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(Phenalene)chromium Tricarbonyl Complexes. Synthesis, Structure, and Thermal Rearrangements

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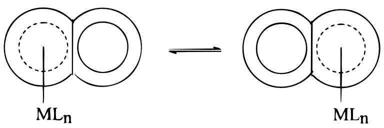
The reaction of phenalene with $Cr(CO)_3Py_3/BF_3{\cdot}OEt_2$ gives a mixture of two isomeric complexes: tricarbonyl(6a,7−9,9a,9b-η^6-phenalene)chromium (**1**) and tricarbonyl (3a,4−6,6a,9b-η^6-phenalene) chromium (**2**). Deprotonation of the mixture of **1** and **2** followed by the treatment with MeI, n-BuI, or D_2O results in the formation of 1-*exo*-*R*-(**1**) complexes **3**−**5** ((**3**) R = Me, (**4**) R = n-Bu, (**5**) R = D). The molecular geometry of the complex **3** was characterized by a single-crystal X-ray diffraction study. Heating of **5** and **3** in toluene or C_6F_6 at temperatures 90−110 °C leads for **5** to deuterium label redistribution over the positions 1-*exo*, 1-*endo*, and 3 by means of sigmatropic shifts of *exo*- and *endo*-hydrogens in nonaromatic ring and inter-ring migrations of chromium tricarbonyl group, whereas for **3** the methyl label distributes over the positions 1-*exo* and 3 via the same processes resulting in the formation of structurally similar isomeric complexes **6**−**8** (**6** = 1-*exo*-methyl-(**2**); **7** = 3-methyl-(**2**); **8** = 3-methyl-(**1**)), respectively, through the same processes as for isomerization of **5**, excluding *exo*-hydrogen migrations. The mechanisms of these rearrangements are discussed.

1. Introduction

π-Complexes of transition metals with unsaturated and aromatic ligands, in which the metal uses for bonding only part of the ligand sites accessible for coordination, are quite labile and characterized by different dynamic processes. Among the most thoroughly studied reactions are haptotropic rearrangements in the course of which the metal migrates from one position of the ligand to another.[1−6] In some cases metal movement over the ligand is accompanied by reversible migration of hydrogen atoms (or R group) between the metal and *endo*-position of the unsaturated ligand. These processes are considered as an intramolecular oxidative addition−reductive elimination reaction and usually treated from the viewpoint of *endo*-CH bond activation. Both types of rearrangements are closely related to the catalytic activity of complexes. Thus the investigation of their intramolecular nonrigidity is of considerable interest from theoretical and practical points of view.[7,8]

For the complexes of transition metals with polycyclic aromatic ligands the inter-ring haptotropic rearrangements are quite common, and in the course of such processes, the organometallic or metal carbonyl group ML_n moves along the plane of the π-system of the ligand from one ring to another (eq 1). Migrations of ML_n



(1)

between two aromatic six-membered rings have been studied in detail for the derivatives of naphthalene, acenaphthene, acenaphthylene, biphenylene, and biphenyl (η^6, η^6-rearrangements) as well as similar metal shifts between five- and six-membered rings in the complexes of indenyl and fluorenyl anions and their heteroanalogues (η^6, η^5-rearrangements).[4−6] Fast reversible migrations of a $Mn(CO)_3$ group between two five-membered rings in derivatives of indeno[1,2-*a*]-indene were described.[9] The fast migrations of PdL_2 fragments over the η^3-phenalenyl ligand periphery[10] and shifts of $Ni(PR_3)_2$ groups in η^2-5-alkyl and 5,10-dialkylanthracene complexes[11] were also studied.

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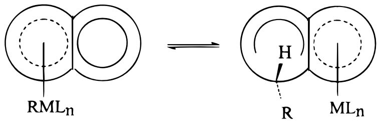
Table 1. ^{1}H NMR Chemical Shifts (ppm) of Complexes 1 and 2

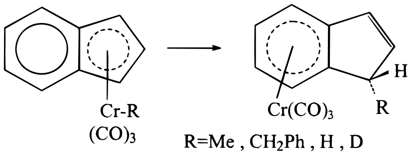
		hydrogen atoms position									
compd	solvent	H^1_{exo}	H^1_{endo}	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9
1	C_6D_6	3.01	3.164	5.60	6.20	6.33	6.68−6.72	6.68−6.72	5.11	4.76	4.41
	C_6F_6	4.01	4.02	6.30	6.66	6.98	7.37	7.33	5.90	5.64	5.37
2	C_6D_6	3.26	3.54	5.58	5.73	4.52	4.76	5.26	6.74−6.85	6.74−6.85	6.45
	C_6F_6	4.18	4.09	6.34	6.40	5.29	5.63	6.06	7.45	7.49	7.31

Special types of rearrangements comprise "ricochet" inter-ring haptotropic rearrangements (eq 2). In these processes the metal shifts from one ring to another are accompanied by the simultaneous migrations of either hydrogen atom or alkyl group from the metal to one of the *endo*-positions of the ligand.



(2)

The first examples of rearrangements (2), in which both these isomers were identified, were observed by the authors in the course of the thermal rearrangements of (σ-alkyl)(η^5-indenyl)- or (σ-alkyl)(η^5-fluorenyl)chromium tricarbonyl complexes (eqs 3 and 4).[12,13]



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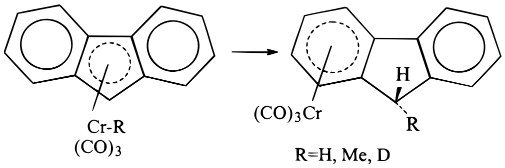
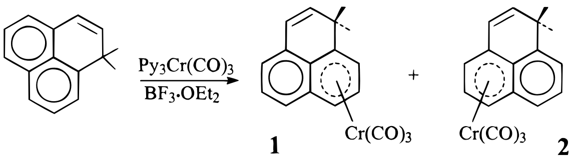


(4)

During our earlier investigation of thermal rearrangements of 1-*exo*-d_1-(**1**) we found that along with η^6,η^6-inter-ring migrations of the $Cr(CO)_3$ group typical for naphthalene complexes redistribution of the deuterium label over the phenalene ligand positions also took place in the ligand. Such process can be interpreted in terms of direct participation of the metal atom via intermediate formation of the hydride group H−ML$_n$. At the same time, it is impossible to exclude an opportunity of accomplishment of hydrogen atom sigmatropic shifts without direct participation of the metal atom. To study these processes in detail and to reveal the extent of metal atom participation in such reactions, we have synthesized a number of new tricarbonyl chromium complexes of substituted phenalenes and thoroughly investigated their structures and kinetics of their thermal rearrangements. These results are reported in the present paper.

2. Results and Discussions

2.1. Synthesis of Isomeric Tricarbonyl(η^6-phenalene)chromium Complexes. Tricarbonyl(6a,7−9,-9a,9b-η^6-phenalene)chromium (**1**) was first obtained by Boudjouk[14] with the yield of 21% in the reaction of $Cr(CO)_3(CH_3CN)_3$ with phenalene at 45 °C, and it was isolated by chromatography and sublimation. We used the Ofele reaction[15] to prepare **1** and obtained two isomeric complexes **1** and **2** in a total yield of 44% in the ratio **1**:**2** = 2:3 (eq 5).



(5)

The complexes **1** and **2** were separated by chromatography and completely characterized. Chromium tricarbonyl complexes of substituted phenalenes are orange-red or red crystals quite stable in the solid state. Therefore, they can be stored for a long time in sealed tubes under argon atmosphere. The complexes are readily soluble in aromatic solvents (benzene, toluene, hexafluorobenzene), have low solubility at room temperatures in alkanes, and can be crystallized from them. Solutions of the complexes are quite sensitive to light and air oxygen. In polar (THF, ether) and chlorine-containing solvents, the complexes demonstrate limited stability (see Experimental Section).

The AB part of the complex spin system in the strong-field region of the ^{1}H NMR spectrum of **1** in C_6D_6 belongs to a geminal pair of protons at C_1. It will be shown below that conversion of **1** to the corresponding anion **9** through interaction with BuLi followed by the treatment of **9** with D_2O leads exclusively to the formation of *exo*-1-*d*-(**1**) (eq 6). After completion of this reaction the strong-field signal in the AB part disappears, which allows us to assign it to an *exo*-proton at C_1. The assignment of other signals was done by means of double resonance experiments and observation of the nuclear Overhauser effect (NOE).

The complete analysis of spectra of **1** and **2** in C_6F_6 was done with the aid of double resonance experiments and iterative calculations. The parameters obtained are presented in Tables 1 and 2; the ^{13}C chemical shifts are given in Table 3. For the assignment of carbon signals the DEPT procedure was used.

Hydrogen and carbon signals of metal-coordinated six-membered rings of **1** and **2** undergo upfield shifts typical for π-complexes of transition metals.[16] Moreover, considerable decrease of absolute values of spin−spin couplings of coordinated rings protons is observed. It is especially evident for the long-range couplings, which indicate a considerable shifting of π-electron density toward the metal. Differences of spin−spin coupling

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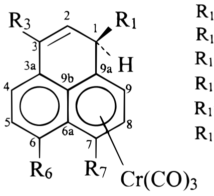
Table 2. Spin−Spin Coupling Constants J_{HH} in ^{1}H NMR Spectra of Compounds 1 and 2 in Hz (±0.05 Hz) (solvent C_6F_6, 400 MHz)

H atoms	compd	H^1_{exo}	H^1_{endo}	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9
H^1_{exo}	**1**		−24.94	3.65	−2.42	1.06	<0.1	0.39			−0.91
	2		−25.43	2.82	−2.46	0.59			1.06	<0.1	−1.72
H^1_{endo}	**1**	−24.49		4.57	−1.99	1.05	<0.1	0.39			−0.81
	2	−25.43		4.20	−2.06				0.93	<0.1	−1.62
H^2	**1**	3.65			10.03	0.59		0.46			
	2				9.98						
H^3	**1**	−2.42	−1.99	10.03		0.52			<0.1		
	2	−2.46	−2.06	9.98		0.27			0.2		
H^4	**1**	1.06	1.05	0.59	0.52		6.86	1.07			
	2	0.59	0.46		0.27		6.11	1.09			
H^5	**1**	<0.1	<0.1			6.86		8.68			
	2					6.11		6.72			
H^6	**1**	0.39	0.39	0.46		1.07			0.2		
	2					1.09	6.72		0.23		
H^7	**1**				<0.1					6.73	1.05
	2	1.06	0.93		0.2			0.23			1.09
H^8	**1**								6.73		6.16
	2	<0.1	<0.1						8.63		7.00
H^9	**1**	−0.91	−0.81						1.05	6.16	
	2	−1.72	−1.62						1.09	7.00	

Table 3. ^{13}C NMR Chemical Shifts of Chromium Tricarbonyl Complexes of Phenalenes and Their Derivatives in C_6D_6



$R_1=R_3=R_6=R_7=H$	**1**
$R_1=R_3=R_6=R_7=H$	**2***
$R_1=Me, R_3=R_6=R_7=H$	**3**
$R_1=n\text{-}Bu, R_3=R_6=R_7=H$	**4**
$R_1=R_6=Me, R_3=R_7=H$	**11**
$R_1=R_6=H, R_3=R_7=Me$	**14 ***

*- $Cr(CO)_3$ Bonded with atoms-3a,4,5,6,6a,9b

	chem shift δ (±0.02 ppm)					
C	**1**	**2**	**3**	**4**	**11**	**14**
C_1	30.68	31.26	35.81	41.06	35.44	30.96
C_2	123.69	129.00	124.45	123.84	123.95	128.40
C_3	125.97	128.65	124.91	125.61	124.51	133.00
C_4	126.76	88.87	127.37	126.73	128.46	92.01
C_5	128.38	89.86	129.81	129.21	133.15	87.32
C_6	129.23	93.12	135.12	133.19	133.98	86.03
C_7	88.77	126.11	89.81	89.33	85.88	128.88
C_8	89.74	125.79	90.03	89.39	89.56	125.88
C_9	93.02	124.57	93.69	92.99	92.91	125.32
C_{3a}	133.62	101.68	133.92	133.49	131.14	101.69
C_{6a}	100.78	99.70	100.14	100.05	99.72	102.54
C_{9a}	103.75	135.75	106.23	109.16	110.68	133.32
C_{9b}	105.45	106.71	110.38	100.58	105.09	105.88
CO	232.99	232.99	233.48	233.93	232.98	233.07
CH_3			27.23	13.99	19.37 26.82	18.26 18.96
CH_2				23.03 27.30 40.23		

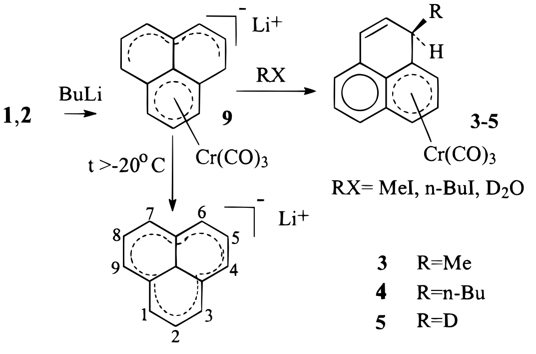
with H_{1-exo} and H_{1-endo} are also quite characteristic. If one takes into account the sign, the *exo*-proton has smaller couplings $^3J_{1,2}$, $^4J_{1,3}$, and $^4J_{1,9}$ than those of *endo*-proton (3.65 and 4.57 Hz, −2.42 and −1.99 Hz, and −0.91 and −0.81 Hz, respectively). This effect can be used for stereochemical assignments.

3-d_1-Phenalene prepared through phenalanone reduction with $LiAlD_4$ followed by dehydration of deuterated phenalanol gives in the Ofele reaction a mixture of d_1-(**1**) and d_1-(**2**) of the same **1**/**2** ratio as found in reaction 5 for deuterium-free phenalene. In both complexes the deuterium label is randomly distributed over the positions 1-*exo*, 1-*endo*, 3, 4, 6, 7, and 9. It can be assumed that deuterium scrambling takes place in phenalene under the action of BF_3·OEt_2 before phenalene coordination to the metal. Such facile redistribution is well-known for the substituted phenalenes under base or acid catalysis conditions.[17] Chromium tricarbonyl complexes of phenalene **1** and **2** as well as substituted phenalenes are much less sensitive to the action of acidic reagents than the corresponding free ligands. In the separate experiments we have found that 1-*exo*-methyl-(**1**) (**3**) and 1-*exo*-d_1-(**1**) (**5**) can be quantitatively recovered without isomerization under treatment with $Py_3Cr(CO)_3$ and BF_3·OEt_2 in the typical conditions of the Ofele reaction (25 °C, 1 h).

Complexes **1** and **2** have been fully characterized through a combination of mass, IR, and NMR spectroscopes. Presumably, the authors of the paper[14] dealt also with a mixture of complexes **1** and **2** obtained in reaction of $Cr(CO)_3(CH_3CN)_3$ with phenalene. However, the use of only ^{1}H NMR with the working frequency of 100 MHz in isotropic $CDCl_3$ gives no possibility to detect the presence of two isomers. This explains also a lower melting point measured for **1** in this paper as compared with melting point obtained in our experiments.

2.2. Metalation of the Complexes 1 and 2.

n-Butyllithium easily converts both isomeric complexes **1** and **2** into an anion (**9**) at −70 °C in THF. The lithium salt of **9** in THF is unstable above −20 °C and decomposes with the formation of phenalenyl anion (eq 6). ^{1}H NMR of the lithium salt of **9** indicates that it has a symmetric structure with the complete delocalization of the negative charge between both noncoordinated six-membered rings.



(6)

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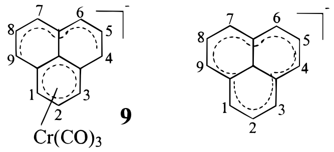
Table 4. NMR ^1H Data for 9 and the Phenalenide Anion (THF-d_8, − 40 °C, 400 MHz)



compd	chem shift (ppb) of H's					spin−spin coupling consts (Hz)		
	$H_{1,3}$	H_2	$H_{4,9}$	$H_{5,8}$	$H_{6,7}$	$J_{(1,2)} = J_{(2,3)}$	$J_{(4,5)} = J_{(8,9)}$	$J_{(5,6)} = J_{(7,8)}$
9	4.521	5.23	5.517	6.53	6.02	5.91	6.78	7.19
phenalenide anion	5.195	5.93	5.195	5.93	5.195	7.32	7.32	7.32

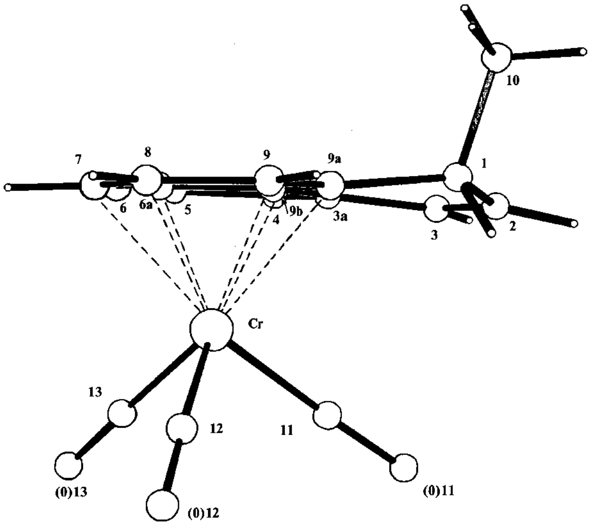


Figure 1. Crystallographic structure of complex **3**.

The analysis of spectra (Table 4) recorded at different temperatures shows that below −20 °C there are no inter-ring migration of $Cr(CO)_3$ between six-membered rings in anion **9** fast enough on the NMR time scale.

2.3. Interaction of 9 with Electrophilic Reagents. The interaction of **9** with electrophilic reagents (D_2O, MeI, n-BuI) at low temperatures occurs regio- and stereoselectively with the formation of 1-*exo*-derivatives (eq 6).

It should be noted that in the reaction with MeI along with expected complex **3** the 1-*exo*-butylphenalene complex (**4**) can be obtained in low yield. This is believed to be a consequence of exchange reaction of butyllithium taken in excess with methyl iodide to give n-BuI followed by the reaction of the latter with **9** to yield **4**.

Regioselectivity of the reaction was strictly confirmed by means of complete X-ray analysis of **3** (Figure 1). In the ^1H NMR spectrum of 1-*exo*-d_1-(**1**) (**5**) in C_6D_6, no signal is observed at 3.01 ppm, which allows one to make the reliable assignment in the AB part of the spectrum of **1**, whereas in the ^2D NMR spectrum of **5** only one singlet is observed at 3.01 ppm. Parameters of ^1H and ^{13}C NMR spectra of **3** and other substituted chromium tricarbonyl complexes of phenalene are presented in Tables 5 and 3, respectively.

2.4. Single-Crystal X-ray Diffraction Study of 3. The structure of the molecule of **3** was confirmed by a single-crystal X-ray diffraction study and presented in Figure 1. Figure 2 shows the projection of the $Cr(CO)_3$ group onto the plane of the aromatic ligand. Bond lengths and angles are presented in Tables 6 and 7. The distance between the chromium atom and the mean plane of η^6-cycle A (1.746 Å) is equal to that in tricarbonyl(η^6-naphthalene)chromium (1.747 Å)[18] and just slightly longer than in tricarbonyl (η^6-benzene)chromium (1.726 Å)[19] in accordance with the smaller π-donating ability of annelated ligands. Orientation of $Cr(CO)_3$ to the "naphthalene" fragment in complex **3** (fused cycles A and B) is similar to that in η^6-$C_{10}H_8Cr(CO)_3$: the carbonyl groups are disposed above the C(6a)−C(7), C(8)−C(9), and C(9a)−C(9b) bonds. Cycles A and B are approximately planar although they show small wavelike distortions typical for annelated π-ligands (the C(6a) and C(9) atoms in cycle A and the C(5) and C(9) atoms in cycle B are shifted on 0.02−0.03 Å from the chromium atom).

The annelated atoms of the η^6-cycle in η^6-$C_{10}H_8Cr(CO)_3$ are shifted farther away from chromium than the peripheral ones (average distances are 2.32 and 2.02 Å, respectively, which is also typical for annelated arene π-ligands[20]). This feature is less obvious in **3**. Nonaromatic cycle C with the C(2)=C(3) double bond has a sofa conformation. The C(1) atom is displaced from the C(2)-(C(3)C(3a)C(9b)C(9a) plane by 0.23 Å in the direction opposite to the chromium atom. The C(10) atom is also shifted out of this plane by 1.65 Å thus indicating that the methyl substituent has a pseudoaxial *exo*-orientation. The distance Cr−H(1-*endo*) in **3** is equal 3.42 Å which exceeds the sum of covalent radii of chromium and hydrogen by 1.86 Å. The rich experimental data on the structures with agostic bonds show that the direct agostic interaction between the metal and C−H bond can only exist if the difference between the M−H distance and the sum of the covalent radii of metal and hydrogen does not exceed 0.6 Å.[21] Thus, in the chromium tricarbonyl complexes of phenalene there is no effective interaction of the chromium atom with the C_1−H_{endo} bond in the ground state of the molecule. This conclusion is also supported by spectral data indicating neither an upfield shift of agostic hydrogen in ^1H NMR nor any deviations in the ν_{CH} region of IR spectra of such complexes.[22]

2.5. Deprotonation of Substituted Phenalene−Chromium Tricarbonyls and the Reactions of Corresponding Anions. Deprotonation of **1** and **2** proceeds as a stereoselective *exo*-attack of the base on

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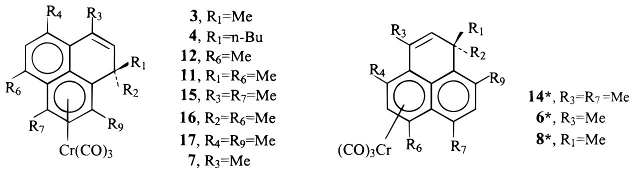
Table 5. NMR ^{1}H Data (400 MHz, C_6D_6) of Chromium Tricarbonyl Complexes of Phenalene Derivatives[a]



3, R_1=Me
4, R_1=n-Bu
12, R_6=Me
11, R_1=R_6=Me
15, R_3=R_7=Me
16, R_2=R_6=Me
17, R_4=R_9=Me
7, R_3=Me

14*, R_3=R_7=Me
6*, R_3=Me
8*, R_1=Me

R_i=H if R_i not defined.

	3	**4**	**12**	**11**
R_1^{exo}	0.84	0.7 (CH_3)	3.12	0.90
	$J_{(CH_3,R_2)} = 7.3$	1.27; 1.04; 0.88 (CH_2)	$J_{(R_1,R_2)} = 24.3$	$J_{(R_1R_2)} = 7.27$
R_2^{endo}	3.17	3.31	3.20	3.20
	$J_{(R_2,CH_3)} = 7.3$	$J_{(CH_2,CH_2)} = 5.9$	$J_{(R_1,R_2)} = 24.3$	$J_{(R_1R_2)} = 7.27$
		$J_{(R_2,9)} = 0.8$		
H_2	5.64	5.79	5.58	5.67
	$J_{(1,2)} = 4.7$	$J_{(1,2)} = 4.9$	$J_{(2,3)} = 10.2$	$J_{(2,R_2)} = 4.64$
	$J_{(2,3)} = 10.1$	$J_{(2,3)} = 10.0$	$J_{(2,R_1)} \approx J_{(2,R_2)} = 4.3$	$J_{(2,3)} = 9.77$
R_3	6.19	6.35		6.23
	$J_{(2,3)} = 10.1$	$J_{(1,3)} = 1.4$	6.18	$J_{(2,3)} = 9.77$
	$J_{(3,R_2)} = 1.35$	$J_{(2,3)} = 10.0$	$J_{(2,3)} = 10.2$	$J_{(3,4)} = 0.92$
R_4	6.40	6.43		6.38
	$J_{(4,5)} = 6.0$	$J_{(4,5)} = 6.1$	6.35	$J_{(4,5)} = 7.08$
	$J_{(4,6)} = 2.0$	$J_{(4,6)} = 2.2$		
				6.57
H_5	~6.70−6.80	~6.71−6.78	6.57	$J_{(4,5)} = 7.08$
R_6	~6.70−6.80	~6.71−6.78	2.05	2.09
R_7	5.15	5.18		
	$J_{(7,8)} = 6.5$	$J_{(7,8)} = 6.5$	5.83	5.25
	$J_{(7,9)} = 0.9$	$J_{(7,9)} = 1.1$	$J_{(7,8)} = 6.3$	$J_{(7,8)} = 6.9$
H_8	4.81	4.83	4.78	4.83
	$J_{(7,8)} \approx J_{(8,9)} = 6.5$	$J_{(7,8)} = 6.5$	$J_{(8,9)} \approx J_{(7,8)} = 6.3$	$J_{(7,8)} = 6.9$
		$J_{(8,9)} = 6.2$		$J_{(8,9)} = 6.2$
R_9	4.55	4.64		
	$J_{(8,9)} = 6.5$	$J_{(7,9)} = 1.1$	4.45	4.63
	$J_{(7,9)} = 0.9$	$J_{(8,9)} = 6.2$	$J_{(8,9)} = 6.3$	$J_{(8,9)} = 6.2$
	$J_{(R_2,9)} = 0.9$	$J_{(R_2,9)} = 0.8$		

	6	**7**	**19**[b]	**20**[b]
R_1^{exo}		3.13		
	3.31	$J_{(R_1,R_2)} = 23.5$	1.21 (CH_3)	3.66
R_2^{endo}			3.61 (H)	
	3.56	3.28	$J_{(H,CH_3)} = 7.4$	3.66
H_2	5.46	5.49	5.75	
	$J_{(2,CH_3)} = 1.7$	$J_{(2,1)} = 4.5$	$J_{(2,CH_3)} = 2.0$	5.58
H_3	4.61		6.44	
	$J_{(4,5)} = 6.3$	1.75	$J_{(2,3)} = 9.6$	1.91
	$J_{(4,6)} = 1.1$			
H_4		6.58		
	6.61	$J_{(4,6)} = 1.6$	6.98	6.98
		$J_{(4,5)} = 6.3$		
H_5	4.80		H_5−H_9 7.10−7.35 (M)	H_5−H_9 7.10−7.35 (M)
	$J_{(5,6)} = 6.7$	6.78		
H_6	4.88	6.76		
H_7		5.12		
	5.36	$J_{(7,9)} = 1.0$		
H_8		4.79		
	6.72−6.84	$J_{(8,9)} = 6.5$		
		$J_{(7,8)} = 6.9$		
H_9	6.72−6.84	4.47		

	14	**15**	**16**	**17**
R_1^{exo}	3.35	3.12	3.53	2.89
	$J_{(R_1,R_2)} = 25.7$	$J_{(R_1,R_2)} = 24.9$	$J_{(R_1,R_2)} = 7.3$	$J_{(R_1,R_2)} = 22.3$
R_2^{endo}	3.57	3.17		3.26
	$J_{(R_1,R_2)} = 25.7$	$J_{(R_1,R_2)} = 24.9$	1.30	$J_{(R_1,R_2)} = 22.3$
H_2				5.75
	5.49	5.51		$J_{(2,R_2)} = 3.96$
				$J_{(2,3)} = 10.16$
R_3				6.54
	1.63	1.80		$J_{(2,3)} = 10.16$
				$J_{(R_2,3)} = 2.15$
R_4		6.72		1.85
	4.87	$J_{(4,5)} = 7.13$		

Table 5 (Continued)

	14	15	16	17
H_5	~4.87	6.85 $J_{(4,5)} = 7.13$ $J_{(5,6)} = 8.9$		6.58 $J_{(5,6)} = 8.67$
R_6	5.47	7.48 $J_{(5,6)} = 8.9$	1.83	6.72 $J_{(5,6)} = 8.67$
R_7	2.18	2.20		5.28 $J_{(7,8)} = 6.80$
H_8	6.71 $J_{(R_7,8)} = 1.0$ $J_{(8,9)} = 7.11$	4.59 $J_{(8,9)} = 6.16$		4.72 $J_{(7,8)} = 6.80$
R_9	6.52 $J_{(8,9)} = 7.11$ $J_{(9,1)} = 1.70$	4.73 $J_{(8,9)} = 6.16$		1.59

[a] Asterisk indicates shifts measured in toluene-d_8. [b] **19** and **20** are ligands appearing in the course of decomposition of complexes **3** and **6**, respectively.

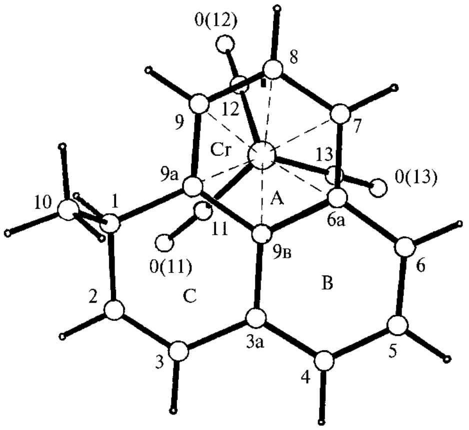


Figure 2. Projection of the $Cr(CO)_3$ group on the plane of the arene ligand.

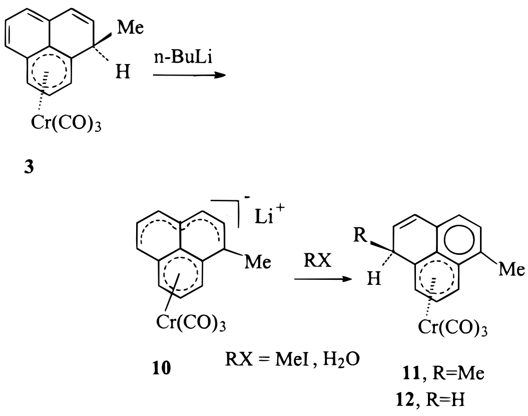
Table 6. Interatomic Distances *r* in Molecule 3 (Å) (Figure 1)

distances	*r*(*E*)	dist	*r*(*E*)
Cr−C(6a)	2.304(5)	C(1)−C(10)	1.530(9)
Cr−C(7)	2.229(6)	C(2)−C(3)	1.31(1)
Cr−C(8)	2.205(7)	C(3)−C(3a)	1.450(9)
Cr−C(9)	2.219(7)	C(3a)−C(4)	1.360(9)
Cr−C(9a)	2.241(6)	C(3a)−C(9b)	1.437(9)
Cr−C(9b)	2.273(6)	C(4)−C(5)	1.43(1)
Cr−C(11)	1.830(6)	C(5)−C(6)	1.33(1)
Cr−C(12)	1.826(6)	C(6)−C(6a)	1.425(8)
Cr−C(13)	1.829(6)	C(6a)−C(7)	1.43(1)
O(11)−C(11)	1.156(7)	C(6a)−C(9b)	1.443(9)
O(12)−C(12)	1.157(8)	C(7)−C(8)	1.38(1)
O(13)−C(13)	1.159(8)	C(8)−C(9)	1.40(1)
C(1)−C(2)	1.502(9)	C(9)−C(9a)	1.395(9)
C(1)−C(9a)	1.522(9)	C(9a)−C(9b)	1.420(9)

Table 7. Bond Angles *ω* in Molecule 3 (deg) (Figure 1)

angle	*ω*	angle	*ω*
C(11)CrC(12)	87.1(3)	C(6)C(6a)C(9b)	118.4(6)
C(11)CrC(13)	91.4(3)	C(7)C(6a)C(9b)	117.9(6)
C(12)CrC(13)	86.8(3)	C(6a)C(7)C(8)	120.9(6)
C(2)C(1)C(9a)	111.8(5)	C(7)C(8)C(9)	120.7(7)
C(2)C(1)C(10)	109.7(5)	C(8)C(9)C(9a)	120.8(6)
C(9a)C(1)C(10)	109.0(5)	C(1)C(9a)C(9)	120.1(5)
C(1)C(2)C(3)	124.6(6)	C(1)C(9a)C(9b)	120.1(5)
C(2)C(3)C(3a)	122.0(6)	C(9)C(9a)C(9)	119.5(6)
C(3)C(3a)C(4)	122.1(6)	C(3a)C(9b)C(6a)	118.7(5)
C(3)C(3a)C(9b)	117.8(5)	C(3a)C(9b)C(9a)	121.2(5)
C(4)C(3a)C(9b)	119.9(6)	C(6a)C(9b)C(9a)	120.1(5)
C(3a)C(4)C(5)	120.4(6)	CrC(11)O(11)	177.6(5)
C(4)C(5)C(6)	121.4(6)	CrC(12)O(12)	177.2(5)
C(5)C(6)C(6a)	121.0(6)	CrC(13)O(13)	179.5(6)
C(6)C(6a)C(7)	123.6(6)		

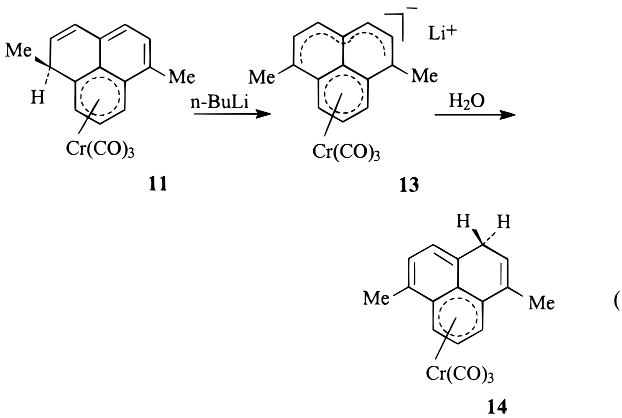
the geminal pair of methylene hydrogens. The Ofele reaction (eq 5) carried out for 3-d_1-phenalene gave a mixture of isotopomeric d_1-(**1**) and d_1-(**2**), both products containing the deuterium label equally distributed over the 1-*exo*, 1-*endo*, 3, 4, 6, 7, and 9 positions. The action of n-BuLi at −70 °C in THF on this mixture followed by quenching with H_2O resulted in a formation of complex **1** containing no deuterium in the 1-*exo* position, whereas deuterium distribution over other positions was not changed. Complex **3** possessing only on *endo*-hydrogen is deprotonated slower than **1** and **2** because of more difficult access of the base to the hydrogen. In this case, it is necessary to increase the temperature up to −40 °C. Anion **10** formed by deprotonation interacts with electrophyles exclusively at the C_6 *exo*-position affording **11** in the reaction with MeI and **12** with H_2O (eq 7).



(7)

At the same time, dimethyl complex **11** after deprotonation gives anion **13**, which then reacts with water at C_3 or C_4 to give **14** rather than at C_1 or C_6 to give *endo*-methyl complexes (eq 8).

The absence among the reaction products of eqs 7 and 8 other complexes except **11**, **12**, and **14** indicates that at low temperatures (−70 °C) no inter-ring haptotropic rearrangements take place in anions **9**, **10**, and **13**. The anion **10**, which was kept in THF at −20 °C for 2 h, was subsequently treated with H_2O and gave a mixture of all five possible isomers differing in the methyl group position in six-membered rings. This result shows that inter-ring haptotropic rearrangements in anion **10** take place at this temperature but proceed slowly on the



(8)

NMR time scale. These experiments will be described in detail in following publications. Parameters of ^{1}H and ^{13}C NMR of the complexes described above are presented in Tables 5 and 3, respectively.

2.6. Thermal Isomerization of Tricarbonylchromium Complexes of Phenalenes. Thermal isomerization of tricarbonyl chromium complexes of phenalenes has been investigated at different conditions. The experiments described earlier[23] were carried out in decane. The solutions of individual complexes **1** and **2** in this solvent were heated under an atmosphere of purified argon at temperatures from 80 to 140 °C during 10−15 h. The isomerization of the complexes took place to give an equilibrium mixture **1**:**2** = 87:13 (140 °C) regardless of the starting isomer. The mixture of the complexes was isolated by chromatography and analyzed by ^{1}H NMR. However, in a considerable number of such experiments the destruction of the complexes was observed accompanied by the formation of suspension of tiny greenish particles consisting probably of the chromium oxide. The extent of the destruction depended on the grade of argon purification, temperature, and duration of heating. All these factors influenced the reproducibility of the results. Therefore another technique was applied in this study. Thermal isomerizations were carried out in C_6F_6 or toluene solution (toluene-d_8 in the case of **3**) in the NMR tubes. Solubility of the complexes was high enough to determine precisely the concentrations of all reaction products up to very high degrees of interconversion. Special measures were carried out to purify solvents and to prepare samples (see Experimental Section) in order to avoid even traces of oxygen and moisture.

2.6.1. Thermal Isomerization of the Complex (5). Thermal isomerizations of **5** were studied in C_6F_6 at 80, 85, 90, 100, and 110 °C and in the mixture of toluene−C_6F_6 (9:1 w/w) at 90, 100, and 110 °C. For the determination of concentrations of products formed NMR ^{2}H{^{1}H} spectroscopy was used. The ^{19}F signal of C_6F_6 was used for locking in both cases. Since a considerable number of the signals of different intensities are overlapped in the spectra, the conventional procedure of integration does not provide desirable accuracy for the determination of concentrations. In this case, the technique based on the deconvolution of spectra was used. A complete spectral contour was presented as the sum of lines having the Lorenz shape along with the correction of the phase and magnet field inhomogenity (see Experimental Section for details). Unequivocal assignment of the signals in the NMR ^{2}H spectrum was done according to the corresponding proton spectra (see Table 1). Toluene is a very convenient solvent for the investigation of thermal isomerization of **5** by NMR ^{2}H-{^{1}H} due to the high enough solubility of the starting complex at room temperature. Moreover, due to the ASIS-effect the separations between signals are large enough for accurate integration, whereas a singlet of CH_2D and three singlets in the aromatic region (corresponding to three nonequivalent deuteron positions in the aromatic ring), arising from natural abundance deuterium in the solvent, can serve as reference signals both for the determination of the signals positions and for integration. The main drawback of this solvent is the side reaction of phenalene substitution in **5** for toluene. Such a reaction of ligand exchange in chromium tricarbonyl complexes is well-known and has been thoroughly investigated from the kinetic point of view.[24] As substitution reactions proceed at moderate temperatures quite slowly, the kinetics of thermal isomerizations, which take place simultaneously, can be investigated in detail. The evolution of the spectra of **5** on heating its toluene solution at 90 °C is presented in the Figure 3.

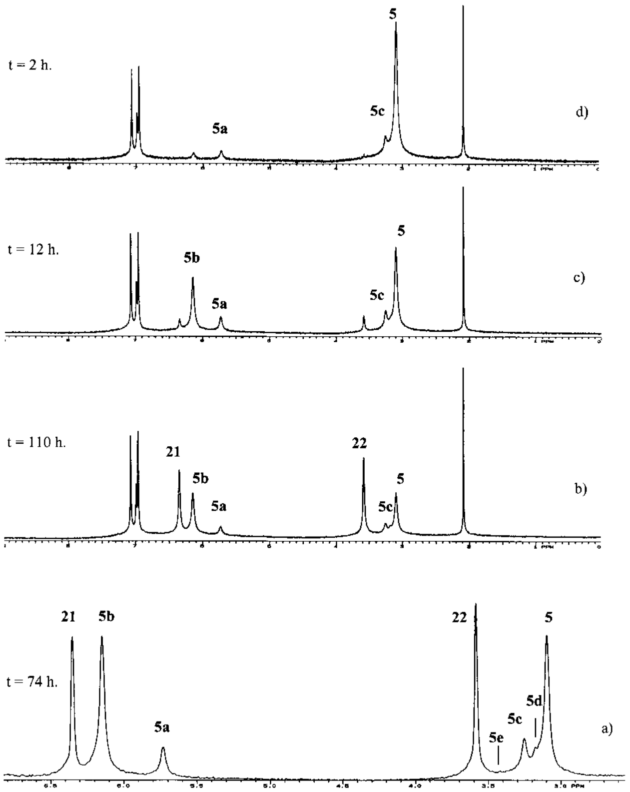


Figure 3. ^{2}H{^{1}H} NMR spectral evolution for the complex **5** in the course of thermal rearrangement.

On the first steps of interconversion a signal of (phenalene)chromium tricarbonyl containing deuterium in the position 3 (**5a**) initially appears along with the singlet of starting **5** (see Scheme 1). The complex **5a** is formed due to sequential [1,5]-sigmatropic shifts of *endo*-hydrogen in **5** (Figure 3c,d). At the same time the signal

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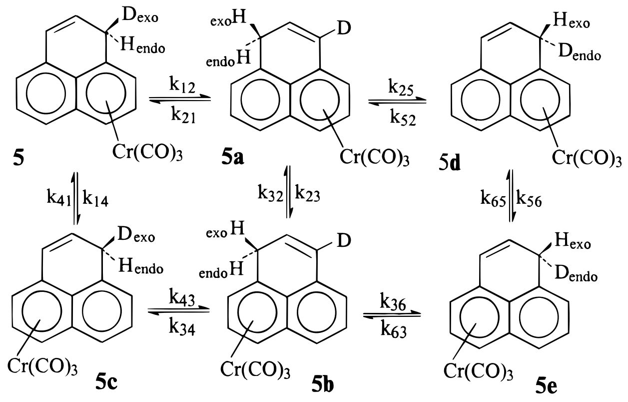
[23] Oprunenko, Yu. F.; Malyugina, S. G.; Babushkina, O. Ya.; Ustynyuk, Yu. A.; Ustynyuk, N. A. *Organomet. Chem. USSR* **1989**, *2*, 599−604.

[24] Traylor, K. G.; Stewart, K. J. *J. Am. Chem. Soc.* **1986**, *108*, 6977.

Scheme 1. Thermal Isomerization of Complex 5



$k_{12}=k_{34}$ $k_{23}=k_{41}$ $K_{12}\cdot K_{23}=1$ $K_{12}=1/K_{23}$
$k_{21}=k_{43}$ $k_{32}=k_{14}$ $k_{25}=k_{52}/K_{12}=k_{52}\,K_{23}$

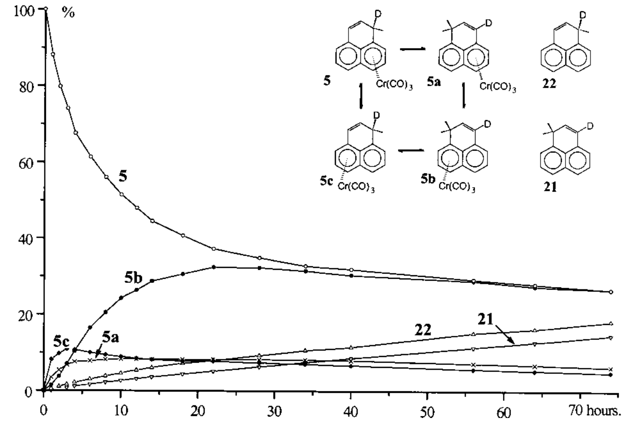


Figure 4. Kinetic curves of thermal isomerization of **5** and phenalene ligands appearing in toluene-d_8 at 110 °C.

of isomer **5c** appears at 3.22 ppm. This isomer forms as a result of an η^6,η^6-haptotropic shift of the $Cr(CO)_3$ group in **5**. Then the signal of isotopomer **5b** arises in low field at 6.13 ppm. **5b** appears due to the η^6,η^6-haptotropic shift of the $Cr(CO)_3$ group in **5a**. The signal intensity of **5b** in the ^{2}D NMR spectrum increases more rapidly in comparison with the intensity of the signal of **5a** (Figure 3b,c). After this the signals of isotopomers of phenalene-d_1 **21** and **22** appear. These substances are formed as a result of the ligand exchange reactions in **5**−**5e**. As a product of these ligand exchanges (η^6-toluene)chromium-d_8 tricarbonyl was detected by TLC. Finally after 20 h of heating the detailed analysis of the spectra allowed one to detect the signal of relatively low intensity belonging to (1-*endo*-d_1-phenalene)chromium tricarbonyl (**5d**) (Figure 3a). The formation of **5d** is thought to be a result from the [1,5]-shift of 1-*exo*-proton in **5a**. The evolution of concentrations of complexes in the reaction mixture is presented in Figure 4 including the concentration of complex **5d**, which arose at the final stage of isomerization. The signal intensity of the complex **5d** is enough for its reliable identification, but it is too low for kinetic calculations. The summary set of all the above processes is presented in Scheme 1.

It is worthwhile to note that ^{1}H NMR spectra of phenalene in toluene-d_8 and C_6F_6 were thoroughly analyzed with the use of double resonance and homonuclear Overhauser experiments to furnish reliable assignment of the signals of deuterium in isotopomers of phenalene-d_1. As a result of these experiments, some errors in assignment reported in a previous paper[25] were corrected.

The kinetic curves of interconversion of **5**, **5a**, **5b**, and **5c** are completely described in terms of the model of reversible reaction of the first order. There are no doubts that all these processes occur intramolecularly because if $Cr(CO)_3$ dissociates from the ligand it should be immediately trapped by toluene existing in a great excess. In the course of investigation of thermal isomerization of **5** in C_6F_6 additional confirmations of intramolecularity of [1,5]-migration of hydrogen atoms and of η^6,η^6-haptotropic rearrangement were obtained. It was shown that a 2-fold decrease in concentrations of **5** does not practically change the rates of these processes. Similarly, no changes in rates take place on the addition of 10 equiv of hexamethylbenzene which serves as effective trap of $Cr(CO)_3$. The data presented above show that thermal isomerization of chromium tricarbonyl complexes of phenalenes comprises several consecutive and parallel reversible and irreversible reactions. Therefore we need to choose a kinetic model and to determine its parameters. Traditionally with a view to confirm the uniqueness of solution, the following values are used as criteria: residual variance of calculated and experimental curves, standards, and pair linear correlation coefficients of searching parameters. However in the case of a complex kinetic scheme similar to that previously described, an indefinite solution is possible. In mathematic terms this may be expressed by the properties of the Jacobian: Jacoby's matrix of particular derivatives of the responses with respect to the parameters $Xi, j = \partial xi/\partial pj$. The rows of this matrix will not be independent. This means that the model is strictly locally unidentifiable and there is an infinitive field of parameter values for the same responses in the limits of experimental errors. Thus it is not sufficient to have only the criteria mentioned above for uniqueness of solution. In connection with this we used the calculation procedure[26] of numeric investigation of parameter identification of nonlinear models (see Experimental Section).

We tested different models of the kinetic scheme by means of this procedure. A necessity of such a type has appeared in particular when exchange reactions of phenalene on toluene in **5**, **5a**, **5b**, and **5c** were investigated. These processes were characterized by independent constants of pseudo-first-order. Nevertheless it was found that the values of the obtained constants were strongly correlated and the procedure we used strictly determined the unidentifiability of the model parameters. Therefore we accepted the exchange rates to be of equal values. This assumption has not resulted in any considerable deterioration of theoretical and experimental curve convergence. In the Table 8 are presented rate constants of the main processes shown on the Scheme 2 for the temperatures of 90, 100, and 110 °C in toluene.

Thermal isomerization of **5** in the solution of C_6F_6 occurs in many respects very similar to the above

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[25] Frendenberger, V.; Prinsbach, H.; Schneidenger, U. *Helv. Chim. Acta* **1967**, *50*, 1087.

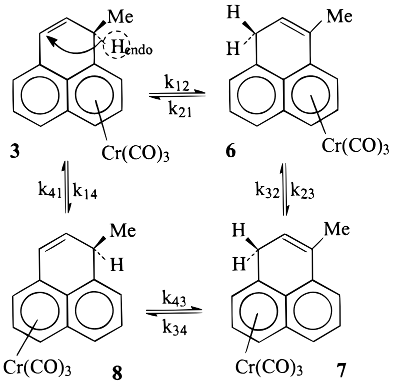
[26] Gorsky, V. G.; Katsman, E. A.; Klebanova, F. D.; Grigor'ev, A. A. *Theor. Exp. Chem.* **1987**, N2, 191−197.

Table 8. Rate Constants of Thermal Rearrangements of Tricarbonyl(η^6-D-phenalene)chromium at Different Temperatures in Toluene (s^{-1})

t, °C	10^4k_{12}	10^4k_{21}	10^4k_{23}	10^4k_{32}	10^6k_{25}	10^6k_{52}	K_{23}	10^6k_L[a]
90	0.05 ± 0.01	0.24 ± 0.01	0.52 ± 0.03	0.11 ± 0.03	0.77 ± 0.01	0.16 ± 0.01	4.79 ± 0.14	0.58 ± 0.01
100	0.17 ± 0.01	0.75 ± 0.01	0.97 ± 0.06	0.22 ± 0.06	1.59 ± 0.01	0.36 ± 0.01	4.41 ± 0.10	1.73 ± 0.03
110	0.53 ± 0.02	2.35 ± 0.02	2.88 ± 0.18	0.65 ± 0.18	7.73 ± 0.07	1.74 ± 0.07	4.44 ± 0.12	10.44 ± 0.19

[a] k_L = rate constant of complex **5** dissociation into the ligand.

Scheme 2. Thermal Isomerization of Complex 3



described process in toluene solution. Here also for the high degrees of interconvertion (6 h and more) the isotopomers of phenalene-d_1 appear. In this case it is hard to explain their appearance by the exchange reaction of phenalene ligand for C_6F_6. It is well-known that arenes containing electron-withdrawing substituents have reduced ability to coordinate the $Cr(CO)_3$ group and when the ring contains three such substituents, the synthesis of their chromium tricarbonyl complexes starting from arene by common methods in reactions with $Cr(CO)_6$, $(NH_3)_3Cr(CO)_3$, $(CH_3CN)_3Cr(CO)_3$, or $Py_3Cr(CO)_3$ become impossible.[27] Chromium difluorobenzenes tricarbonyls have been prepared from difluorobenzenes, but the attempts to introduce $C_6H_3F_3$ isomers in the synthesis failed.[28] Nevertheless chromium tricarbonyl complexes with several electron-withdrawing groups can be prepared by indirect methods using substitution reactions of a coordinated ligand. They are stable enough complexes. For example (η^6-hexachlorbenzene) chromium tricarbonyl was described.[29] We failed to detect (hexafluorobenzene)chromium tricarbonyl by TLC or by NMR spectroscopy. As was already mentioned, the addition of hexamethylbenzene (10-fold C_6Me_6 excess relative to **5**) into the solution of the complex has no considerable influence on the rates of free ligands formation. But in this case the formation of (hexamethylbenzene)chromium tricarbonyl was detected by TLC. Special precautions to exclude even traces of oxygen which is very soluble in C_6F_6 (storing of C_6F_6 in a vacuum line over a potassium mirror, vacuum transportation of the solvent directly to the sample tube just before use, multiply degassing the samples) were undertaken to provide the stability of the complex at high temperatures. The samples remained clear and the lines did not increase their widths, which indicates the absence of paramagnetic particles. The corresponding kinetic parameters are listed in Table 8.

A distinctive peculiarity of thermal isomerization of **5** in the solution of C_6F_6 is an appearance of isotopomers of d_1-(**1**) and d_1-(**2**) containing a deuterium label in the coordinated ring in the reaction mixture after the long duration of the process (100 h at 110 °C in pure C_6F_6, 200 h at 110 °C in C_6F_6 with the addition of hexamethylbenzene). The similar rearrangement in toluene does not afford these isotopomers. This fact supports the idea that in C_6F_6 solution coordinatively unsaturated and high reactive particles are formed which are capable to induce redistribution of the deuterium label through all 1-*exo*, 1-*endo*, 3, 4, 6, 7, and 9 positions of the phenalene ring in free phenalene as it takes place in the Ofele reaction (see above). After this (phenalene)-chromium tricarbonyl complexes with deuterium in the coordinated ring are formed in bimolecular reactions of such ligands. It is possible to suppose that C_6F_6 coordinates "hot $Cr(CO)_3$" particles by fluorine lone pairs but not by π-electron systems. Such collision complexes can exist in C_6F_6 solution as a dynamic system in which very fast exchange of C_6F_6 molecules permanently proceeds between the coordination sphere of chromium and bulk solvent.

The thermodynamic parameters of the processes shown in Scheme 1 for thermal rearrangements in toluene are summarized in Table 9.

2.6.2. Thermal Isomerization of Complex 3. Thermal isomerization of **3** in toluene-d_8 and hexafluorobenzene in the temperature range of 90−110 °C proceeds similarly to thermal isomerization of **5** with the formation at the first step of the isomer with the vinylic position of the methyl group (**6**) due to [1,5]-migration of the *endo*-hydrogen H_1. As the result of inter-ring shift of the $Cr(CO)_3$ group in **6**, isomer **7** appears. Similarly due to the shift of the chromium tricarbonyl group in **3** and H-*endo* in **7** correspondingly appears **8**. The interconversion of methyl-substituted complexes is shown in Scheme 2.

All signals of four isomeric complexes **3** and **6**−**8** were detected in the spectrum of the reaction mixture. The respective assignments of the signals were done by means of ^1H NMR with the use of double resonance and experiments on the nuclear Overhauser effect (NOE). Kinetic scheme models were investigated by means of the same procedure whereas the parameter calculations were performed by applying the same program as for **5**. Corresponding thermodynamic parameters are given in Table 10. It should be noted that we did not observed a [1,5]-sigmatropic shift of the *exo*-hydrogen in **7**. This process should lead to the complex of the structure with the *endo*-orientation of the Me group.

2.6.3. Thermal Isomerization of 14. Comparatively mild heating (80 °C) of **14** in decane leads to the formation of **15** (Scheme 3) due to the shift of the $Cr(CO)_3$ group. Complex **15** was isolated by TLC and characterized by ^1H NMR with the ratio **14**:**15** = 93:7 (after 18 h). If the heating is continued at the same

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Table 9. Activation Parameters of Thermal Rearrangements of Tricarbonyl(η^6-D-phenalene)chromium in Toluene

reacn	$\Delta G^{\ddagger}$ (kcal/mol)[a]	$\Delta H^{\ddagger}$ (kcal /mol)[b]	$\Delta S^{\ddagger}$ (cal/(deg·mol))[b]	E_a (kcal/mol)[b]	log A (s^{-1})[b]
1 → **2**	30.14 ± 0.05	31.88 ± 0.19	4.63 ± 0.50	32.61 ± 0.19	14.34 ± 0.11
2 → **1**	29.04 ± 0.01	30.75 ± 0.50	4.67 ± 1.37	31.51 ± 0.50	14.35 ± 0.30
2 → **3**	28.85 ± 0.04	22.84 ± 4.07	−15.79 ± 10.90	23.58 ± 4.12	9.88 ± 2.39
3 → **2**	29.76 ± 0.47	23.74 ± 3.49	−15.35 ± 9.34	24.48 ± 3.47	9.75 ± 2.05
2 → **5**	31.90 ± 0.01	31.01 ± 7.31	−1.78 ± 19.64	31.76 ± 7.32	12.94 ± 1.29
5 → **2**	33.01 ± 1.64	32.12 ± 6.60	−1.80 ± 17.72	33.86 ± 6.59	12.93 ± 3.87

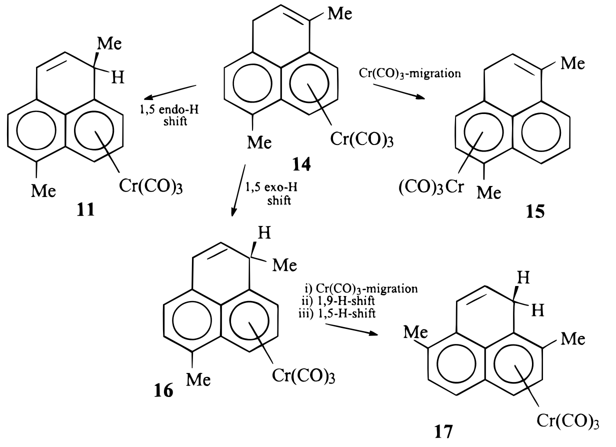
[a] At 100 °C, $\Delta G^{\ddagger} = 4.576T\,(10.32 + \log T - \log k)$. [b] Calculated by the least-squares method (LSM).

Table 10. Activation Parameters of Thermal Rearrangements of 3 in Toluene-d_8 (^{1}H NMR)

reacn	$\Delta G^{\ddagger}$ (kcal/mol)[a]	$\Delta H^{\ddagger}$ (kcal /mol)[b]	$\Delta S^{\ddagger}$ (cal/(deg·mol))[b]	E_a (kcal/mol)[b]	log A (s^{-1})[b]
1 → **2**	29.60 ± 0.02	29.72 ± 0.02	−1.76 ± 0.50	30.46 ± 0.03	13.39 ± 0.02
2 → **1**	30.48 ± 0.06	27.70 ± 8.60	−7.90 ± 2.3	28.44 ± 8.6	11.33 ± 5.15
2 → **3**	28.39 ± 0.05	27.04 ± 2.05	−3.43 ± 5.02	27.78 ± 2.05	12.58 ± 1.20
3 → **2**	29.25 ± 0.47	17.60 ± 3.20	−28.17 ± 7.20	18.40 ± 3.25	6.59 ± 1.89

[a] At 100 °C, $\Delta G^{\ddagger} = 4.576T\,(10.32 + \log T - \log k)$. [b] Calculated by the least-squares method (LSM).

Scheme 3. Product of Thermal Isomerization of 14 (Decane, 80−140 °C)



temperature for an additional 10 h, the isomer **11** is formed (ratio of isomers is **14**:**15**:**11** = 75:18:7). This isomer could be formed either directly from **14** by [1,5]-sigmatropic shift of *endo*-hydrogen or as the result of a two-step process in **15** comprising both [1,5]-sigmatropic shift of hydrogen and inter-ring haptotropic rearrangement of the Cr(CO)$_3$ group. Under more drastic conditions (140 °C, 18 h, decane) **14** yields **16**, which differs from **11** only by the *endo*-configuration of the methyl group at the sp^3-hybridized carbon atom of the phenalene ligand.

Complex **16** was identified by NOE measurement (irradiation of the corresponding doublet of the methyl group leads to an increase of the signal intensity in the range of coordinated ring protons). Additionally, from the reaction mixture complex **17** was isolated by TLC and characterized by NMR. This isomer contains both a methyl group in the aromatic rings and sp^3-hybridized carbon in the nonsubstituted ring with the Cr(CO)$_3$-group being located near the sp^3-carbon. It is important to note that a complex with such a structure can appear from **11** as a result of consecutive Cr(CO)$_3$ migration and 1,9- and 1,5-sigmatropic hydrogen shifts. The ratio of the complexes in the reaction mixture is **14**:**17**:**15**:**11**:**16** = 12:39:36:8:5.

2.6.4. Kinetic and Thermodynamic Parameters of Inter-Ring η^6,η^6-Haptotropic Rearrangements in (Phenalene)chromium Tricarbonyl Complexes. Using the data obtained it is possible to make reliable conclusions concerning η^6,η^6-haptotropic rearrangements in (phenalene)chromium tricarbonyl complexes. Thermodynamic and activation parameters obtained are in good agreement with the literature data available for chromium tricarbonyl complexes of substituted naphthalenes. For these complexes, the free activation energies are in the range of 26−30 kcal/mol.[5,30] The insensitivity of the processes to the change of solvent, variation in concentrations, and addition of the ligands capable to coordinate the transition metal as well as kinetic data leave no doubt that the migrations of the Cr(CO)$_3$ group in **5** and **3** proceed intramolecularly. In both equilibria presented in Schemes 1 and 2 the thermodynamically more stable isomers contain a Cr(CO)$_3$ group connected with the six-membered ring having an sp^3-hybridyzed carbon in the α-position which also corresponds to the relative stabilities reported for (naphthalene)chromium tricarbonyls.

2.6.5. Kinetic and Thermodynamic Parameters of [1,5]-Migrations of Hydrogen in (Phenalene)chromium Tricarbonyl Complexes. The data on the rates of [1,5]-sigmatropic migrations of hydrogen in (phenalene)chromium tricarbonyl complexes are of considerable interest. There are only indirect indications on the occurrence of this migration in free phenalene.[31] It takes place only under rigid conditions above 170 °C. However, it is possible to estimate the activation parameters of this process from the activation energy of SiMe$_3$ group migration in (trimethylsilyl)phenalene, which is 27 kcal/mol.[32] We have previously elaborated a simple scheme enabling the comparison of free activation energies of prototropic and metallotropic [1,5]-shifts in different cyclic systems with a satisfactory accuracy.[33] Using this approximation the value of 36 kcal/mol could be obtained for [1,5]-shifts of hydrogen in phenalene from the corresponding data for shifts of SiMe$_3$ which corresponds to the temperature interval under which migration of hydrogen takes place. Comparing this value with free activation energies for [1,5]-sigmatropic rearrangements of hydrogen in **3** and **5**, one can note a

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sharp decrease in the activation barriers which is more pronounced for *endo*-hydrogen. This effect is commonly observed for the complexes of transition metals with monocyclic dienes and trienes.[34] According to the widely accepted view,[35] such rearrangements typically proceed in these complexes via the intermediate formation of agostic bonds and hydride intermediates.

As it was shown above, distance Cr−H(*endo*) and Cr−C_1 are too long for the realization of the agostic interaction in the ground state of **3** and **5**. But it is possible that it takes place in the transition state, and this could be elucidated by a detailed quantum chemical investigation. It is quite important to note that [1,5]-migration of the *exo*-hydrogen atom was firmly established in **5**. So it can be stated that the coordination of the $Cr(CO)_3$ group to phenalene considerably facilitates the process of [1,5]-sigmatropic shifts of hydrogen. This is probably explained by the considerable charge separation in the transition state. The hydrogen atom in the transition state carries a high positive charge. Possibly a powerful electron withdrawal effect of the $Cr(CO)_3$ group has to promote such polarization thus increasing the mobility of the hydrogen atom. Detailed DFT quantum chemical calculations, which were started by us recently, will shed more light on this problem. We have not carried out the detailed investigation of the exchange reactions of phenalene ligand in **3** and **5** for other arenes. But it is possible to note that rates observed are in a good agreement with the data presented in the literature.[24]

3. Conclusions

It was found in the present study that in the course of heating of 1-*exo*-substituted (phenalene)chromium tricarbonyl complexes few concurrent processes simultaneously occur. The intramolecular process that is characterized by the smallest activation barrier and proceeds most rapidly is the η^6,η^6-inter-ring haptotropic rearrangement resulting in interconversion of isomers differing by the position of chromium tricarbonyl groups in the six-membered rings of the phenalene ligand. Suprafacial [1,5]-shift of hydrogen atom H(1-*endo*) proceeds with a slightly greater activation energy. This process does not involve the formation of agostic and hydride intermediates. Concurrent intermolecular ligand exchange processes in complexes with aromatic solvents (toluene, C_6F_6) and the same processes with resulting free substituted phenalenes lead to the complexes containing a label in the coordinated ring. Together these processes lead to the redistribution of the label through the positions 1, 3, 4, 6, 7, and 9. Detailed analysis of the data makes it possible to find that migration of H(1-*exo*) proceeds slower than the corresponding migration of H(1-*endo*).

4. Experimental Section

All operations, except thin-layer chromatography, were performed in a purified argon atmosphere. All solvents (ether, decane, THF, hexafluorobenzene) were purified by refluxing over K/Na alloy and distilled from it under argon just prior use. If not specially mentioned, chromatography was carried out on silica 40/100 μ from Chemapol (Bratislava, Czech Republic). IR spectra were recorded on a UR-20 spectrometer from Carl Zeiss in heptane. NMR spectra were recorded on a Varian VXR-400 spectrometer (400 MHz for ^1H). The assignments of the signals in ^1H NMR spectra were done with the help of double resonance (in some cases COSY techniques was used) and Overhauser effect measurements by means of the NOEDIF procedure which is included in the software of the spectrometer. The assignment of the signals in ^{13}C NMR spectra were done with the help of DEPT and by the comparison with the spectra of model compounds. Mass spectra were recorded on a MAT-112S under an electron impact of 70 eV.

Synthesis of the Complexes 1 and 2. An amount of 13.8 g (97 mmol) of freshly distilled $BF_3{\cdot}OEt_2$ was added to a mixture of 5.7 g (21.4 mmol) of phenalene and 8 g (21.4 mmol) of $Cr(CO)_3Py_3$ in 75 mL of ether at −10 °C. After the stirring at 25 °C for 1 h, water was added. Solution was washed three times with water and dried over anhydrous $MgSO_4$. After the ether was removed in vacuo, the residue was chromatographed on a 3 × 40 silica gel column using petroleum ether/benzene mixture as eluent. From the red zone 3.8 g (44%) of the mixture **1** and **2** was obtained after recrystallization (benzene/heptane), with the ratio **1**:**2** = 40:60 (according to ^1H NMR data). The complete separation of more mobile **2** from **1** was done with the help of thin-layer chromatography on silica using as eluent the mixture 10:1 hexanes−ether. Complex **1** crystallizes from heptane as red prisms, mp 168−170 °C. Literature data: 116−118 °C.[14] Both isomeric complexes **1** and **2** exhibit in electron impact (EI) mass spectra molecular ion peaks of moderate intensity (*m*/*e* 302), fragmentation of which occurs through consecutive release of CO groups. The difference in fragmentation of **1** and **2** consists of the fact that in the mass spectrum of **2** a low-intensity peak of M − CO (*m*/*e* 274) is observed, whereas it is absent in the mass spectrum of **1**. The most intensive peak in the mass spectra of the both isomers belongs to Cr (*m*/*e* 52), followed by *m*/*e* 218 (M − 3CO) and *m*/*e* 165 (M − $HCr(CO)_3$ − phenalenyl cation). Mass spectra of **1**: *m*/*e* 302 (20.47%, M^+), 246 (12.32%, M − 2CO), 218 (70.13%; M − 3CO), 165 (52.46%, M − $HCr(CO)_3$), 52 (100%, Cr). IR spectra (ν_{CO} of **1** or **2**): 1904, 1918, 1976 cm^{-1}. ^1H and ^{13}C NMR data are presented in Tables 1−3. Anal. Calcd for a mixture of **1** and **2**, $C_{16}H_{10}CrO_3$: C, 62.60; H, 3.36; Cr, 17.65. Found: C, 63.58; H, 3.31; Cr, 17.22.

Synthesis of the Li Salt of 9. The mixture of **1** and **2** in THF was treated at −70 °C with BuLi in hexane, and the ratio of (**1** + **2**)/BuLi = 1:3. The stirring of the reaction mixture at −70 °C for 15 min results in the appearing of the deep red color of the Li salt of **9**. ^1H NMR data are presented in Table 4.

Synthesis of the Complexes 3−5 and 1 from 9. To the solution of **9** obtained from 0.2 g (0.49 mmol) of the mixture of **1** and **2** in 30 mL of THF was added at −70 °C 0.1 mL of H_2O in 5 mL of THF. The solvent was slowly heated to ambient temperature, solvent was removed in vacuo, and residue was chromatographed on the plates with silica gel with the use of the mixture 10:1 hexanes−ether as eluent. A total of 0.18 g (90%) of the complex **1** was obtained.

Similarly from 0.16 g (0.4 mmol) of the mixture of **1** and **2** and 0.1 mL of D_2O, 0.15 g (93%) of the complex **5** was obtained whereas from 0.17 g (0.42 mmol) of the mixture of **1** and **2** and 1.2 g of MeI 0.1 g (57%) of the complex **3** was obtained after TLC.

3 crystallizes from hexane as red plates, mp 153−154 °C. Mass spectra (*m*/*e*): 316 (24.1%, M^+); 260 (18.8%, M − 2CO); 246 (11.65%; M − CO − CH_2 − CO); 233 (31.44%, M − 2CO − C_2H_3); 232 (89.56%, M − 3CO); 230 (25.3%, M − 3CO − 2H); 217 (16.5%, M − 3CO − Me); 180 (12.61%, M − $Cr(CO)_3$); 179 (55.29%, M − $HCr(CO)_3$); 178 (10.32%, M − $H_2Cr(CO)_3$); 165 (56.68%, M − $CH_3Cr(CO)_3$); 52 (100%, Cr). ^1H and ^{13}C data are presented in Tables 5 and 3. IR spectrum (ν_{CO}): 1905, 1918, 1977 cm^{-1}.

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By the interaction of **9** obtained from 0.20 g (0.5 mmol) of the mixture of **1** and **2** with stored over copper chips and freshly distilled from potassium carbonate butyl iodide (0.18 g, 1 mmol), 0.20 g (70%) of complex **4** was obtained. Mass spectra of **5** (*m*/*e*): 303 (17.13%, M$^+$); 247 (13.29%, M − 2CO); 220 (22.79%; M + 1 − 3CO); 219 (52.39%, M − 3CO); 218 (14.54%, M − 1 − 3CO); 166 (31.48%, M − HCr(CO)$_3$); 165 (18.48%, M − 1 − HCr(CO)$_3$); 52 (100%, Cr). IR spectrum (ν_{CO}): 1905, 1918, 1977 cm^{-1}.

Preparation of Anion 10 by the Deprotonation of (1-*exo*-Methylphenalene)chromium Tricarbonyl (3). The preparation of **10** was carried out similarly to the synthesis of anion **9** (see above) by the reaction of the solution of **3** in THF (0.3−0.5 mmol, 15−20 mL THF) with a hexane solution of n-BuLi taken in 3-fold excess relative to **3**. The formation of the lithium salt of **10** (deep red color of the mixture) was complete after 15 min of stirring at −40 °C.

Protonation and Methylation of 10. Protonation and methylation of **10** was carried out similarly to analogous reactions of anion **9** (see above). From 0.12 g (0.29 mmol) of **10** and 0.1 mL of H$_2$O, 0.09 g (75%) of the complex **12** was obtained. ^{1}H and ^{13}C NMR data are presented in Tables 5 and 3. IR (ν_{CO}): 1906, 1918, 1978 cm^{-1}.

Similarly from 0.2 g (0.48 mmol) of **3** and 1.4 g of MeI, 0.18 g (87%) of the complex **11** was obtained as red needles. Mp: 120−122 °C (from pentane). Mass spectrum (*m*/*e*): 330 (14.24%, M$^+$); 274 (14.26%, M − 2CO); 247 (11.7%, M − 2CO − C$_2$H$_3$); 246 (87.8%, M − 3CO); 244 (28.2%, M − 3CO − 2H); 231 (12.94%, M − 3CO − CH$_3$); 230 (12.56%, M − 3CO − CH$_2$); 194 (12.7%, M − Cr(CO)); 193 (59.13%, M − HCr(CO)); 179 (100%, M − CH$_3$Cr(CO)3); 178 (30.06%, M − HCr(CO)$_3$ − CO$_3$); 165 (5.36%, M − CH$_3$Cr(CO)$_3$ − CH$_2$); 152 (7.88%, M − Cr(CO)$_3$ − C$_3$H$_6$); 52 (79.11%, Cr). ^{1}H and ^{13}C NMR data are presented in Tables 5 and 3. IR (ν_{CO}): 1905, 1914, 1975 cm^{-1}.

Synthesis of the Complex 14. Deprotonation of **11** and treatment of the appeared anion **13** with water were carried out as was described above for the synthesis of the complexes **1** and **12**.

From 0.15 g (0.35 mmol) of **11**, 0.12 g (80%) of the complex **14** was obtained. TLC was carried out on the plates with silica using 20:1 hexanes−ether as eluent, and then column chromatography was done with “Silpearl” in 100:1 and 50:1 hexanes−ether as eluent. ^{1}H NMR data are presented in Table 5. IR (ν_{co}): 1904, 1917, 1978 cm^{-1}.

Thermal Isomerizations of (Phenalene)chromium Tricarbonyl Complexes. Decane, toluene, toluene-*d*$_8$, and C$_6$F$_6$ were freed from water and oxygen by storing on a potassium mirror, further distillation, and repeating three times the freeze−pump−thaw cycle at 10^{-5} mm in a vacuum system.

Complexes 5 and 3. The solutions of 12 mg of **5** or **3** in C$_6$F$_6$ (in some cases to hexafluorobenzene was added toluene to increase the solubility of the complex and to increase considerably the differences in chemical shifts thus facilitating precise integration of the spectra) were heated in sealed 5 mm or 10 mm o.d. standard sample tubes (respectively for registration of ^{1}H and ^{2}D NMR spectra) in the temperature range from 80 to 120 °C in a thermostat with the accuracy of temperature maintained ±0.5 °C. After corresponding time intervals sample tubes were lifted out of the thermostat and cooled rapidly to ambient temperature with cold water, and then ^{1}H and ^{2}D NMR spectra were recorded for these samples. For the stabilization of the resonance conditions in the course of spectra registration the corresponding signals of deuterium from TMS-*d*$_{12}$ and fluorine from C$_6$F$_6$ were used. The special probe was created by Dr. V. A. Roznyatovsky for the registration of the ^{2}D NMR spectra with the high accuracy and for locking on ^{19}F. For the complex **3** when measurements were carried out in toluene-*d*$_8$ the control for the concentration changes was done with the help of ^{1}H NMR and locking on ^{2}D from the solvent whereas all other operations were carried out similarly to described above.

To 100 mg of the complex at 50 °C decane was added until complete dissolution of the complex, and solvent was heated at fixed temperatures for the corresponding time intervals. To change decane for hexane the solution was placed on a small column with silica and the complex was eluted with benzene. The crystals obtained after recrystalization from the mixture of benzene−heptane were washed with pentane and dried in a vacuum, and product ratios were determined by ^{1}H and ^{2}D NMR.

Thermal Isomerization of 14. A solution of 0.1 g of **14** in 20 mL of decane was heated for 18 h at 80 °C. After the treatment described above, the residue was chromatographed on the column with “Silpearl” with the hexanes−ether mixture gradually increasing the ether proportion from 1 to 2%. A 0.01 g (10%) amount of complex **15** was obtained. The sample of the complex **15** prepared as described above was heated in decane at 140 °C for 18 h. After evaporation of decane complexes were chromatographed on Silufol plates with hexanes−ether (30:1). Three deep red bands were separated. Two upper bands contained according to ^{1}H NMR complexes **15** and **17** whereas the lower band contained a mixture of complexes **11**, **14**, and **16**. ^{1}H and ^{13}C NMR data are presented in Tables 5 and 3.

X-ray Crystallographic Study of (3). An X-ray crystallographic study was carried out on an automatic four-round “Hilger & Watts” diffractometer at 20 °C (Mo Kα irradiation), and calculations were performed on an “Eclipse S/200” computer with the help of INEXTL[36] software. Crystallographic data: C$_{17}$H$_{12}$CrO$_3$, monoclinic, $a = 12.059(1)$ Å, $b = 8.665(1)$ Å, $c = 13.711(1)$ Å, $\beta = 101.48(1)°$, $V = 1404.0(2)$ Å^3, space group $P2_1/c$, $Z = 4$, $d_{calc} = 1.50$ g/cm, μ(Mo Kα) = 8.6 cm^{-1}. The intensities of 902 independent observed reflections with $I > 2\sigma(I)$ were measured by the method of $\theta/2\theta$-scanning. The structure was solved by the heavy-metal method. All non-hydrogen atoms were refined by the full-matrix least-squares technique in anisotropic approximation (taking into account atoms H which were fixed in calculated positions): $R = 0.032$, $R_w = 0.029$; weighting scheme $W = (\sigma^2_F + 10^{-4}F^2)^{-1}$; merit coefficient $S = 1.28$. Coordinates of the atoms and equivalent isotropic heat factors $B_{eq} = {}^1/_3\sum_{ij}B_{ij}a_i{}^*a_i{}^*(a_ia_j)$ are presented in the Supporting Information.

Procedure for Determination of Kinetic Parameters. Some analytical expressions involving the base of the algorithm[26] are briefly described here. The smooth dependence of current concentrations of searching parameters allows one to determine the numeric Jacobian $X(k)$ of $N{\cdot}s$ dimension, where N is the total number of responses and s is the number of searching parameters,

$$X_{ij} = \partial x_i/\partial k_j$$

The informational Fisher's matrix could be written by the following:

$$M(k) = X^T(k){\cdot}D^{-1}{\cdot}X(k)$$

Here D is the dispersion matrix of responses. In the common case the range, n, of the matrix $X(k)$ is satisfied by the relation $n \le s$.

Matrix $M(k)$ is degenerate, and the vector of searching parameters cannot be obtained unambiguously if the local unidentifiability is present, $n < s$. At the same time a numeric reparametrization is possible with the new set of parameters, q, and n as their number. A new Fisher's matrix

$$M(\theta) = X^T(\theta){\cdot}D^{-1}{\cdot}X(\theta)$$

can be calculated for the set q. The connection between the

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matrixes is given by the equation

$$M(\theta) = (B)^T\cdot M(k)\cdot B^{-1}$$

where the B matrix fulfills the transformation of the Jacobian $X(k)$ to the form that the first n columns would be basic ones, and the B matrix looks like the next expression:

$$B = \partial q/\partial k$$

The calculation procedure allows one to obtain the B matrix by a numeric way, and the form of this matrix indicates the type of identifiability of the model in question. If searching parameters can be identified unambiguously, then the corresponding column and row of the B matrix consist of one element not equal to zero; their values are equal to units. This condition is not fulfilled for the old set if the parameters cannot be identified. The last have more than one not equal to zero derivatives with respect to the new parameters. Thus we have the possibility to distinguish cases of uniqueness for problem solution.

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Supporting Information Available: A table of atomic coordinates and U values (1 page). Ordering information is given on any current masthead page.

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