group is coordinated to the asymmetrically substituted ring, which is accomplished by the shift of double bonds in the ligand, to afford tricarbonyl-[1,4,5,6,8,10-hexamethyl-η^6-(10a, 1—5)heptalene]-chromium (**6**) as the only mononuclear complex. Under more drastic conditions (Raush's reaction, 80 °C), **1** ↔ **2** interconversion proceeds faster than the reaction of individual bond isomers with coordinatively unsaturated "hot" particles $(solv)_nCr(CO)_3$. In this case, all of the four possible isomeric mononuclear complexes (**6—9**) and two binuclear complexes (**10** and **11**) are formed. The structures of complexes **6—11** have been studied by NMR and mass spectrometry, the structure of **6** has been established by X-ray diffraction analysis. Heating a solution of **6** in octane at 115 °C results in the isomerization of **6** into complex **7** through the intracycle 1,2-shift of the $Cr(CO)_3$ group and also in its conversion into complex **8**, which is the first example of interring $\eta^6 \rightarrow \eta^6$-haptotropic rearrangement in nonplanar seven-membered π-systems.

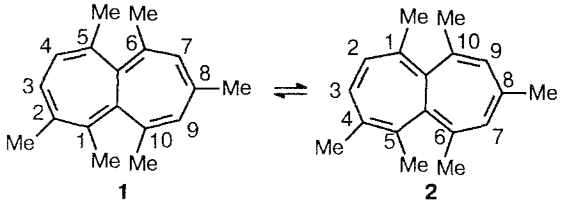
Key words: heptalene; tricarbonylchromium complexes of hexamethylheptalenes; intra- and interring haptotropic rearrangements; X-ray diffraction analysis.

The chemistry of heptalenes, which are nonplanar 12π-electron systems with localized double bonds, has been studied in detail.[1—14] The results of X-ray diffraction analyses of substituted heptalenes demonstrate that each of the seven-membered cycles in these compounds adopts a boat conformation. The conjugation in each of the seven-membered cycles is rather efficient, since the torsion angles between the planes of the double bonds do not exceed 30—35°, whereas there is virtually no conjugation between the double bonds of two different

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2220—2226, December, 1994.

cycles because the corresponding torsion angles[2—4,8,9,13] are close to 60° or 120°. Similar to 8π- and 12π-annulenes, heptalene readily undergoes bond isomerization, the kinetics of which has been studied for a series of substituted compounds.[5,8,12,14] For unsubstituted heptalene, the activation barrier to the 1,2-shift of the multiple bonds is only 3.5 kcal mol^{-1} (Refs. 2, 14). For substituted heptalenes, the values of these barriers depend substantially on the type of substituents and their positions in the rings. These barriers have maximum values in heptalenes with substituents in positions 1, 5, 6, and 10. In particular, the bond isomerization of 1,2,5,6,8,10-hexamethylheptalene (**1**) occurs with an activation energy of 26.7 kcal mol^{-1}, and in an equilibrium mixture at temperatures from 70 to 95 °C, bond isomers **1** and **2** are present in the ratio of ~1 : 1.5 (Refs. 5, 12) (Scheme 1).

Scheme 1



A substantially smaller number of works has been devoted to organometallic derivatives of heptalenes.[2,14—16] The η^6-tricarbonylchromium complex of unsubstituted heptalene (**3**),[2] η^4-tricarbonyliron complex (**4**),[16] and *cis* binuclear complex (**5**)[14] (Scheme 2) have been synthesized. Judging from the NMR data, in complex **3**, a rapid 1,2-shift of the tricarbonylchromium group occurs even at room temperature, so that the molecule acquires an effective C_3—C_8 symmetry axis.

The structures of **4** and **5** were established by X-ray structural analysis.[15,16] Intramolecular migration of the $Fe(CO)_3$ groups in these compounds proceeds as a 1,2-shift within the seven-membered ring; this migration has been studied by dynamic NMR methods. The activation parameters for complex **4** are $\Delta G^{\neq}_{273}$ = 11.4±0.1 kcal mol^{-1} ($\Delta H^{\neq}$ = 10.3±0.2 kcal mol^{-1}; $\Delta S^{\neq}$ = −4.2±0.6 e.u.), whereas for **5** these values are substantially larger ($\Delta G^{\neq}$ = 19.8 ± 0.1 kcal mol^{-1}; $\Delta H^{\neq}$ = 24.0±0.6 kcal mol^{-1}; $\Delta S^{\neq}$ = 15.1±1.6 e.u.).[16] In the latter case, it was not establisged whether the shift of two carbonylmetal groups occurs simultaneously or sequentially. From the above-mentioned data it follows that carbonylmetal complexes of heptalene **3—5** are similar in their dynamic behavior to the corresponding cyclooctatetraene complexes.[17—19] They easily undergo intraring haptotropic shifts of the carbonylmetal groups; however, interring haptotropic rearrangements for these compounds have not been reported previously.

The present work is devoted to the synthesis of new carbonylchromium complexes of substituted heptalenes and to the study of their structures and rearrangements.

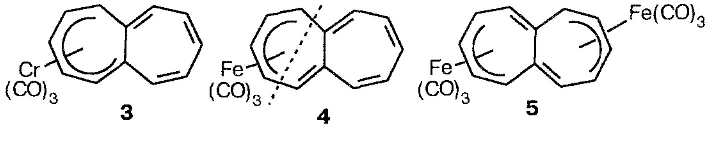
Synthesis of tricarbonylchromium complexes from isomeric hexamethylheptalenes 1 and 2

Tricarbonylchromium complexes of polyenes and aromatic compounds can be obtained under mild conditions according to Öfele's reaction[20] by adding an unsaturated compound to an equimolar amount of a $Py_3Cr(CO)_3/BF_3 \cdot OEt_2$ mixture in diethyl ether at ~0 °C. 1,2,5,6,8,10-Hexamethylheptalene **1**, as a pure isomer,[5] enters into this reaction at +10 °C, which can be easily detected from the appearance of a typical cherry color. The IR spectrum of complex **6** shows ν(CO) absorption bands at 1886, 1900, and 1970 cm^{-1}; the intensities of these bands reach maximum within 40 min. After chromatographic separation on silica gel, it is possible to isolate mononuclear complex **6** in an 80 % yield and binuclear complex **10** in a 12 % yield with respect to consumed compound **1**, and also about 80 % of the unchanged ligand as a mixture of bond isomers **1** and **2** in the ratio of 1 : 1.7, which is close to the equilibrium value under these conditions (Scheme 3).

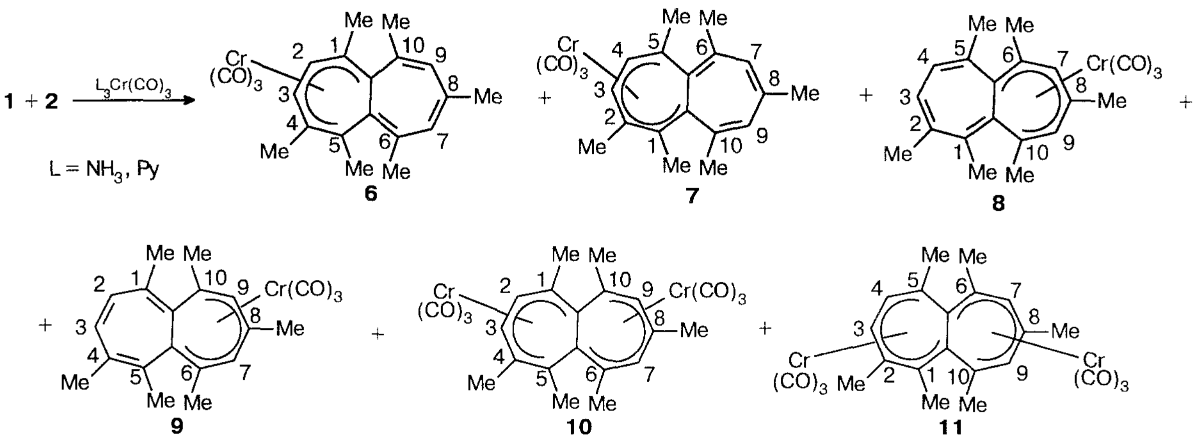
If Öfele's reaction is performed under the same conditions with ligands **1** and **2** taken in the ratio of 5.8 : 1, about 80 % of the mixture of ligands is recovered; the ratio of bond isomers in the mixture is close to the equilibrium value. Complex **6** was obtained as the major reaction product (56 % with respect to the consumed ligand). We also managed to isolate three more mononuclear complexes **7—9** and binuclear complex **10** (yield 9 % with respect to the consumed ligand). The total yield of the mononuclear complexes was 74 %, and the ratio **6** : **7** : **8** : **9** = 1 : 0.09 : 0.18 : 0.045.

If Öfele's reaction is performed using a mixture of bond isomers **1** and **2** with a predominance of more stable **2** (the ratio of 1 : 2.5) at +30 °C, 90 % of the

Scheme 2



Scheme 3



mixture is recovered unchanged. According to the NMR data, the ratio of bond isomers in this mixture is 1 : 3.3. This implies that the mixture of bond isomers is additionally enriched with the more stable isomer **2** over the equilibrium ratio. In this experiment, complexes **6—9** were obtained as reaction products in the ratio 1 : 0.74 : 0.49 : 0.43; binuclear complex **10** was also present in a trace amount.

The results of the three above-described experiments allow one to draw the following conclusions: 1. Of the two bond isomers of hexamethylheptalene, the less thermodynamically stable **1** is more reactive toward the intermediate, coordinatively unsaturated "hot" particles $(Et_2O)_nCr(CO)_3$, which appear in Öfele's reaction. 2. The $Cr(CO)_3$ group is coordinated predominantly to the asymmetrically substituted seven-membered ring, which is accompanied by a 1,2-shift of the double bonds in the ligand.

Rausch's reaction is most often used for preparing different tricarbonylchromium π-complexes. In this reaction, the tris-ammine complex, $(NH_3)_3Cr(CO)_3$, is used as the starting compound, and the reaction is carried out by heating in dioxane.[21] We studied the reaction of **1** and a mixture of **1** and **2** in the ratio of 1 : 2 with an equimolar amount of $(NH_3)_3Cr(CO)_3$ in boiling dimethoxyethane. At 80 °C, interconversion of bond isomers **1** and **2** proceeds rather rapidly; therefore, the results of experiments are independent of whether a single isomer or mixtures of isomers in different ratios were used as starting compounds. In both cases, we obtained mixtures of all four isomeric mononuclear complexes **6—9** in the ratio of 1 : 0.59 : 0.4 : 0.37 in a

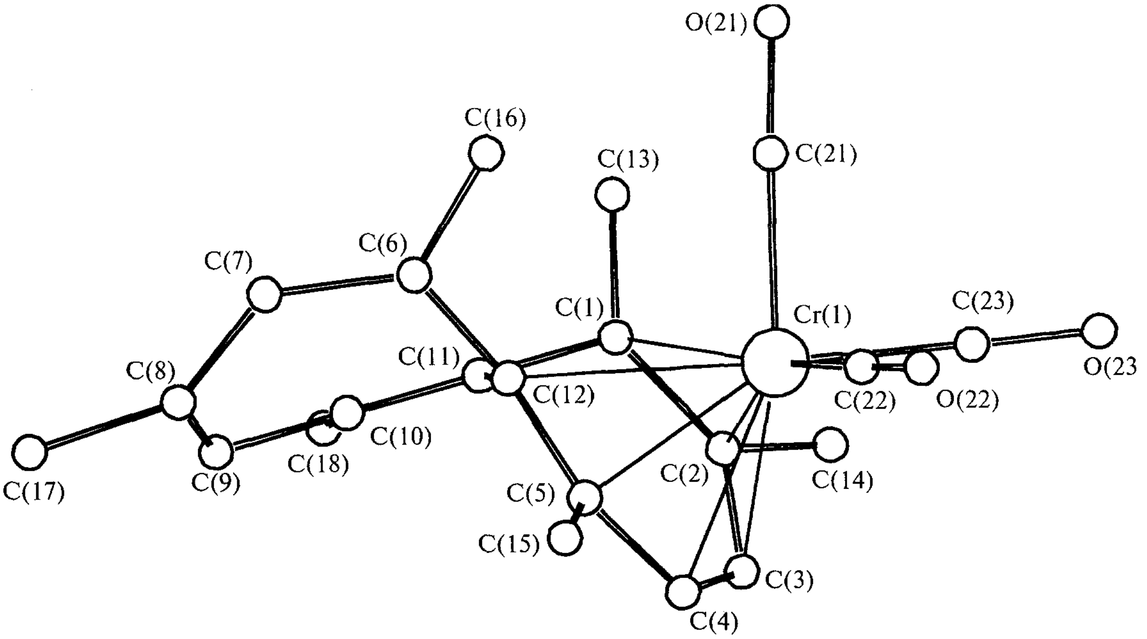


Fig. 1. The structure of complex **6** in the crystal.

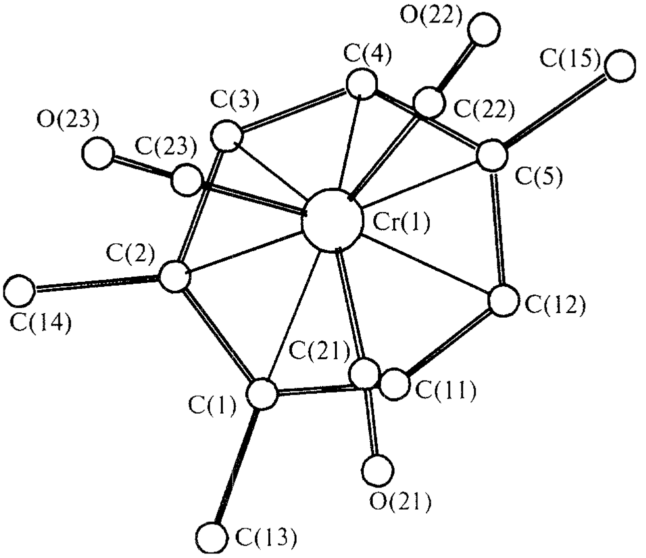


Fig. 2. The projection of the tricarbonylchromium fragment onto the mean plane of the seven-membered cycle.

total yield of ~40 % with respect to the consumed hexamethylheptalene, and two isomeric binuclear complexes **10** and **11** in the ratio of 1 : 0.9 in a yield of ~10 % with respect to the consumed **1** and **2**.

Structures of tricarbonylchromium complexes of hexamethylheptalenes

The structure of complex **6** was established by X-ray diffraction analysis (Tables 1—3), and is shown in Fig. 1. The projection of the tricarbonylchromium fragment onto the mean plane of the seven-membered cycle to which this fragment is coordinated, is shown in Fig. 2.

The coordination of the $Cr(CO)_3$ group slightly changes the geometry of the seven-membered cycle to which this group is bonded: pronounced flattening of the cycle occurs. The dihedral angle between the C(2)C(3)C(4)C(5) and C(1)C(2)C(5)C(12) planes decreases from 26° to 12°, whereas in the noncoordinated nucleus, this angle virtually coincides with the average value for a series of substituted heptalenes.[4,8,13] The geometry of the seven-membered cycle involved in coordination is similar to the known geometry[22] of the (7-phenyltropilidene)$Cr(CO)_3$ complex. Coordination causes the single bond lengths to decrease by an average of 0.016 Å, whereas the multiple bond lengths increase by 0.044 Å (the average length is 1.384 Å). The geometry of the seven-membered ring that is not involved in bonding with the chromium atom, changes insignificantly. Of the Cr—C bonds, four short bonds (2.18—2.26 Å) with the C(2)—C(5) atoms and two longer bonds (2.35—2.41 Å) with the C(1) and C(12) atoms may be distinguished (see Table 2).

Table 1. Atomic coordinates for structure **6**

Atom	*x*	*y*	*z*
Cr	0.25110(6)	0.16298(4)	0.11371(3)
O(21)	0.6284(3)	0.1540(3)	0.1563(2)
O(22)	0.1869(4)	0.0779(2)	0.2558(1)
O(23)	0.2807(4)	−0.0600(2)	0.0825(2)
C(1)	0.3242(4)	0.2615(2)	0.0169(2)
C(2)	0.1952(4)	0.1915(2)	−0.0046(2)
C(3)	0.0410(4)	0.1877(3)	0.0273(2)
C(4)	−0.0013(4)	0.2344(3)	0.0893(2)
C(5)	0.0968(4)	0.3016(2)	0.1390(2)
C(6)	0.3522(4)	0.4121(3)	0.1790(2)
C(7)	0.3407(4)	0.5145(3)	0.1725(2)
C(8)	0.2395(4)	0.5727(2)	01171(2)
C(9)	0.2034(4)	0.5428(2)	0.0479(2)
C(10)	0.2531(4)	0.4490(2)	0.0144(2)
C(11)	0.2773(3)	0.3597(2)	0.0492(1)
C(12)	0.2460(4)	0.3474(2)	0.1253(1)
C(13)	0.4963(5)	0.2552(3)	−0.0083(2)
C(14)	0.2137(6)	0.1127(3)	−0.0629(2)
C(15)	0.0274(5)	0.3237(3)	0.2095(2)
C(16)	0.4659(6)	0.3634(3)	0.2411(2)
C(17)	0.1833(5)	0.6770(3)	0.1395(2)
C(18)	0.2647(5)	0.4576(3)	−0.0655(2)
C(21)	0.4825(4)	0.1596(3)	0.1415(2)
C(22)	0.2105(5)	0.1132(3)	0.2021(2)
C(23)	0.2680(4)	0.0270(3)	0.0929(2)
H(3)	−0.043(3)	0.145(2)	0.006(2)
H(4)	−0.114(3)	0.212(2)	0.104(1)
H(7)	0.403(3)	0.554(2)	0.207(1)
H(9)	0.150(3)	0.587(2)	0.017(1)
H(131)	0.534(4)	0.187(2)	−0.008(2)
H(132)	0.574(4)	0.295(3)	0.023(2)
H(133)	0.492(4)	0.284(3)	−0.053(2)
H(141)	0.136(4)	0.055(3)	−0.060(2)
H(142)	0.335(6)	0.086(4)	−0.058(2)
H(143)	0.183(5)	0.146(3)	−0.107(2)
H(151)	−0.058(5)	0.276(3)	0.218(2)
H(152)	0.115(5)	0.316(3)	0.251(2)
H(153)	−0.026(6)	0.382(4)	0.207(2)
H(161)	0.500(4)	0.409(3)	0.276(2)
H(162)	0.556(5)	0341(3)	0.222(2)
H(163)	0.420(5)	0.304(3)	0.257(2)
H(171)	0.122(4)	0.669(3)	0.168(2)
H(172)	0.133(5)	0.717(3)	0.102(2)
H(173)	0.281(6)	0.717(4)	0.159(2)
H(181)	0.247(4)	0.393(3)	−0.089(2)
H(182)	0.171(4)	0.503(3)	−0.088(2)
H(183)	0.370(4)	0.484(3)	−0.074(2)

The results of the X-ray structural study demonstrate that when the tricarbonylchromium complex is formed, the seven-membered cycle of heptalene involved in coordination undergoes changes in geometry, which are also commonly observed in other complexes. It is particularly remarkable that the effect of the η^4-coordination of the $Fe(CO)_3$ group on the geometry both of the heptalene ligand and of the seven-membered cycle of cycloheptatriene is more significant than that of the η^6-coordination of $Cr(CO)_3$. In tricarbonyliron complexes, very strong flattening of the ligand occurs. The structures of these complexes may be very likely considered as the combination of a planar butadiene-

Table 2. Bond angles for structure **6**

Angle	ω/deg	Angle	ω/deg
C(1)—Cr—C(2)	35.0(1)	Cr—C(2)—C(1)	77.5(2)
C(1)—Cr—C(3)	65.8(1)	Cr—C(2)—C(3)	69.2(2)
C(1)—Cr—C(4)	85.5(1)	Cr—C(2)—C(14)	125.2(2)
C(1)—Cr—C(5)	85.6(1)	C(1)—C(2)—C(3)	122.5(3)
C(1)—Cr—C(12)	62.4(1)	C(1)—C(2)—C(14)	120.8(3)
C(1)—Cr—C(21)	83.8(1)	C(3)—C(2)—C(14)	116.6(3)
C(1)—Cr—C(22)	166.4(1)	Cr—C(3)—C(2)	73.0(2)
C(1)—Cr—C(23)	109.4(1)	Cr—C(3)—C(4)	72.0(2)
C(2)—Cr—C(3)	37.8(1)	C(2)—C(3)—C(4)	130.5(3)
C(2)—Cr—C(4)	70.8(1)	Cr—C(4)—C(3)	70.9(2)
C(2)—Cr—C(5)	92.0(1)	Cr—C(4)—C(5)	74.1(2)
C(2)—Cr—C(12)	85.4(1)	C(3)—C(4)—C(5)	129.8(3)
C(2)—Cr—C(21)	109.9(1)	Cr—C(5)—C(4)	68.6(2)
C(2)—Cr—C(22)	156.1(1)	Cr—C(5)—C(12)	78.8(2)
C(2)—Cr—C(23)	87.7(1)	Cr—C(5)—C(15)	126.8(2)
C(3)—Cr—C(4)	37.1(1)	C(4)—C(5)—C(12)	123.2(3)
C(3)—Cr—C(5)	70.1(1)	C(4)—C(5)—C(15)	116.8(3)
C(3)—Cr—C(12)	84.2(1)	C(12)—C(5)—C(15)	120.0(3)
C(3)—Cr—C(21)	147.7(1)	C(7)—C(6)—C(12)	118.5(3)
C(3)—Cr—C(22)	120.6(1)	C(7)—C(6)—C(16)	120.9(3)
C(3)—Cr—C(23)	93.2(1)	C(12)—C(6)—C(16)	120.5(3)
C(4)—Cr—C(5)	37.3(1)	C(6)—C(7)—C(8)	127.9(3)
C(4)—Cr—C(12)	64.6(1)	C(7)—C(8)—C(9)	124.5(3)
C(4)—Cr—C(21)	156.1(2)	C(7)—C(8)—C(17)	115.5(3)
C(4)—Cr—C(22)	94.0(1)	C(9)—C(8)—C(17)	119.8(3)
C(4)—Cr—C(23)	117.3(1)	C(8)—C(9)—C(10)	128.7(3)
C(5)—Cr—C(12)	34.1(1)	C(9)—C(10)—C(11)	123.4(3)
C(5)—Cr—C(21)	120.3(1)	C(9)—C(10)—C(18)	114.9(3)
C(5)—Cr—C(22)	85.8(1)	C(11)—C(10)—C(18)	121.6(3)
C(5)—Cr—C(23)	151.2(1)	C(1)—C(11)—C(10)	125.3(3)
C(12)—Cr—C(21)	91.5(1)	C(1)—C(11)—C(12)	112.5(2)
C(12)—Cr—C(22)	105.2(1)	C(10)—C(11)—C(12)	122.1(3)
C(12)—Cr—C(23)	171.7(1)	Cr—C(12)—C(5)	67.1(2)
C(21)—Cr—C(22)	91.5(2)	Cr—C(12)—C(6)	127.7(2)
C(21)—Cr—C(23)	86.4(2)	Cr—C(12)—C(11)	90.8(2)
C(22)—Cr—C(23)	82.9(2)	C(5)—C(12)—C(6)	122.7(3)
Cr—C(1)—C(2)	67.5(2)	C(5)—C(12)—C(11)	119.0(2)
Cr—C(1)—C(11)	93.0(2)	C(6)—C(12)—C(11)	115.9(3)
Cr—C(1)—C(13)	122.7(2)	Cr—C(21)—O(21)	176.6(3)
C(2)—C(1)—C(11)	118.0(3)	Cr—C(22)—O(22)	176.8(3)
C(2)—C(1)—C(13)	122.5(3)	Cr—C(23)—O(23)	177.4(3)
C(11)—C(1)—C(13)	117.5(3)		

tricarbonyliron fragment fused to a tropone-type moiety (see Scheme 2, complex **4**).

The structure of complex **6** was confirmed also by mass spectrometry. Fragmentation of the molecular ion of this complex and of a series of tricarbonylchromium complexes of heptalene by electron impact proceeds in the standard way through the consecutive loss of CO groups. The peak at *m/z* 290 $[M-3CO]^+$ has the maximum intensity in the spectrum.

The structures of all of the other complexes **7—11** were established by NMR. The coordination of the $Cr(CO)_3$ group causes the expected shift of the resonance signals for the olefinic protons of the coordinated ring to higher field by 1.5—2.0 ppm. A slight decrease in the coupling constant $^3J_{H,H}$ was also observed on coordination. Parameters of the NMR spectra are presented in Table 4. The signals were assigned using two-dimensional COSY and NOESY experiments. It will be impossible to conclude whether binuclear complexes **10** and **11** are *cis* or *trans* isomers until a complete X-ray diffraction analysis is performed.

Table 3. Bond lengths for structure **6**

Bond	*d*/Å	Bond	*d*/Å
Cr—C(1)	2.356(3)	C(2)—C(14)	1.519(5)
Cr—C(2)	2.229(3)	C(3)—C(4)	1.391(5)
Cr—C(3)	2.178(3)	C(4)—C(5)	1.426(4)
Cr—C(4)	2.192(3)	C(5)—C(12)	1.377(4)
Cr—C(5)	2.264(3)	C(5)—C(15)	1.524(5)
Cr—C(12)	2.411(3)	C(6)—C(7)	1.340(5)
Cr—C(21)	1.833(3)	C(6)—C(12)	1.481(4)
Cr—C(22)	1.846(4)	C(6)—C(16)	1.509(5)
Cr—C(23)	1.820(4)	C(7)—C(8)	1.436(4)
O(21)—C(21)	1.151(4)	C(8)—C(9)	1.346(4)
O(22)—C(22)	1.143(5)	C(8)—C(17)	1.505(5)
O(23)—C(23)	1.155(4)	C(9)—C(10)	1.451(4)
C(1)—C(2)	1.385(4)	C(10)—C(11)	1.333(4)
C(1)—C(11)	1.483(4)	C(10)—C(18)	1.515(4)
C(1)—C(13)	1.502(5)	C(11)—C(12)	1.486(4)
C(2)—C(3)	1.430(5)		

Thermal conversions of complex 6

Complex **6** remains unchanged when heated in benzene for 2 h at 80 °C. No formation of free heptalene and benzenetricarbonylchromium due to ligand exchange was observed. However, when heated for 5 h in octane in a sealed tube at 115 °C, complex **6** partly isomerizes and decomposes. According to the NMR data, thermolysis affords 38.5 % free heptalenes **1** and **2** in the ratio 1 : 2.4, whereas 37 % of complex **6** is recovered. Complex **7** (6 %) was formed through the 1,2-intraring shift of the $Cr(CO)_3$ group, and complex **8** (18.5 %) was formed as a result of interring rearrangement.

Heating complex **6** in *o*-dichlorobenzene at 130 °C for 3 h mainly causes its decomposition to afford a mixture of ligands **1** and **2** in the ratio 1 : 2 in a yield of 85 %. In addition, a small amount of complex **7**, which apparently possesses higher thermal stability, was detected.

The rearrangement of complex **6** into complex **8** is the first example of the interring haptotropic shift of the carbonylmetal group in complexes of nonplanar 12π-systems. However, based on the obtained results, it is impossible to conclude whether intra- or intermolecular isomerization of complex **6** occurs.

Experimental

All operations were carried out under an atmosphere of dry argon; ether and dimethoxyethane were purified by a long reflux over sodium benzophenone ketyl and were freshly distilled before use. IR spectra were recorded on a UR-20

Table 4. Parameters of the ^{1}H NMR spectra of hexamethylheptalene complexes (δ, *J*/Hz)

Compound	Solvent	
	C_6D_6	$CDCl_3$
6	5.796 (br.s, 1 H, H(9)); 5.576 (s, 1 H, H(7)); 5.18 (d, 1 H, H(3), ^3J = 6.8); 4.39 (d, 1 H, H(2), ^3J = 6.8); 2.26 (d, 3 H, 8-Me, J = 1.0); 1.784 (s, 3 H, 1-Me); 1.76 (s, 3 H, 4- or 5-Me); 1.745 (d, 3 H, 10-Me, ^5J = 0.84); 1.696 (d, 3 H, 6-Me, ^4J = 1.21); 1.24 (s, 3 H, 5- or 4-Me)	6.067 (br.s, 1 H, H(9)); 5.736 (br.s, 1 H, H(7)); 5.708 (d, 1 H, H(3), ^3J = 6.8); 4.867 (d, 1 H, H(2), ^3J = 6.8); 2.337 (d, 3 H, 4-Me); 2.277 (d, 3 H, 6-Me, ^4J = 1.2); 2.024 (br.s, 3 H, 1-Me); 1.942 (s, 3 H, 5-Me); 1.903 (d, 3 H, 8-Me, ^4J = 1.2); 1.527 (s, 3 H, 10-Me)
7	5.753 (s, 1 H, H(7)); 5.558 (s, 1 H, H(9)); 5.061 (d, 1 H, H(3), ^3J = 8.8); 4.668 (d, 1 H, H(4), ^3J = 8.8); 2.209 (s, 3 H, Me); 1.739 (br.s, 6 H, 2 Me); 1.689 (s, 3 H, Me); 1.680 (d, 3 H, Me, J = 0.8); 1.165 (s, 3 H, Me)	6.03 (br.s, 1 H, H(7)); 5.72 (br.s, 1 H, H(9)); 5.678 (d, 1 H, H(3), ^3J = 9.0); 5.305 (d, 1 H, H(4), ^3J = 9.0); 2.249 (br.s, 3 H, 6-Me, ^4J = 1.0); 2.142 (s, 3 H, 2-Me); 2.029 (s, 3 H, 1-Me); 1.919 (s, 3 H, 5-Me); 1.887 (d, 3 H, 8-Me, ^4J = 1.0); 1.456 (s, 3 H, 10-Me)
8	4.746 (s, 1 H, H(7)); 4.38 (s, 1 H, H(9)); 5.828 (br.s, 2 H, H(3 or 4)); 2.22 (s, 3 H, Me); 1.93 (s, 3 H, Me); 1.82 (s, 3 H, Me); 1.68 (s, 3 H, Me); 1.539 (s, 3 H, Me); 1.26 (d, 3 H, Me, ^5J = 0.8)	5.22 (br.s, 1 H, H(7)); 4.825 (br.s, 1 H, H(9)); 6.00 (d, 1 H, H(3), ^3J = 7.0); 2.425 (br.s, 3 H, 8-Me); 2.199 (br.s, 3 H, 5-Me); 2.083 (br.s, 3 H, 10-Me); 1.962 (s, 3 H, 6-Me); 1.81 (br.s, 3 H, 2-Me); 1.565 (s, 3 H, 1-Me)
9	4.82 (s, 1 H, H(7)); 4.38 (s, 1 H, H(9)); 5.62 (d, 1 H, H(2), ^3J = 12.4); 5.935 (d, 1 H, H(3), ^3J = 12.4); 2.20 (s, 3 H, Me); 1.958 (s, 3 H, Me); 1.80 (s, 3 H, Me); 1.69 (s, 3 H, Me); 1.57 (s, 3 H, Me); 1.25 (s, 3 H, Me)	5.825 (br.s, 1 H, H(7)); 4.83 (br.s, 1 H, H(9)); 5.08 (d, 1 H, H(2), ^3J = 11.7); 6.08 (d, 1 H, H(3), ^3J = 11.7); 2.425 (br.s, 3 H, 8-Me); 2.19 (br.s, 3 H, 5-Me); 2.05 (br.s, 3 H, 10-Me); 1.90 (s, 3 H, 6-Me); 1.88 (br.s, 3 H, 4-Me); 1.565 (br.s, 3 H, 1-Me)

spectrophotometer. NMR spectra were obtained on Varian VXR-400 and Bruker AMX-600 instruments. Mass spectra were measured on a MAT-112S instrument with direct introduction of a sample into the ion source, and the energy of the ionizing electrons was 70 eV. Adsorption HPLC was used for separating complexes **6**—**9**. Conditions were chosen using a Spherisorb-NH_2 analytical column (4.6×250 mm) with hexane as the mobile phase (the rate of elution was 1 mL min^{-1}); detection was carried out at λ = 222 and 254 nm. Separation was performed on an analogous Spherisorb-NH_2 preparative column, 5 μm (20×250 mm), with hexane as the mobile phase. The rate of elution was 8 mL min^{-1}, and elution time was 14.44 min for complexes **8** and **9** and 15.9 min for complexes **6** and **7** (detection at λ = 254 nm). Other compounds were chromatographed on Silica gel 60, 0.04—0.063 mm (Merck). The yields of complexes are given with respect to the consumed ligand.

Hexamethylheptalenes **1** and **2** were prepared according to the known procedure.[5]

Reaction of 1 with $Py_3Cr(CO)_3$. $BF_3 \cdot Et_2O$ (0.32 g, 2.2 mmol) was added to a mixture of compound **1** (0.18 g, 0.76 mmol) and $Py_3Cr(CO)_3$ (0.24 g, 0.65 mmol) in 30 mL of ether at −20 °C. The reaction starts at T > +10 °C. The reaction mixture was gradually warmed to room temperature and stirred for ~40 min. Then the solution was washed twice with water, and the ether layer was dried with $MgSO_4$. After removal of the ether *in vacuo*, the residue was chromatographed on a column with silica gel. The first, yellow fraction was eluted with light petroleum, and 0.14 g of a mixture of ligands **1** and **2** (1 : 1.7) was isolated. Elution of the second, red fraction with a 3 : 1 light petroleum—benzene mixture afforded 0.05 g of practically pure complex **6** in a yield of 80 %, m.p. 165—166 °C (from benzene—heptane). IR (THF, ν(CO)/cm^{-1}): 1886, 1900, and 1970. Mass spectrum, m/z (I_{rel} (%)) : 374 $[M]^+$(16), 346 $[M-CO]^+$(11), 318 $[M-2CO]^+$(11), 290 $[M-3CO]^+$(100), 288 $[M-3CO-2H]^+$(28.5), 236 $[M-Cr(CO)_3-2H]^+$(2), 145 $[M-Cr(CO)_3-6CH_3-3H]^+$(11), 52 Cr^+(93). The third, yellow fraction was eluted with a 3 : 1 light petroleum—benzene mixture and contained $PyCr(CO)_5$. Elution of the last, red fraction with a 2 : 1 light petroleum—benzene mixture afforded 0.01 g of complex **10** in a yield of 12 %, m.p. 183—185 °C (from benzene—heptane). IR (THF, ν (CO)/cm^{-1}): 1895 and 1965. Mass spectrum, m/z (I_{rel} (%)): 510 $[M]^+$(18), 482 $[M-CO]^+$(1), 454 $[M-2CO]^+$(5), 426 $[M-3CO]^+$(5), 398 $[M-4CO]^+$(31), 370 $[M-5CO]^+$(9), 342 $[M-6CO]^+$(100), 340 $[M-6CO-2H]^+$(23.4), 290 $[M-Cr(CO)_6]^+$(12), 288 $[M-Cr(CO)_6-2H]^+$(14.5), 52 Cr^+(100). ^{1}H NMR (C_6D_6, δ, *J*/Hz): 4.29 and 4.31 (br.s, H(7) and H(9); 5.00 and 4.25 (d, H(2) and H(3), J = 7.2); methyl groups: 2.03 (s); 1.97 (d, J = 0.70); 1.84 (s); 1.59 (s); 1.28 (s); 1.25 (s).

Reaction of a mixture of 1 + 2 (ratio 5.8 : 1) with $Py_3Cr(CO)_3$. $BF_3 \cdot Et_2O$ (0.23 g, 1.65 mmol) was added to a mixture of **1** + **2** (0.12 g, 0.5 mmol) and $Py_3Cr(CO)_3$ (0.19 g, 0.5 mmol) in 25 mL of ether at −20 °C. Then the temperature of the reaction mixture was rapidly increased to +20 °C, and the mixture was kept for ~40 min. Workup and isolation of products were carried out as described above. A mixture (0.09 g) of ligands **1** and **2** in the ratio of 1 : 1.5, a mixture (0.035 g, 74 %) of complexes **6**—**9** in the ratio of 1 : 0.09 : 0.18 : 0.045, $PyCr(CO)_5$, and complex **10** with traces of isomeric complex **11** (yield 0.0055 g, 9 %) were obtained.

Reaction of a mixture of 1 + 2 (ratio 1 : 2.5) with $Py_3Cr(CO)_3$. $BF_3 \cdot Et_2O$ (0.37 g, 2.6 mmol) was added to a mixture of hexamethylheptalenes **1** + **2** (0.19 g, 0.8 mmol) and $Py_3Cr(CO)_3$ (0.28 g, 0.75 mmol) in 30 mL of ether at −20 °C. The mixture was warmed to room temperature, an additional amount of $Py_3Cr(CO)_3$ was added, the temperature was adjusted to +30 °C, and the reaction mixture was stirred at this temperature for ~40 min. Workup and isolation of products were carried out as described above. A mixture (0.17 g) of ligands **1** + **2** in the ratio 1 : 3.3, a mixture of complexes **6—9** (0.02 g, 64 %) (the ratio of isomers was 1 : 0.74 : 0.49 : 0.43), $PyCr(CO)_5$, and traces of binuclear complex **10** were obtained.

Reaction of 1 with $(NH_3)_3Cr(CO)_3$. A mixture of compound **1** (0.2 g, 0.84 mmol) and $(NH_3)_3Cr(CO)_3$ (0.15 g, 0.8 mmol) in 15 mL of dimethoxyethane was boiled for 3 h. After removal of the solvent *in vacuo*, the residue was chromatographed on a column with silica gel. The first, yellow fraction was eluted with light petroleum, and 0.1 g of a mixture of ligands **1** + **2** in the ratio 1 : 2.7 was obtained. Elution of the second, red fraction with a 3 : 1 light petroleum—benzene mixture afforded a mixture (0.06 g, 38 %) of four complexes; the ratio of isomers **6** : **7** : **8** : **9** = 1 : 0.59 : 0.41 : 0.37. The third, red fraction was eluted with a 2 : 1 light petroleum—benzene mixture and a mixture (0.02 g, 9.3 %) of complexes **10** and **11** in the ratio 1 : 0.9 was obtained. ^1H NMR of complex **11** (C_6D_6, δ, J/Hz): 4.20 and 4.32 (s, H(7) and H(9)); 4.23 and 4.91 (d, H(3) and H(4), J = 9.2); methyl groups: 2.05 (d, J = 0.63); 1.98 (d, J = 0.64); 1.86 (s); 1.59 (s); 1.20 (s); 1.13 (s). The fourth, yellow fraction was $NH_3Cr(CO)_5$.

Reaction of a mixture of 1 + 2 (ratio 1 : 2) with $(NH_3)_3Cr(CO)_3$. A mixture (0.22 g, 0.92 mmol) of isomers **1** + **2** and $(NH_3)_3Cr(CO)_3$ (0.175 g, 0.92 mmol) in 25 mL of dimethoxyethane was boiled for 1.5 h. Workup and isolation of products were carried out as described above. The first fraction was a mixture (0.1 g) of ligands **1** + **2** (1 : 2.4). The second fraction was a mixture (0.08 g, 42.3 %) of complexes **6—9**, the ratio of isomers was 1 : 0.57 : 0.43 : 0.36. The third fraction was a mixture (0.03 g, 12 %) of complexes **10** and **11** (1 : 0.86). The fourth, yellow fraction was $NH_3Cr(CO)_5$.

X-ray diffraction study of complex 6 was performed on an automated CAD-4 diffractometer (Mo-Kα, ω-scanning technique) with the use of a single crystal with dimensions of 0.4×0.3×0.25 mm. The monoclinic unit-cell parameters (a = 7.907(2), b = 13.010(3), c = 18.719(3) Å, β = 97.85(2)°) were determined by automatic indexing and were refined with the use of 22 reflections (13° < θ < 15°). The space group is $P2_1/c$, Z = 4, d_{calc} = 1.304 g cm^{-3}. The intensities of 5114 reflections in the range of θ < 25° and $-9 < h < 9$, $-15 < k < 15$, and $0 < l < 22$ were measured. After the averaging of equivalent reflections (R_{int} = 0.014), 2368 reflections with $I > 2\sigma(I)$ were used for solving the structure. Coordinates for chromium and six carbon atoms bonded with the chromium atom were determined by the direct method and the remaining atoms were located in subsequent electron density syntheses. The structure was refined with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms (314 variables) to R = 0.035, R_w = 0.034. Atomic coordinates are given in Table 1; bond lengths and bond angles are listed in Tables 2 and 3.

We would like to thank N. S. Kulikov for measuring mass spectra and L. A. Aslanov for helpful discussion of the results of X-ray diffraction analysis.

The Research Group from the Moscow State University gratefully acknowledges the support of this work by the International Science Foundation (Grant No. MQ 5000) and the Russian Foundation for Basic Research (Project No. 94-03-08325).

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Received April 18, 1994