

Tricarbonylchromium complexes with phenalene. Synthesis, structure, and thermal rearrangements

N. G. Akhmedov,^a E. A. Katsman,^a S. G. Malyugina,^a V. I. Mstislavsky,^a Yu. F. Oprunenko,^a V. A. Roznyatovsky,^a
Yu. A. Ustynyuk,^{a*} A. S. Batsanov,^b and N. A. Ustynyuk^b

^aDepartment of Chemistry, M. V. Lomonosov Moscow State University,
Vorob'evy Gory, 119899 Moscow, Russian Federation.

Fax: 007 (095) 939 0283. E-mail: yopr@nmr.chem.msu.su

^bA. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.

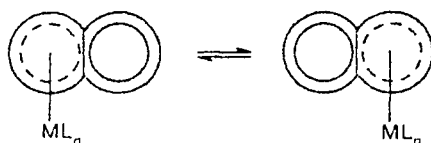
Fax: 007 (095) 135 5085

The reaction of phenalene with $\text{Cr}(\text{CO})_3\text{Py}_3\cdot\text{BF}_3\cdot\text{OEt}_2$ afforded a mixture of two isomeric complexes, tricarbonyl(6a,7-9,9a,9b- η^6 -phenalene)chromium (1) and tricarbonyl(3a,6a,9b,4-6- η^6 -phenalene)chromium (2). Deprotonation of the mixture of compounds 1 and 2 followed by treatment with MeI, BuⁿI, or D₂O gave complexes *exo*-1-R-1 (3-5: R = Me (3), Buⁿ (4), or D (5)). The molecular geometry of complex 3 was established by X-ray structural analysis. Heating of complex 5 in toluene or C₆F₆ at 90–110 °C resulted in redistribution of deuterium among positions *exo*-1, *endo*-1, and 3 in the resulting complexes of types 1 and 2 via sigmatropic shifts of the H_{*exo*} and H_{*endo*} atoms in the nonaromatic ring as well as via inter-ring migrations of the tricarbonylchromium group. In the case of 3, the methyl label is distributed among positions *exo*-1 and 3 to form isomeric complexes with similar structures (*exo*-1-Me-2 (6), 3-Me-2 (7), and 3-Me-1 (8), respectively) via processes analogous to those observed in the case of isomerization of compound 5 (except for migration of the H_{*exo*} atom). The mechanisms of these rearrangements are discussed.

Key words: phenalene, tricarbonylchromium complexes, intra- and intermolecular haptotropic rearrangements; X-ray structural analysis; ¹H and ¹³C NMR spectra.

π -Complexes of transition metals with unsaturated and aromatic ligands, in which only part of the ligand positions accessible for coordination are involved in bonding with the metal atom, are characterized by high lability, which is manifested in the variety of dynamic processes that occur in these compounds. Among them, intramolecular haptotropic rearrangements, which occur with migration of the metal atom from one position of the ligand to another (Scheme 1), have received the most study (see, for example, reviews 1–6).

Scheme 1



In some cases, the migration of the M metal atom is accompanied by reversible migrations of H atoms (or the R group) between the M atom and the *endo*-positions of

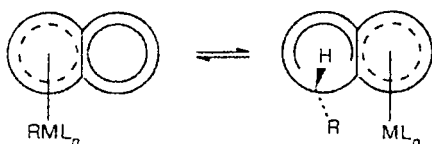
the unsaturated ligand. These processes, which are intramolecular reactions of oxidative addition and reductive elimination, are generally considered from the viewpoint of activation of C–H_{*endo*} bonds. The ease of both types of rearrangements is closely associated with the catalytic activity of the complexes. In this connection, the study of their intramolecular dynamics is of obvious theoretical and practical interest (see reviews 7 and 8).

Inter-ring haptotropic rearrangements in the course of which a ML_{*n*} organometallic or carbonylmetal group migrates along the plane of the π -system of the ligand from one ring to the other are typical of complexes of transition metals with polycyclic aromatic ligands. Presently, migrations of the ML_{*n*} group between two six-membered aromatic rings in derivatives of naphthalene, acenaphthylene, biphenylene, and biphenyl (η^6, η^6 -rearrangements) as well as between the five-membered and six-membered rings in complexes with indenyl and fluorenyl anions and their heteroanalogs (η^6, η^5 -rearrangements) are well studied.^{4–6} Rapid reversible migrations of the Mn(CO)₃ group between two five-membered rings in derivatives of indeno[1,2-*a*]indene,⁹ the rapid migration of the η^3 -bonded PdL₂ fragments from

one six-membered ring of the phenalenyl system to the other,¹⁰ and migrations of the η^2 -bonded $\text{Ni}(\text{PR}_3)_2$ fragments between the six-membered rings of 5-alkyl- and 5,10-dialkylanthracenes were also reported (see Ref. 11 and references therein).

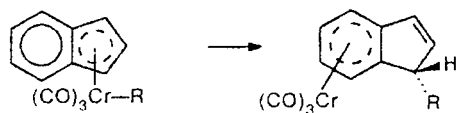
"Ricochet" rearrangements (Scheme 2)⁵ comprise a special class of inter-ring haptotropic rearrangements. In these processes, migrations of the metal atom from one ring to the other are accompanied by simultaneous migrations of the H atom or the alkyl group from the metal atom to one of the *endo*-positions of the ligand.

Scheme 2



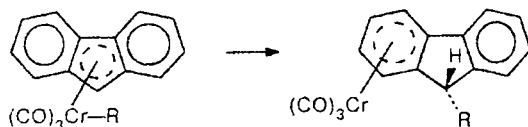
We found the first examples of "ricochet" rearrangements (see Scheme 2) in the case of thermal isomerization of σ -alkyl(η^5 -indenyl or fluorenyl)tricarbonyl complexes of chromium^{12,13} (Schemes 3 and 4).

Scheme 3



R = Me, CH_2Ph , H, D

Scheme 4



R = H, Me, D

When studying thermal rearrangements of complex *exo*-1-D-1,¹² we found that the change in the position of the deuterium label occurs along with the usual η^6, η^6 -inter-ring migration of the $\text{Cr}(\text{CO})_3$ fragment, which was observed in the case of naphthalene derivatives. This may be associated with the direct participation of the metal atom in the process (which involves intermediate formation of the $\text{H}-\text{ML}_n$ group), which occurs as the "ricochet" inter-ring rearrangement (see Scheme 2). However, the possibility of sigmatropic shifts

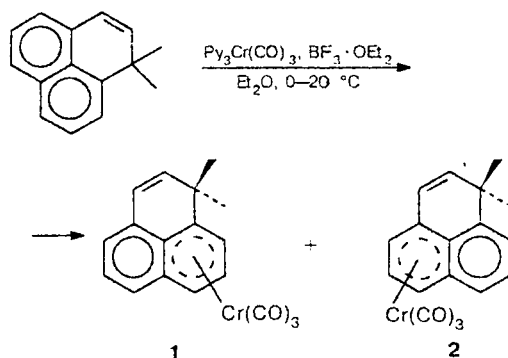
of H atoms without the participation of the metal atom must not be ruled out. With the aim of studying these processes in detail and revealing the extent to which the metal atom is involved in them, in this work we synthesized a series of new tricarbonylchromium complexes with substituted phenalenes and studied their structures and the kinetics of thermal rearrangements.

Results and Discussion

Synthesis of isomeric tricarbonyl(η^6 -phenalene)chromium complexes

Tricarbonyl(6a,7-9,9a,9b- η^6 -phenalene)chromium (**1**) was first synthesized by the reaction of $\text{Cr}(\text{CO})_3(\text{MeCN})_3$ with phenalene at 45 °C and isolated by chromatography and sublimation in 21% yield.¹⁴ We synthesized complex **1** by Öfele's reaction.¹⁵ As a result, two isomers **1** and **2** were obtained in a ratio of 2 : 3 in a total yield of 44% (Scheme 5).

Scheme 5



Complexes **1** and **2** were separated chromatographically and characterized by spectral methods (see the Experimental section).

In the ^1H NMR spectrum of compound **1**, the AB portion of the complex spin system (Fig. 1) in the highest field belongs to the geminal pair of the protons at the C(1) atom. Below is demonstrated that transformation of complex **1** to anion **9** under the action of Bu^nLi followed by treatment of **9** with D_2O yields exclusively complex *exo*-1-D-1 (Scheme 6). In this case, the high-field signal in the AB part of the NMR spectrum of complex **1** (in C_6D_6) disappears, which allows one to assign this signal to the *exo*-proton at the C(1) atom. The assignment of other signals was made using the double resonance method and Overhauser effect experiments.

The solvent has a pronounced effect on the positions of the signals in the ^1H NMR spectra of the tricarbonylchromium complexes with phenalene. In particular, in

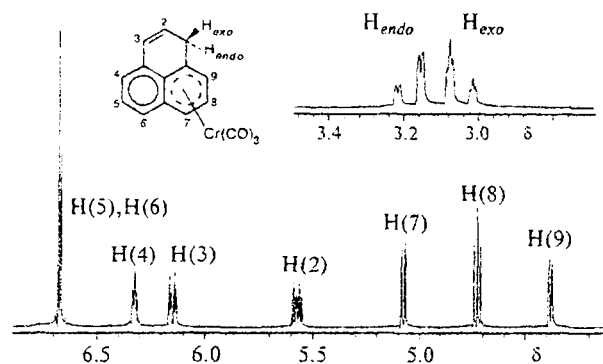


Fig. 1. ^1H NMR spectrum (400 MHz) of tricarbonyl(6a,7-9.9a,9b- η^6 -phenalene)chromium (**1**) in C_6D_6 .

going from C_6D_6 to C_6F_6 , all resonance signals shift downfield by 0.5–1.1 ppm. Therefore, hexafluorobenzene does not exhibit the ASIS effect (the aromatic solvent-induced shift)¹⁶ typical of other aromatic sol-

vents. The largest downfield shift is observed for the signal of the *exo*-protons at the C(1) atom (δ 1.09 and 0.92 for complexes **1** and **2**, respectively). In the corresponding short-lived "collision complexes,"¹⁷ these protons are directed toward the deuterobenzene molecules located above the plane of the six-membered ring coordinated to the Cr atom. It is interesting that the signals of the *exo*- and *endo*-protons in the spectrum recorded in C_6F_6 change places. A complete analysis of the spectra of complexes **1** and **2** in C_6F_6 was carried out using the double resonance method and iterative calculations. The obtained parameters are given in Tables 1 and 2. The values of δ ^{13}C for complexes **1** and **2** are listed in Table 3. The assignment of the signals in the ^{13}C NMR spectra was made using the DEPT procedure.

The signals of the H and C atoms of the six-membered rings in complexes **1** and **2**, which are involved in coordination to the $\text{Cr}(\text{CO})_3$ fragment, undergo upfield shifts typical of π -complexes of transition metals. In this

Table 1. Chemical shifts in the ^1H NMR spectra of complexes **1** and **2**

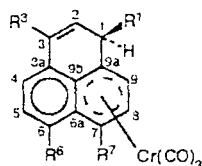
Compound	Solvent	δ									
		H(1) _{exo}	H(1) _{endo}	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)
1	C_6F_6	3.01	3.164	5.60	6.20	6.33	6.68–6.72	6.68–6.72	5.11	4.76	4.41
	C_6D_6	4.01	4.02	6.30	6.66	6.98	7.37	7.33	5.90	5.64	5.37
2	C_6D_6	3.26	3.54	5.58	5.73	4.52	4.76	5.26	6.74–6.85	6.74–6.85	6.45
	C_6F_6	4.18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

Table 2. Spin-spin coupling constants (J_{HH}) in the ^1H NMR spectra (400 MHz) of complexes **1** and **2** (in C_6F_6)

Atom	Compound	$J/\text{Hz} (\pm 0.05)$									
		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	–24.94	—	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. Chemical shifts in the ^{13}C NMR spectra of the tricarbonylchromium complexes with phenalene and its derivatives (in C_6D_6)

Com- pound	δ (± 0.02)															
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(3a)	C(6a)	C(9a)	C(9b)	CO	Me	CH_2
1	30.68	123.69	125.97	126.76	128.38	129.23	88.77	89.74	93.02	133.62	100.78	103.75	105.45	232.99	—	—
2	31.26	129.00	128.65	88.87	89.86	93.12	126.11	125.79	124.57	101.68	99.70	135.75	106.71	232.99	—	—
3	35.81	124.45	124.91	127.37	129.81	135.12	89.81	90.03	93.69	133.92	100.14	106.23	110.38	233.48	27.23	—
4	41.06	123.84	125.61	126.73	129.21	133.19	89.33	89.39	92.99	133.49	100.05	109.16	100.58	233.93	13.99	23.03 27.30 40.23
11	35.44	123.95	124.51	128.46	133.15	133.98	85.88	89.56	92.91	131.14	99.72	110.68	105.09	232.98	19.37 26.82	—
14	30.96	128.40	133.00	92.01	87.32	86.03	128.88	125.88	125.32	101.69	102.54	133.32	105.88	233.07	18.26 18.96	—

**1–4, 11, 14**

1: $\text{R}^1 = \text{R}^3 = \text{R}^6 = \text{R}^7 = \text{H}$
2: $\text{R}^1 = \text{R}^3 = \text{R}^6 = \text{R}^7 = \text{H}$
3: $\text{R}^1 = \text{Me}, \text{R}^3 = \text{R}^6 = \text{R}^7 = \text{H}$

4: $\text{R}^1 = \text{Bu}^n, \text{R}^3 = \text{R}^6 = \text{R}^7 = \text{H}$
11: $\text{R}^1 = \text{R}^6 = \text{Me}, \text{R}^3 = \text{R}^7 = \text{H}$
14: $\text{R}^1 = \text{R}^6 = \text{H}, \text{R}^3 = \text{R}^7 = \text{H}$

Note. In molecules **2** and **14**, the $\text{Cr}(\text{CO})_3$ fragment is bonded to the C(3a), C(4), C(5), C(6), C(6a), and C(9b) atoms.

case, the absolute values of the spin-spin coupling constants of the protons of the coordinated nuclei decrease substantially. This is most pronounced with the long-range spin-spin coupling constants, which is indicative of a substantial shift of the π -electron density to the metal atom. The difference in the spin-spin coupling constants of the $\text{H}(1)_{\text{exo}}$ and $\text{H}(1)_{\text{endo}}$ atoms are also typical. Taking into account the sign, the values of the $^3J_{\text{H}(1),\text{H}(2)}$, $^4J_{\text{H}(1),\text{H}(3)}$, and $^4J_{\text{H}(1),\text{H}(9)}$ constants for the *exo*-protons are slightly lower than those for the *endo*-protons (3.65 and 4.57 Hz; -2.42 and -1.99 Hz; -0.91 and -0.81 Hz, respectively), which can be used for the stereochemical assignments.

Öfele's reaction with 3-D-phenalene (obtained by reduction of phenalanone with LiAlD_4 followed by dehydration of the resulting phenalanol) gave a mixture of complexes **1** and **2** of the same composition. In both isomers, the deuterium label is uniformly distributed among positions *exo*-1, *endo*-1, 3, 4, 6, 7, and 9. Apparently, redistribution of the deuterium label occurs in the phenalene molecule under the action of $\text{BF}_3 \cdot \text{OEt}_2$ prior to formation of the complex because it is well known that substituted phenalenes are readily isomerized under the conditions of acid or basic catalysis.¹⁸ Tricarbonylchromium complexes with phenalene **1** and **2** as well as the complexes of substituted phenalenes are less sensitive to acid agents. Thus, we demonstrated by special experiments that under the conditions of Öfele's reaction, *exo*-1-Me-**1** (**3**) and *exo*-1-D-**1** (**5**) are quantitatively regenerated (without isomerization) by treatment with $\text{Py}_3\text{Cr}(\text{CO})_3$ and $\text{BF}_3 \cdot \text{OEt}_2$, respectively.

The mass spectra of isomeric complexes **1** and **2** (electron impact) have medium intensity molecular ion

peaks at m/z of 302 whose fragmentation occurs through successive elimination of CO groups. The difference in fragmentation is that the mass spectrum of compound **2** has the low intensity peak of the $[\text{M}-\text{CO}]$ fragment (at m/z 274), which is absent in the mass spectrum of isomer **1**.

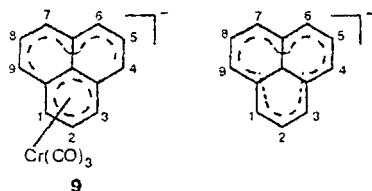
Apparently, the authors,¹⁴ who described complex **1** for the first time, also dealt with a mixture of isomers **1** and **2** formed by the reaction of $\text{Cr}(\text{CO})_3(\text{MeCN})_3$ with phenalene. However, they failed to detect the presence of two isomers in the ^1H NMR spectra recorded on an instrument operating at 100 MHz in a solution of isotropic CDCl_3 . The above-mentioned fact also accounts for the lower melting temperature of complex **1** reported in Ref. 14 than that determined by us.

Metalation of complexes **1** and **2**

When treated with *n*-butyllithium (-70°C , THF), both isomeric complexes **1** and **2** transformed readily to anion **9**. Lithium salt **9** is unstable in THF at a temperature higher than -20°C and produces a phenalene anion through elimination of the $\text{Cr}(\text{CO})_3$ fragment (Scheme 6). The ^1H NMR spectrum of salt **9** (Table 4) is indicative of the symmetrical structure with complete delocalization of the charge over both six-membered rings, which are not involved in coordination to the metal atom. Based on the data of the spectra recorded at different temperatures, it may be concluded that inter-ring haptotropic migrations of $\text{Cr}(\text{CO})_3$ between the six-membered rings (rather rapid within the NMR time scale) do not occur in anion **9** at a temperature up to -20°C .

Table 4. Parameters of the ^1H NMR spectra (400 MHz) of complex **9** and the phenalenyl anion (in THF- d_8 , -40°C)

Com- pound	δ					J/Hz			
	H(1), H(3)	H(2)	H(4), H(9)	H(5), H(8)	H(6), H(7)	$J_{\text{H}(1),\text{H}(2)}$, $J_{\text{H}(2),\text{H}(3)}$	$J_{\text{H}(4),\text{H}(5)}$, $J_{\text{H}(8),\text{H}(9)}$	$J_{\text{H}(5),\text{H}(6)}$, $J_{\text{H}(7),\text{H}(8)}$	
9	4.521	5.23	5.517	6.53	6.02	5.91	6.78	7.19	
Phenalenyl anion	5.195	7.44	5.195	5.20	5.195	7.32	7.32	7.32	



A comparison of the ^1H NMR spectra of salt **9** and the phenalenyl anion (see Table 4) demonstrated that coordination of the $\text{Cr}(\text{CO})_3$ fragment results in upfield shifts of the resonance signals of the H(1, 3) and H(2) protons of the coordinated nucleus by 0.674 and 2.21 ppm, respectively, with a decrease in the vicinal constant $J_{\text{H}(1),\text{H}(2)}$ from 7.32 to 5.91 Hz, which is typical of coordination effects. The signals of the protons of the rings, which are not involved in bonding with metal, H(5, 8), shift upfield by 0.91 ppm, whereas the signals of H(4, 9) and H(6, 7) shift downfield by 0.322 and 0.925 ppm, respectively. The total downfield shift of all the protons of the uncoordinated nuclei in the spectrum of complex **9** compared to the signals of compound **1** indicates that in anion **9**, the negative charge shifts substantially from the ligand to the metal atom. The chemical shifts in the ^1H NMR spectrum of compound **9** are temperature independent. This suggests that lithium salt **9** occurs in THF predominantly as solvent separated ionic pairs.¹⁹

Reaction of complex **9** with electrophilic reagents

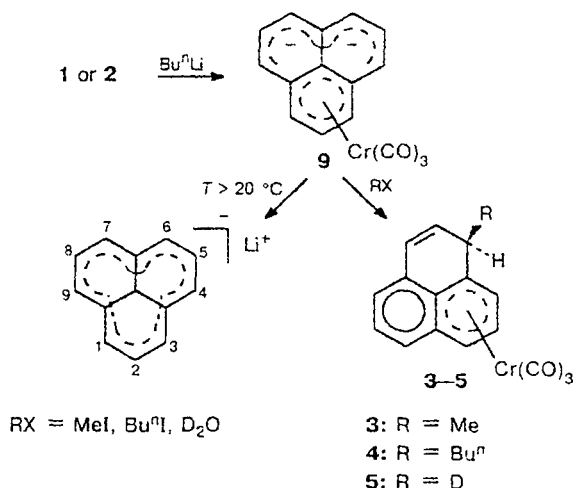
The reactions of salt **9** with electrophilic reagents (MeI, BuⁿI, and D₂O) at low temperatures proceed regio- and stereoselectivity to form the corresponding *exo*-1 derivatives (Scheme 6).

Note that if $\text{RX} = \text{MeI}$ and an excess of BuⁿLi was present in the reaction mixture, compound **4** occasionally formed in small amounts along with the expected complex **3** due to formation of BuⁿI through exchange between butyllithium and methyl iodide.

The regioselectivity of the reaction was confirmed by a complete X-ray structural study of complex **3**. In the ^1H NMR spectrum of complex *exo*-1-D-**1** (**5**), the signal at δ 3.01 is absent, which allows one to make the reliable assignment in the AB portion of the spectrum, whereas in the ^2H NMR spectrum of compound **5**, only one singlet at δ 3.01 is observed. The parameters of the ^1H NMR spectra of methyl derivative **3** and the other

substituted tricarbonylchromium complexes with phenalene are given in Table 5. The chemical shifts in their ^{13}C NMR spectra are listed in Table 3.

Scheme 6



It should be noted that fragmentation of compound **5** under the action of the electron impact also proceeds regioselectively. The $[\text{M}]^+$, $[\text{M}-2\text{CO}]$, $[\text{M}-3\text{CO}]$, and $[\text{M}-\text{HCr}(\text{CO})_3]$ peaks in the mass spectrum of complex **5** are shifted to greater masses by 1 amu compared to the spectrum of compound **1**, i.e., the last-mentioned fragmentation ion forms through migration of the *endo*-proton from the C(1) atom to the chromium atom (Scheme 7).

X-ray structural analysis of complex **3**

The structure of molecule **3** is shown in Fig. 2. The projection of the tricarbonylchromium group onto the

Scheme 7

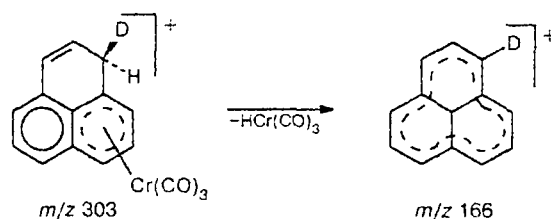
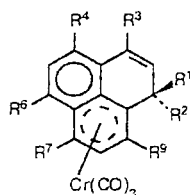
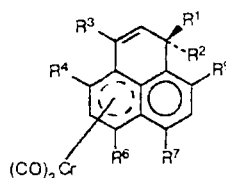


Table 5. Parameters of the ^1H NMR spectra (400 MHz) of the tricarbonylchromium complexes with derivatives of

Compound	δ (J/Hz)				
	R^1_{exo}	R^2_{endo}	H(2)	R^3 , H(3)	R^4 , H(4)
3	0.84 ($J_{\text{CH}_3, \text{R}^2} = 7.3$)	3.17 ($J_{\text{R}^2, \text{CH}_3} = 7.3$)	5.64 ($J_{\text{H}(1), \text{H}(2)} = 4.9$, $J_{\text{H}(2), \text{H}(3)} = 10.1$)	6.19 ($J_{\text{H}(2), \text{H}(3)} = 10.1$, $J_{\text{H}(3), \text{R}^2} = 1.35$)	6.40 ($J_{\text{H}(4), \text{H}(5)} = 6.0$, $J_{\text{H}(4), \text{H}(6)} = 2.0$)
4	0.7 (CH_3); 1.27, 1.04, 0.88 (CH_2)	3.31 ($J_{\text{CH}_2, \text{CH}_2} = 5.9$, $J_{\text{R}^2, \text{H}(9)} = 0.8$)	5.79 ($J_{\text{H}(1), \text{H}(2)} = 4.9$, $J_{\text{H}(2), \text{H}(3)} = 10.0$)	6.35 ($J_{\text{H}(1), \text{H}(3)} = 1.4$, $J_{\text{H}(2), \text{H}(3)} = 10.0$)	6.43 ($J_{\text{H}(4), \text{H}(5)} = 6.1$, $J_{\text{H}(4), \text{H}(6)} = 2.2$)
12	3.12 ($J_{\text{R}^1, \text{R}^2} = 24.3$)	3.20 ($J_{\text{R}^1, \text{R}^2} = 24.3$)	5.58 ($J_{\text{H}(2), \text{H}(3)} =$ 10.2, $J_{\text{H}(2), \text{R}^1} \approx$ $J_{\text{H}(2), \text{R}^2} = 4.3$)	6.18 ($J_{\text{H}(2), \text{H}(3)} = 10.2$)	6.35
11	0.90 ($J_{\text{R}^1, \text{R}^2} = 7.27$)	3.20 ($J_{\text{R}^1, \text{R}^2} = 7.27$)	5.67 ($J_{\text{H}(2), \text{R}^2} = 4.64$, $J_{\text{H}(2), \text{H}(3)} = 9.77$)	6.23 ($J_{\text{H}(2), \text{H}(3)} = 9.77$, $J_{\text{H}(3), \text{H}(4)} = 0.92$)	6.38 ($J_{\text{H}(4), \text{H}(5)} = 7.08$)
14	3.35 ($J_{\text{R}^1, \text{R}^2} = 25.7$)	3.57 ($J_{\text{R}^1, \text{R}^2} = 25.7$)	5.49	1.63	4.87
15	3.12 ($J_{\text{R}^1, \text{R}^2} = 24.9$)	3.17 ($J_{\text{R}^1, \text{R}^2} = 24.9$)	5.51	1.80	6.72 ($J_{\text{H}(4), \text{H}(5)} = 7.13$)
16	3.53 ($J_{\text{R}^1, \text{R}^2} = 7.3$)	1.30	—	—	—
17	2.89 ($J_{\text{R}^1, \text{R}^2} = 22.3$)	3.26 ($J_{\text{R}^1, \text{R}^2} = 22.3$)	5.75 ($J_{\text{H}(2), \text{R}^2} = 3.96$, $J_{\text{H}(2), \text{H}(3)} = 10.16$)	6.54 ($J_{\text{H}(2), \text{H}(3)} = 10.16$, $J_{\text{R}^2, \text{H}(3)} = 2.15$)	1.85
6	3.31	3.56	5.46 ($J_{\text{H}(2), \text{CH}_3} = 1.7$)	4.61 ($J_{\text{H}(4), \text{H}(5)} = 6.3$, $J_{\text{H}(4), \text{H}(6)} = 1.1$)	6.61
7	3.13 ($J_{\text{R}^1, \text{R}^2} = 23.5$)	3.28	5.49 ($J_{\text{H}(2), \text{H}(1)} = 4.5$)	1.75	6.58 ($J_{\text{H}(4), \text{H}(6)} = 1.6$, $J_{\text{H}(4), \text{H}(5)} = 6.3$)
19	1.21 (CH_3)	3.61 (H , $J_{\text{H}, \text{CH}_3} = 7.4$)	5.75 ($J_{\text{H}(2), \text{CH}_3} = 2.0$)	6.44 ($J_{\text{H}(2), \text{H}(3)} = 9.6$)	6.98
20	3.66	3.66	5.58	1.91	6.98

**3, 4, 7, 11, 12, 15–17**

3: $\text{R}^1 = \text{Me}$
4: $\text{R}^1 = \text{Bu}^n$
12: $\text{R}^6 = \text{Me}$
11: $\text{R}^1 = \text{R}^6 = \text{Me}$
15: $\text{R}^3 = \text{R}^7 = \text{Me}$
16: $\text{R}^2 = \text{R}^6 = \text{Me}$
17: $\text{R}^4 = \text{R}^9 = \text{Me}$
7: $\text{R}^3 = \text{Me}$

**6, 8, 14**

14: $\text{R}^3 = \text{R}^7 = \text{Me}$
6: $\text{R}^3 = \text{Me}$
8: $\text{R}^1 = \text{Me}$

Note. The remaining substituents $\text{R} = \text{H}$ (unless otherwise stated). Chemical shifts for complexes **6**, **8**, and **14** were measured in toluene- d_8 . Compounds **19** and **20** are the ligands obtained by decomposition of complexes **3** and **4**, respectively.

plane of the phenalene ligand is shown in Fig. 3. The bond lengths and bond angles are given in Tables 6 and 7, respectively. The distance between the Cr atom and the mean plane of the η^6 -ring *A* (1.746 Å) is equal to that observed in the tricarbonyl(η^6 -naphthalene)chromium molecule (1.747 Å)²⁰ and is somewhat larger than that in the tricarbonyl(η^6 -benzene)chromium mol-

ecule (1.726 Å),²¹ which is consistent with the lower π -donor ability of the condensed ligands. In molecule **3**, the orientation of the $\text{Cr}(\text{CO})_3$ group with respect to the "naphthalene" fragment (rings *A* and *B*) is identical to that in η^6 - $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$. The carbonyl groups are located below the C(6a)–C(7), C(8)–C(9), and C(9a)–C(9b) bonds. The rings *A* and *B* are approximately

phenalene^a 3, 4, 6, 7, 11, 12, 14–17, 19, 20 in C₆D₆

δ (J/Hz)				
H(5)	R ⁶ , H(6)	R ⁷ , H(7)	H(8)	R ⁹ , H(9)
-6.70–6.80	-6.70–6.80	5.15 ($J_{H(7),H(8)} = 6.5$, $J_{H(7),H(9)} = 0.9$)	4.81 ($J_{H(7),H(8)} \approx$ $J_{H(8),H(9)} = 6.5$)	4.55 ($J_{H(8),H(9)} = 6.5$, $J_{H(7),H(9)} = 0.9$, $J_{R^2,H(9)} = 0.9$)
-6.71–6.78	-6.71–6.78	5.18 ($J_{H(7),H(8)} = 6.5$, $J_{H(7),H(9)} = 1.1$)	4.83 ($J_{H(7),H(8)} = 6.5$, $J_{H(8),H(9)} = 6.2$)	4.64 ($J_{H(7),H(9)} =$ 1.1, $J_{H(8),H(9)} = 6.2$, $J_{R^2,H(9)} = 0.8$)
6.57	2.05	5.83 ($J_{H(7),H(8)} = 6.3$)	4.78 ($J_{H(8),H(9)} \approx$ $J_{H(7),H(8)} = 6.3$)	4.45 ($J_{H(8),H(9)} = 6.3$)
6.57 ($J_{H(4),H(5)} = 7.08$)	2.09	5.25 ($J_{H(7),H(8)} = 6.9$)	4.83 ($J_{H(7),H(8)} = 6.9$, $J_{H(8),H(9)} = 6.2$)	4.63 ($J_{H(8),H(9)} = 6.2$)
-4.87	5.47	2.18	6.71 ($J_{R^7,H(8)} \approx 1.0$, $J_{H(8),H(9)} = 7.11$)	6.52 ($J_{H(8),H(9)} = 7.11$, $J_{H(9),H(1)} = 1.70$)
6.85 ($J_{H(4),H(5)} = 7.13$, $J_{H(5),H(6)} = 8.9$)	7.48 ($J_{H(5),H(6)} = 8.91$)	2.20	4.59 ($J_{H(8),H(9)} = 6.16$)	4.73 ($J_{H(8),H(9)} = 6.16$)
—	1.83	—	—	—
6.58 ($J_{H(5),H(6)} = 8.67$)	6.72 ($J_{H(5),H(6)} = 8.67$)	5.28 ($J_{H(7),H(8)} = 6.80$)	4.72 ($J_{H(7),H(8)} = 6.80$)	1.59
4.80 ($J_{H(5),H(6)} = 6.7$)	4.88	5.36	6.72–6.84	6.72–6.84
6.78	6.76	5.12 ($J_{H(7),H(9)} = 1.0$)	4.79 ($J_{H(8),H(9)} = 6.5$, $J_{H(7),H(8)} = 6.9$)	4.47
7.10–7.35 (m, H(5)—H(9))				
7.10–7.35 (m, H(5)—H(9))				

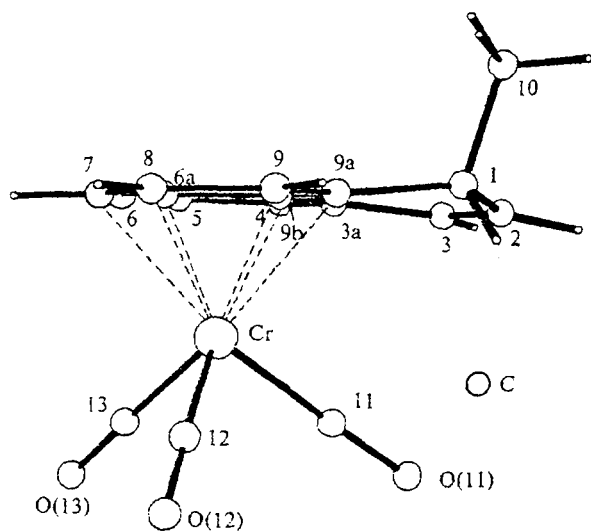


Fig. 2. Molecular structure of complex 3.

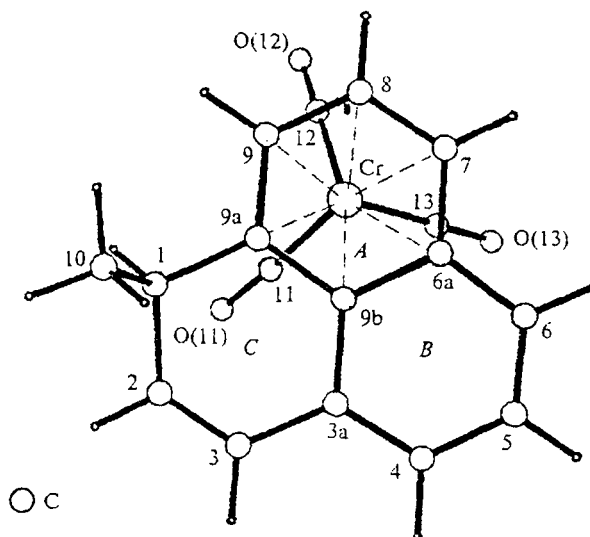


Fig. 3. Projection of the tricarbonylchromium group onto the plane of the phenalene ligand in complex 3.

Table 6. Interatomic distances (*d*) in molecule 3 (see Figs. 2 and 3)

Bond	<i>d</i> /Å	Bond	<i>d</i> /Å	Bond	<i>d</i> /Å	Bond	<i>d</i> /Å
Cr—C(6a)	2.304(5)	Cr—C(12)	1.826(6)	C(1)—C(10)	1.530(9)	C(6)—C(6a)	1.425(8)
Cr—C(7)	2.229(6)	Cr—C(13)	1.829(6)	C(2)—C(3)	1.310(1)	C(6a)—C(7)	1.430(1)
Cr—C(8)	2.205(7)	O(11)—C(11)	1.156(7)	C(3)—C(3a)	1.450(9)	C(6a)—C(9b)	1.443(9)
Cr—C(9)	2.219(7)	O(12)—C(12)	1.157(8)	C(3a)—C(4)	1.360(9)	C(7)—C(8)	1.380(1)
Cr—C(9a)	2.241(6)	O(13)—C(13)	1.159(8)	C(3a)—C(9b)	1.437(9)	C(8)—C(9)	1.400(1)
Cr—C(9b)	2.273(6)	C(1)—C(2)	1.502(9)	C(4)—C(5)	1.430(1)	C(9)—C(9a)	1.395(9)
Cr—C(11)	1.830(6)	C(1)—C(9a)	1.522(9)	C(5)—C(6)	1.330(1)	C(9a)—C(9b)	1.420(9)

Table 7. Bond angles (ω) in molecule 3 (see Figs. 2 and 3)

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

planar although they exhibit weak wave-like distortions (the distances from the Cr atom to the C(6a) and C(9) atoms of the ring *A* and to the C(5) and C(9b) atoms of the ring *B* are somewhat larger (by 0.02–0.03 Å) than the remaining Cr—C distances in these rings) typical of condensed arene π -ligands.²²

In the η^6 -C₁₀H₈Cr(CO)₃ molecule, the distances between the annelated atoms of the η^6 -ring and the Cr atom are larger than those between the peripheral atoms and the Cr atom (the average distances are 2.32 and 2.02 Å, respectively), which is typical of the complexes with condensed π -arene ligands.²³ For compound 3, this tendency is less pronounced. Note that in the η^6 -octamethylnaphthalenetetracarbonylchromium molecule,²⁴ one of the annelated atoms of the arene system is far removed from the Cr atom (2.406 Å), whereas the second atom comes closer to the Cr atom so that five Cr—C distances have close values (average 2.25 Å). The nonaromatic ring *C* with the localized C(2)=C(3) double bond adopts a sofa conformation. The C(1) atom deviates from the C(2)C(3)C(3a)C(9b)C(9a) plane in the opposite direction with respect to the Cr atom by 0.23 Å. The C(10) atom deviates from this plane toward the Cr atom by 1.65 Å, *i.e.*, in such a manner that the methyl substituent has a pseudoaxial *exo* orientation. The Cr—H(1)_{endo} distance in molecule 3 is 3.42 Å, which is 1.86 Å larger than the sum of the covalent radii of the Cr and H atoms. The Cr—C(1) distance is 3.65 Å, which is 0.63 Å larger than the sum of the covalent radii of the Cr and C atoms. Abundant experimental data on the structures of compounds with agostic bonds²⁵ indicate that direct agostic interaction between the metal atom and the C—H bond is possible only if the M—H distance is larger by no more than 0.6 Å than the sum of

the covalent radii of the M and H atoms. Therefore, there is no efficient interaction between the Cr atom and the C—H_{endo} bond at the C(1) atom in the ground state of molecules of the tricarbonylchromium complexes with phenalene. This is also confirmed by the spectral data; that is, upfield shifts typical of agostically bonded H atoms are not observed in the ¹H NMR spectra,²⁶ and the anomalies are absent in the ν (CH) vibration region of the IR spectra.

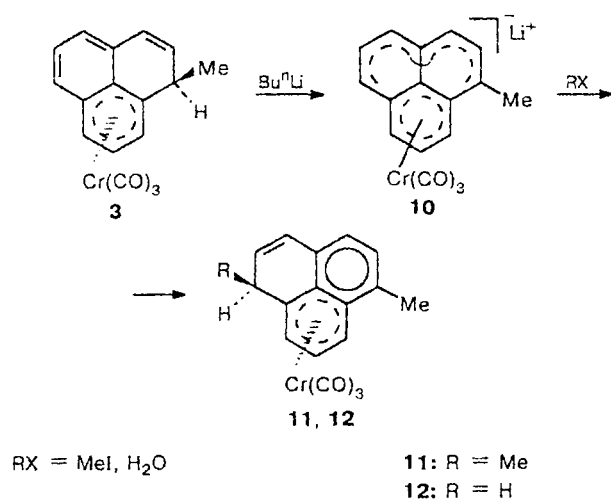
The conformational transition of the C(1) atom in the ring, as a result of which the Me group changes its orientation to pseudoaxial due to the shift of the C(1) atom toward the Cr atom, should not require a substantial expenditure of energy. Based on the results of quantum-chemical calculations by the PM3 method, the energy of the conformation, where the C(1) atom deviates from the C(2)C(3)C(3a)C(9b)C(9a) plane toward the Cr atom by 0.23 Å, differs from that of the initial conformation by no more than 1 kcal mol^{−1}. In this conformation, the calculated Cr—C(1) and Cr—H(1)_{endo} distances are 3.2 and 3.4 Å, respectively, which is also unfavorable for the occurrence of direct agostic interactions.

Deprotonation of substituted tricarbonylchromium complexes with phenalene and reactions of the corresponding anions

Deprotonation of complexes 1 and 2 occurs as the stereoselective *exo*-attack of the base at the geminal pair of the methylene protons. The reaction of a mixture of isotopoisomeric complexes 1 and 2 monodeuterated at positions *exo*-1, *endo*-1, 3, 4, 6, 7, and 9 (which was

prepared by Öfele's reaction from 3-D-phenalene with the equally probable distribution of deuterium among positions *exo*-1, *endo*-1, 3, 4, 6, 7, and 9) with Bu^nLi (-70°C in THF) followed by treatment of the resulting anion with water gave compound **1** in which deuterium is absent at position *exo*-1, whereas the distribution of the deuterium label among the remaining positions *endo*-1, 3, 4, 6, 7, and 9 remains unchanged. Complex **3** containing only *endo*-protons deprotonates more slowly than compounds **1** and **2** because the H_{endo} atom is less accessible to a base. In this case, it is necessary to increase the temperature of the reaction mixture to -40°C . The resulting anion **10** is subjected to electrophilic attack exclusively in the *exo*-position at the C(6) atom to form compounds **11** and **12** under the action of MeI and H_2O , respectively (Scheme 8).

Scheme 8



In turn, deprotonation of complex **11** yields anion **13**. When treated with water, the latter does not form the *endo*-methyl complexes, but reacts exclusively at the C(3) or C(4) atom (added a proton in the *exo*-position) to form complex **14** (Scheme 9).

The absence of any other compounds except for **11**, **12**, and **14** among the reaction products (see Schemes 8 and 9) confirms the fact that inter-ring haptotropic rearrangements do not occur in anions **9**, **10**, and **13** at

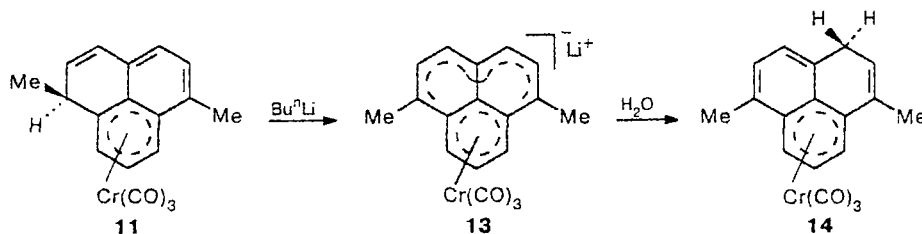
low temperature (-70°C). Storage of lithium salt **10** in THF at -20°C for 2 h followed by treatment with water gave a mixture of all five possible isomeric complexes, which differ in the position of the methyl group in the six-membered rings. The results obtained demonstrated that inter-ring haptotropic rearrangements in anion **10** occur at -70°C , but they proceed slowly within the NMR time scale. These experiments will be discussed in more detail elsewhere. The parameters of the ^1H NMR spectra of the resulting complexes are given in Table 5. The values of $\delta^{13}\text{C}$ are listed in Table 3.

The tricarbonylchromium complexes with substituted phenalenes synthesized by us are orange-red or red crystalline compounds, which are rather stable in the solid state. They can be stored indefinitely in sealed tubes under an atmosphere of inert gas. These complexes are readily soluble in aromatic solvents (benzene, toluene, and hexafluorobenzene) and moderately soluble in alkanes at room temperature, and therefore, are crystallized from alkanes. Solutions of these compounds are very sensitive to light and atmospheric oxygen. In polar (THF and ether) and chlorine-containing solvents, the complexes are moderately stable.

Thermal isomerization of tricarbonylchromium complexes with phenalene

Thermal isomerization of tricarbonylchromium complexes with phenalene was studied under various conditions. In the experiments reported previously,²⁷ solutions of individual complexes **1** and **2** in decane were heated under an atmosphere of purified argon at temperatures from 80 to 140°C for 10–15 h. In this case, the complexes underwent isomerization to form an equilibrium mixture. The ratio of compounds **1** and **2** was 87 : 13 no matter what isomer was taken as the initial. The mixture of the complexes was isolated chromatographically and analyzed by ^1H NMR spectroscopy. However, in a number of experiments, destruction of the complexes was observed, which was accompanied by the appearance of a fine suspension of greenish paramagnetic particles, which are, apparently, chromium oxide. The degree of destruction depended on the carefulness of purification of argon, temperature, and the duration of heating. In this connection, in this work we used an alternative procedure. Thermal isomerization of

Scheme 9



the complexes was carried out in C_6F_6 or toluene (in the case of compound 3, in toluene- d_8) in NMR tubes. The complexes are rather readily soluble in these solvents, which allows one to determine reliably the concentrations of all the reaction products up to deep degrees of transformations. Special procedures for purification of the solvents and for the preparation of samples (see the Experimental section) made it possible to exclude completely traces of oxygen and moisture.

Thermal isomerization of complex 5. Isomerization of complex 5 was studied in a C_6F_6 solution at 85, 100, and 110 °C and in toluene at 90, 100, and 110 °C. The concentrations of the resulting products were determined by $^2H\{^1H\}$ NMR spectroscopy. The spectra were recorded with stabilization of the resonance conditions on the ^{19}F nucleus using the signal of C_6F_6 as the reference. Isomerization in a toluene solution was studied using samples in which 10 vol.% of C_6F_6 were added to stabilize the resonance conditions. The samples were carefully degassed by repeating freezing—evacuation—thawing cycles with the use of a vacuum line at 10^{-5} Torr and were then sealed *in vacuo*. In the recorded spectra, many signals, which are substantially different in intensity, overlap. Therefore, the standard procedure for the integration did not provide the required accuracy of determination of concentrations. Because of this, we used a procedure of analysis based on deconvolution of the spectra (representation of the total spectral profile as the sum of Lorentz lines). The phase and the nonuniformity of the magnetic field were corrected (see the Experimental section). The unambiguous assignment of the signals in the 2H NMR spectrum was made based on the corresponding 1H NMR spectra (see Table 1).

Toluene is a convenient solvent for studying the thermal isomerization of complex 5 by $^2H\{^1H\}$ NMR spectroscopy because this complex is readily soluble in toluene at room temperature. Moreover, owing to the ASIS effect, the distances between the signals are sufficiently large for accurate integration, and the singlet of the CH_2D group and three singlets in the aromatic region (which correspond to three nonequivalent positions of the protons of the aromatic nucleus), which are caused by the solvent with a natural deuterium content, can serve as the standard for determining the positions of the signals and as the standard for integrating these signals. The drawback of toluene as a solvent is the occurrence of the side reaction of replacement of the phenylene ligand in complex 5 by toluene. This ligand exchange in arene complexes of tricarbonylchromium is well known and was studied from the viewpoint of kinetics in detail.²⁸ However, because this exchange occurs rather slowly at moderate temperature, it is possible to study the kinetics of thermal isomerization against the background of this exchange in detail. Evolution of the spectra that occurs in the course of heating of complex 5 in toluene at 100 °C is shown in Fig. 4.

In the early stages of transformations, the signal of the tricarbonyl(phenylene)chromium containing deute-

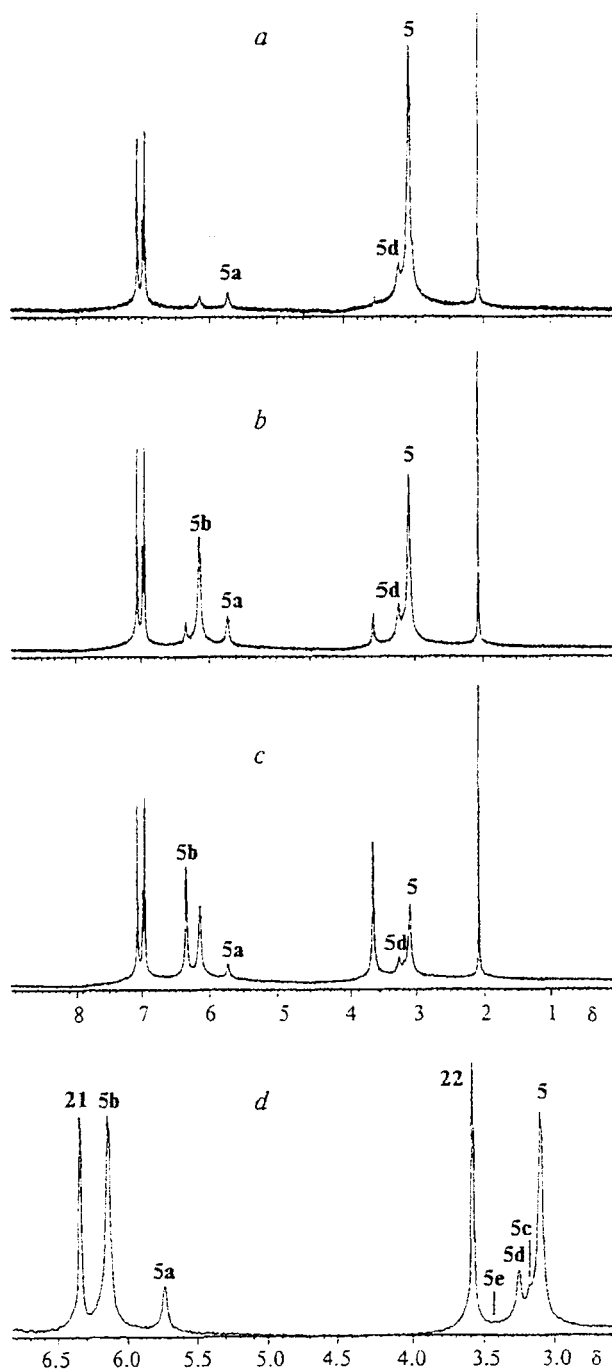


Fig. 4. Evolution of the $^2H\{^1H\}$ NMR spectra of complex 5 in the course of thermal rearrangement in toluene at 100 °C: a, 2 h after the beginning of heating; b, 12 h; c, 110 h; d, the fragment of the spectrum obtained after 74 h. The signals from the natural deuterium content of the solvent are also given. The corresponding kinetic curves are shown in Fig. 5.

rium at position 3 (5a) appears originally along with the singlet of the initial complex 5. This complex forms through the [1,5]-sigmatropic shift of the H_{endo} atom in

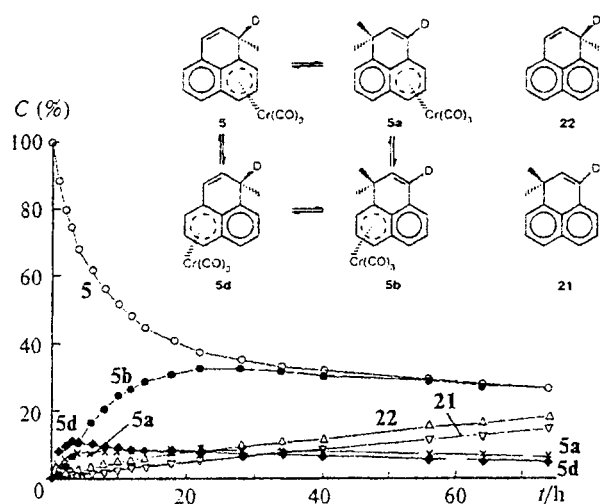


Fig. 5. Kinetic curves of thermal isomerization and dissociation of complex 5 (toluene, 100 °C).

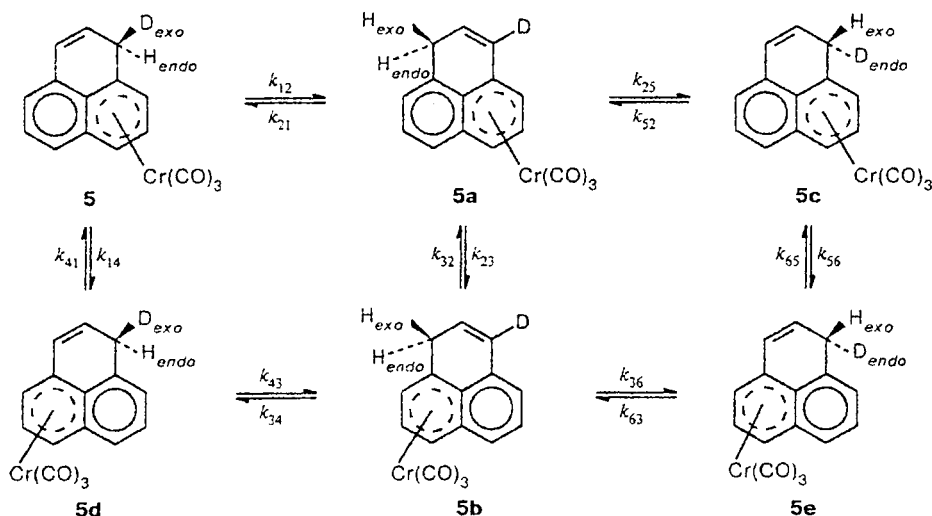
molecule 5 (Scheme 10). Simultaneously, complex 5d forms through the η^6, η^6 -haptotropic shift of the $\text{Cr}(\text{CO})_3$ group (see Fig. 4, a, b). Then, the signal of isotopoisomer 5b, which is formed from complexes 5a and 5d, appears in the low field. The intensity of the signal of this complex in the ^2H NMR spectrum increases more rapidly than that of the signal of 5a (see Fig. 4, b, c). An analysis of the spectrum makes it possible to detect the rather low-intensity signals of *endo*-1-D-tricarbonyl(6a,7-9,9a,9b- η^6 -phenalene)chromium 5c and *endo*-1-D-tricarbonyl(3a,6a,9b,4-6- η^6 -phenalene)chromium 5e (see Fig. 4, d), which form via the [1,5]-shift of the

$\text{H}(1)_{\text{exo}}$ proton in molecules 5a and 5b. The change in the concentrations of the complexes that formed with time is shown in Fig. 5. The intensity of the signal of complex 5e is sufficient to identify it reliably but is too small to determine the changes in the concentration of 5e with time with an accuracy necessary for kinetic studies. All the processes that occur in the system are shown in Scheme 10. Note that with the aim of assigning reliably the signals of deuterium in isotopoisomers of phenalene- d_1 , we analyzed the ^1H NMR spectra of phenalene in toluene- d_8 and C_6F_6 using the double resonance method and internuclear Overhauser effect experiments. In the course of these studies, we rectified the errors of the assignment of the signals made in Ref. 29.

The kinetic curves of interconversions of complexes 5, 5a, 5b, and 5c are adequately described within the framework of the model of reversible first-order reactions. There is no question that these processes occur as intramolecular reactions because in the case of elimination of the $\text{Cr}(\text{CO})_3$ fragment, it will be immediately captured by toluene, which is present in high excess. Studies of the thermal isomerization of compound 5 in C_6F_6 provided additional supporting evidence for the intramolecular character of both the [1,5]-migration of the H atom and the η^6, η^6 -haptotropic rearrangement. It was demonstrated that the rates of these processes remained virtually unchanged when the concentration of complex 5 decreased by half as well as when 10 equivalents of hexamethylbenzene, which can efficiently capture $\text{Cr}(\text{CO})_3$, were added.

The above-considered data indicate that the processes of thermal isomerization of tricarbonylchromium complexes with phenalene involve several consecutive

Scheme 10



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

and concurrent reversible and irreversible reactions. In this connection, it was necessary to choose the kinetic model and to determine the parameters. The values of the residual dispersion of the correspondence between the calculated and experimental kinetic curves, the standard deviations of the desired parameters, and the matrix of the pair linear correlations are conventionally used as the criteria of uniqueness of solution of this nonlinear inverse problem. However, in complex kinetic schemes analogous to that described above, solutions can be nonunique. From the viewpoint of mathematics, this manifests itself in the fact that the columns of the Jacobian matrix of partial derivatives of responses with respect to the parameters, $X_{ij} = \partial x_i / \partial k_j$, are not independent. What this means is the model is not rigorously locally identifiable, *i.e.*, there is a continuous range of values of the parameters for which a single value of the responses is available within the total experimental error. In these cases, the above-mentioned criteria are lacking. Because of this, we used the calculation procedure³⁰ for the numerical study of the identifiability of the parameters of nonlinear models (see the Experimental section) and analyzed different models of the kinetic scheme using this procedure. In particular, we also considered the cases where the reactions of replacement of the phenalene ligand by toluene in complexes **5**, **5a**, **5b**, and **5c** are characterized by the individual pseudo-first-order constants. However, it was established that the values of the constants obtained in this case are substantially correlated, and the procedure used by us unambiguously indicated that the parameters of the model are nonidentifiable. In this connection, the rate constants of the ligand exchange for complexes **5**, **5a**, **5b**, and **5c** were assumed to be equal, which did not lead to a substantial deterioration of the convergence between the experimental and theoretical curves.

The rate constants of the major processes (see Scheme 10) at 90, 100, and 110 °C are given in Table 8.

Thermal isomerization of complex **5** in C_6F_6 proceeds in many ways analogously to that described above for the case of the toluene solution. In this case, at high degrees of transformations (6 h and more), the isotopomers of phenalene- d_1 also appear. However, it is hard to attribute their formation to the exchange of the phenalene ligand for C_6F_6 .

It is well known that arenes containing electron-withdrawing groups exhibit reduced ability to coordinate the $Cr(CO)_3$ fragment, and if the arene molecule con-

tains three halogen atoms, it is impossible to carry out the direct synthesis of its tricarbonylchromium complexes.³¹ Thus, only tricarbonylchromium complexes with difluorobenzene can be prepared by the direct synthesis.³² However, complexes of this type synthesized by alternative procedures are rather stable. In particular, hexachlorobenzene tricarbonylchromium was described in Ref. 33. It should be noted that we failed to detect hexafluorobenzene tricarbonylchromium by spectral methods or TLC. As mentioned above, we also found that addition of hexamethylbenzene (a tenfold excess with respect to complex **5**) has no pronounced effect on the rate of formation of the free ligands. In this case, the tricarbonylchromium complex with hexamethylbenzene was detected in the reaction mixture by TLC. The precautions taken (C_6F_6 was kept *in vacuo* over a potassium mirror and was transferred into a tube immediately before use; the samples were repeatedly degassed) made it possible to exclude oxidative destruction of compound **5** under the action of oxygen dissolved in C_6F_6 . The samples turned transparent, and the line widths in the spectra remained unchanged, which is indicative of the absence of paramagnetic particles. The corresponding kinetic parameters are given in Table 8.

The characteristic feature of thermal isomerization of complex **5** in C_6F_6 is that after long duration of the processes (100 h at 110 °C in pure C_6F_6 and 200 h at 110 °C in C_6F_6 with the addition of hexamethylbenzene), isotopomers **1** and **2** containing deuterium labels in the coordinated nuclei appeared in the reaction mixture. When the process was carried out in toluene, isotopomers were not detected. This suggests that in a C_6F_6 solution, coordinatively unsaturated highly reactive particles, which may cause redistribution of the deuterium label among all *amphi*-positions of the phenalene ring in the free phenalene, appear, much as under the condition of Öfele's reaction followed by the bimolecular reaction with this ligand, the tricarbonylchromium complexes with phenalene, which contain deuterium in the coordinated ring, form. It is not inconceivable that it is the resulting $C_6F_6Cr(CO)_3$, which should very readily exchange C_6F_6 for another arene ligand, that acts as such particle. The thermodynamic parameters of the reactions (shown in Scheme 10) in toluene are given in Table 9.

Thermal isomerization of complex 3. Thermal isomerization of **3** in deuteriotoluene and hexafluorobenzene in the temperature range 90–110 °C occurs analogously to

Table 8. Rate constants of thermal rearrangements of complex **5** in toluene at various temperatures

$T/^\circ C$	$k_{12} \cdot 10^{-4}$	$k_{21} \cdot 10^{-4}$	$k_{23} \cdot 10^{-4}$	$k_{32} \cdot 10^{-4}$	$k_{25} \cdot 10^{-6}$	$k_{52} \cdot 10^{-6}$	K_{33}	$k_L \cdot 10^{-6*}$
	s^{-1}							
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

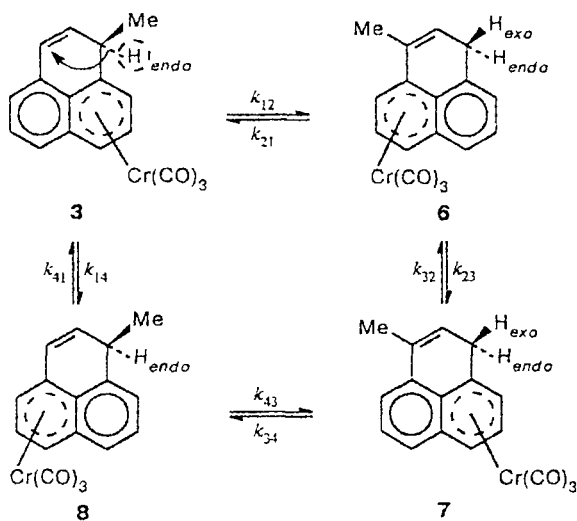
* Here, k_L is the rate constant of elimination of the ligand from complex **5**.

Table 9. Activation parameters of thermal rearrangements of complex **5** in toluene

Reaction	ΔG^\ddagger ^a	ΔH^\ddagger ^b	ΔS^\ddagger ^b	E_a ^b	$\log A$ ^b
	kcal mol ⁻¹	kcal mol ⁻¹	/cal mol ⁻¹ deg ⁻¹	/kcal mol ⁻¹	/s ⁻¹
5 → 5a	30.14±0.05	31.88±0.19	4.63±0.50	32.61±0.19	14.34±0.11
5a → 5	29.04±0.01	30.75±0.50	4.67±1.37	31.51±0.50	14.35±0.30
5a → 5b	28.85±0.04	22.84±4.07	-15.79±10.90	23.58±4.12	9.88±2.39
5b → 5a	29.76±0.47	23.74±3.49	-15.35±9.34	24.48±3.47	9.75±2.05
5a → 5c	31.90±0.01	31.01±7.31	-1.78±19.64	31.76±7.32	12.94±1.29
5c → 5a	33.01±1.64	32.12±6.60	-1.80±17.72	33.86±6.59	12.93±3.87

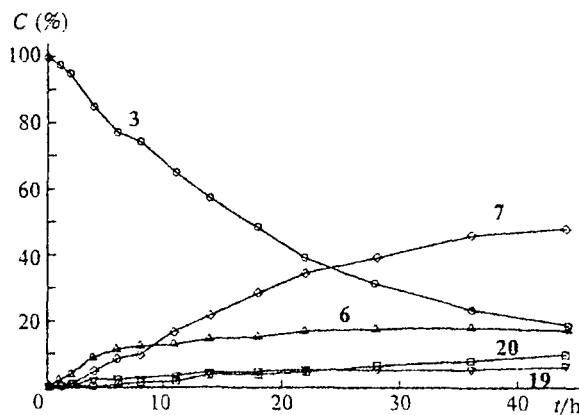
^a At 100 °C, $\Delta G^\ddagger = 4.576T(10.32 + \log T - \log k)$. ^b Calculated using the least-squares method.

that described above for complex **5**. In the initial stage, the isomer containing the Me group in the vinyl position (**6**) forms due to [1,5]-migration of the H(1)_{endo} atom. The inter-ring shift of the organometallic group, which results in complex **7**, proceeds somewhat more slowly. Analogously, compound **8** forms due to the shift of the tricarbonylchromium group of complex **3** and the H_{endo} atom of compound **7**. The interconversion of the methyl isomers is described by Scheme 11.

Scheme 11

All signals of the resulting four isomeric methyl complexes **3**, **6**, **7**, and **8** are observed in the NMR spectrum of the reaction mixture. The assignment of the signals was made based on the spectra and nuclear Overhauser effect experiments.

The kinetic curves for the methyl isomers were constructed using precision integration of the signals of the corresponding methyl groups of the isomeric complexes in deuteriotoluene with the use of the program for the analysis of the total spectral profile, which is applied in studies of rearrangements of complex **5** (Fig. 6). Models

**Fig. 6.** Kinetic curves of thermal isomerization of complex **3** (toluene-d₈, 90 °C).

of the kinetic scheme were studied using the same procedure. The parameters were calculated using the same program as in the case of complex **5**. The rate constants are given in Table 10. The corresponding activation parameters are listed in Table 11. Note that in the case of complex **8**, we did not observe the [1,5]-sigmatropic shift of the H_{exo} atom with the formation of the complex analogous to **5c** containing the Me group in the *endo*-orientation.

Thermal isomerization of complex 14. Heating of compound **14** in decane (80 °C) afforded complex **15** due to the shift of the Cr(CO)₃ fragment. Heating during 18 h afforded compounds **14** and **15** in a ratio of 93 : 7. Subsequent storage of the mixture at the same temperature for 10 h gave isomer **11** (**14** : **15** : **11** = 75 : 18 : 7), which formed either immediately from complex **14** through the [1,5]-sigmatropic shift of the H_{endo} atom or from compound **15** as a result of the two-stage reaction involving both the [1,5]-sigmatropic shift of the hydrogen atom and the inter-ring haptotropic rearrangement of the Cr(CO)₃ fragment, which is consistent with the ratio of the corresponding rates of isomerization of monomethyl complex **3** (see Table 11). Under more severe conditions (140 °C, 18 h), complex **14** in decane also gave isomer **16**, which differs from **11** only by the *endo* configuration of the Me group at the

Table 10. Rate constants of thermal rearrangements of complex 3 in toluene- d_8 at various temperatures

$T/^\circ\text{C}$	$k_{12} \cdot 10^{-5}$	$k_{21} \cdot 10^{-5}$	$k_{23} \cdot 10^{-5}$	$k_{32} \cdot 10^{-5}$	K_{12}	K_{23}
	s^{-1}					
90	1.14 \pm 0.03	0.67 \pm 0.03	7.34 \pm 0.62	3.51 \pm 0.62	1.71 \pm 0.14	2.09 \pm 0.15
100	3.53 \pm 0.08	1.08 \pm 0.08	18.15 \pm 1.19	5.69 \pm 1.19	3.27 \pm 0.41	3.19 \pm 0.23
110	10.34 \pm 0.24	4.97 \pm 0.24	54.98 \pm 4.64	13.34 \pm 0.13	2.08 \pm 0.13	4.12 \pm 0.25

Table 11. Activation parameters of thermal rearrangements of complex 3 in toluene- d_8 (^1H NMR)

Reaction	ΔG^\ddagger ^a	ΔH^\ddagger ^b	ΔS^\ddagger ^b	E_a ^b	$\log A$ ^b
	kcal mol^{-1}		$/\text{cal mol}^{-1} \text{ deg}^{-1}$	$/\text{kcal mol}^{-1}$	$/\text{s}^{-1}$
3 \rightarrow 6	29.60 \pm 0.02	29.72 \pm 0.02	-1.76 \pm 0.50	30.46 \pm 0.03	13.39 \pm 0.02
6 \rightarrow 3	30.48 \pm 0.06	27.70 \pm 8.60	-7.90 \pm 2.30	28.44 \pm 8.60	11.33 \pm 5.15
6 \rightarrow 7	28.39 \pm 0.05	27.04 \pm 2.05	-3.43 \pm 5.02	27.78 \pm 2.05	12.58 \pm 1.20
7 \rightarrow 6	29.25 \pm 0.47	17.60 \pm 3.20	-28.17 \pm 7.20	18.40 \pm 3.25	6.59 \pm 1.89

^a At 100 $^\circ\text{C}$, $\Delta G^\ddagger = 4.576T (10.32 + \log T - \log k)$.^b Calculated using the least-squares method.

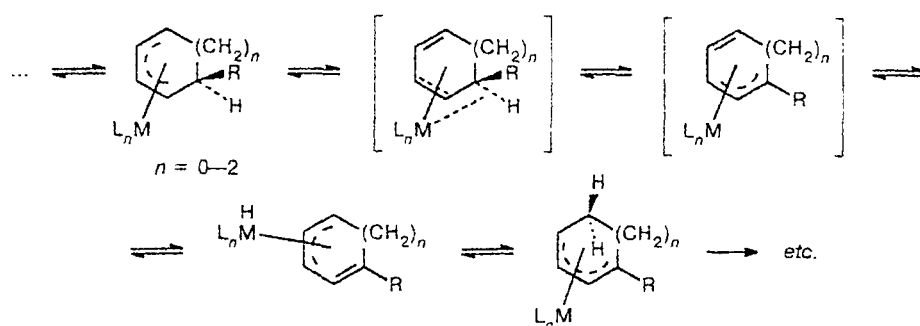
sp^3 -hybridized C atom of the phenalene ligand. Isomer 16 was identified in the reaction mixture using nuclear Overhauser effect experiments. In addition, signals of isomer 17, which has the structure of complex 1 and contains Me groups in the aromatic rings, were observed in the spectrum (compound 17 was isolated chromatographically and was identified by NMR spectroscopy). It should be noted that a complex with such a structure can appear only as a result of an intermolecular exchange analogous to the process, which causes formation of tricarbonylchromium complexes with phenalene, which contains the D atom in the coordinated ring, in the course of thermal isomerization of complex 5. The ratio of complexes 14, 17, 15, 11, and 16 in the reaction mixture was 12 : 39 : 36 : 8 : 5.

Kinetic and thermodynamic parameters of inter-ring η^6, η^6 -haptotropic rearrangements in the tricarbonylchromium complexes with phenalene. The kinetic measurements were carried out for a limited number of temperatures. Therefore, the separation of the entropy and enthalpy contributions given in Tables 9 and 11 is arbitrary. However, based on all the data obtained, a number of reliable conclusions can be made about the inter-ring η^6, η^6 -haptotropic rearrangements in the tricarbonylchromium complexes with phenalene. The corresponding activation and thermodynamic parameters, which we determined for compounds 3 and 5, agree well with each other and with the published data for the complexes of substituted naphthalenes whose free activation energies are in the range of 26–30 kcal mol^{-1} (see Refs. 5 and 34). The process is insensitive to the solvent, concentration of the complex, and admixtures of a ligand capable of participating in coordination. These facts along with the kinetic data unam-

biguously indicate that the migration of the $\text{Cr}(\text{CO})_3$ fragment in complexes 5 and 3 proceeds as an intramolecular reaction. In both equilibria shown in Schemes 10 and 11, the isomers in which the $\text{Cr}(\text{CO})_3$ group is bonded to the six-membered ring containing the sp^3 -hybridized C atom at the α -position are thermodynamically more favorable, which also corresponds to the usual effect of substituents on the relative stability of isomers.

Kinetic and thermodynamic parameters of [1,5]-migrations of hydrogen in tricarbonylchromium complexes with phenalene. The data on the rates of [1,5]-sigmatropic migrations of the hydrogen atom in tricarbonylchromium complexes with phenalene are of great interest. There is indirect evidence³⁵ that this migration occurs in free phenalene. It occurs under severe conditions at a temperature higher than 170 $^\circ\text{C}$. However, the activation parameters of this process can be estimated from the value of the activation energy of migration of the SiMe_3 group in phenalene ($\sim 27 \text{ kcal mol}^{-1}$).³⁶ Previously, we have developed a simple procedure that makes it possible to compare the free activation energies of prototropic and metallotropic [1,5]-shifts in various cyclic systems with adequate accuracy.³⁷ The approximate estimate of the free activation energy of the [1,5]-H-shift in phenalene, which was made using this procedure based on the corresponding data on migration of SiMe_3 , gave the value of 36 kcal mol^{-1} , which corresponds to the conditions under which these shifts occur. A comparison of this value with the free activation energies for [1,5]-sigmatropic rearrangements in molecules of complexes 3 and 5 demonstrated that the activation barriers to the migration of the H atoms decrease sharply (this decrease is

Scheme 12



most pronounced for the H_{endo} atoms). This effect is generally observed for complexes of transition metals with monocyclic dienes and trienes.³⁸

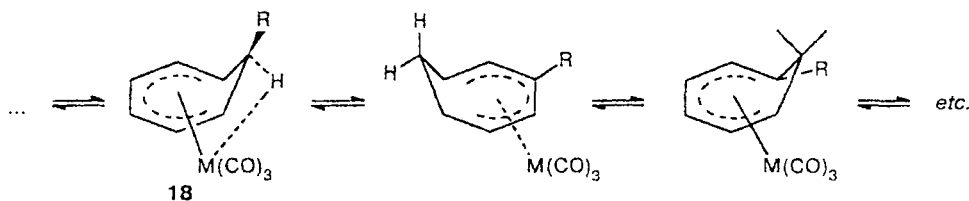
According to the commonly accepted and well supported viewpoint,³⁹ migrations of hydrogen atoms in molecules of complexes of monocyclic or open dienes with transition metals generally proceed *via* intermediate formation of complexes with agostic bonds and hydride intermediates (Scheme 12). In this case, the final result of the rearrangement is isomerization of the complex, which manifests itself in the change in the position of the radical-label R with respect to the diene fragment. These transformations occur most readily in the case of electron-deficient 16-electron complexes in which activation barriers are so low that rearrangements occur rapidly (within the NMR time scale) and result in the appearance of the typical reversible temperature dependences of the 1H and ^{13}C NMR spectra (see Ref. 40).

Generally, the thermal isomerization of selectively labeled 18-electron η^6 -cycloheptatriene and η^5 -cyclohexadienyl complexes of transition metals requires more severe conditions than those in the case of the rearrangement of formally 16-electron compounds shown in Scheme 12. The activation energy of this process (Scheme 13) for the η^6 -cycloheptatriene complexes⁴¹ (18) is $\sim 24 \text{ kcal mol}^{-1}$, which is somewhat lower than the corresponding value for the free ligand (28 kcal mol^{-1}).⁴² For these processes (see Scheme 13), intermediate agostic and hydride forms were not detected. However, the stereospecific migration of the H_{endo} atoms (but not the H_{exo} atoms) was reliably established.⁴³ To the contrary, the agostic form was detected by NMR spectroscopy

at low temperature in the case of the tricarbonylchromium complex with benzocycloheptatriene. At higher temperature, this form is involved in the agostic exchange.⁴⁴ Generally, the appearance of the agostic interaction in the transition state was also supposed when there is no direct experimental evidence confirming this interaction. In this case, a substantial difference in the activation energy of migration of identical substituents in the complex (generally, H atoms) occupying *endo*- and *exo*-positions with respect to the metal atom is considered as the strongest argument in favor of the direct M—H interaction.

As demonstrated above, the Cr— H_{endo} and Cr—C(1) distances are too large, and therefore, agostic interactions in complexes 3 and 5 do not occur. However, this interaction can occur in the transition state. It is significant that the [1,5]-migration of the H_{exo} atom was unambiguously detected in complex 5. Therefore, it can be concluded that coordination of $Cr(CO)_3$ fragments in phenalene promotes substantially the [1,5]-sigmatropic shifts of the hydrogen atom. Apparently, this is determined by the fact that the transition state in these processes is characterized by a substantial charge separation. In this case, the H atom carries a noticeable positive charge. The strong electron-withdrawing effect of the $Cr(CO)_3$ group is favorable for this polarization increasing the lability of the H atom. We did not carry out a detailed study of exchange reactions of the phenalene ligand for another arene in complexes 3 and 5. It can only be noted that the observed rates of this process and the data reported in the literature²⁸ are of the same order.

Scheme 13



M = Mo or Cr; and R = Me or Ph

Therefore, it was established that when 1-*exo*-substituted phenalene complexes are heated, several concurrent reactions proceed simultaneously. The lowest activation barrier occurs in the case of the intramolecular η^6, η^6 -inter-ring haptotropic rearrangement, which proceeds more rapidly and leads to interconversion of the isomer that differs in the position of the tricarbonylchromium fragment in the six-membered rings of the phenalene ligand. The activation energy of the suprafacial [1,5]-shift of the $H(1)_{endo}$ atom is somewhat higher, and this shift occurs without formation of agostic and hydride intermediates. The concurrent reactions of the intermolecular ligand exchange in complexes with aromatic solvents (toluene or C_6F_6) and the analogous processes with the participation of substituted phenalenes that are formed afford complexes containing the label in the coordinated ring. In sum, the above-mentioned transformations determine the distribution of the label among positions 1, 3, 4, 6, 7, and 9. A detailed analysis of the kinetic data made it possible to establish that the migration of the $H(1)_{exo}$ atom proceeds substantially more slowly than that of the $H(1)_{endo}$ atom.

Experimental

All operations, except for TLC, were carried out under an atmosphere of purified argon. The solvents (ether, decane, THF, and hexafluorobenzene) were boiled over a K/Na alloy, which was washed free of aromatic hydrocarbon, and distilled before use. Unless otherwise stated, chromatographic isolation of the resulting complexes was carried out on 40/100 μ silica gel (Chemapol, Bratislava).

The IR spectra were recorded on a UR-20 spectrometer (Karl Zeiss) in heptane. The NMR spectra were measured on a Varian VXR-400 spectrometer (400 MHz for 1H). The assignments in the 1H NMR spectra were made based on double homonuclear resonance (in some cases, the COSY procedure was used) and Overhauser effect measurements using the NOEDIF procedure, which was realized in the software of the spectrometer. The assignments in the ^{13}C NMR spectra were made using the DEPT procedure and by comparing with the spectra of the model compounds. The mass spectra were recorded on a MAT-112S instrument (ionizing voltage 70 eV).

Decane, toluene, toluene- d_8 , and C_6F_6 used for thermal isomerization of the tricarbonylchromium complexes of phenalene were freed from water and oxygen by keeping over a potassium mirror followed by distillation and freezing—evacuation (to 10^{-5} Torr)—thawing repeated three times.

Tricarbonyl(6a,7—9,9a,9b- η^6 -phenalene)chromium (1) and tricarbonyl(3a,6a,9b,4—6- η^6 -phenalene)chromium (2). Freshly distilled $BF_3 \cdot OEt_2$ (13.8 g, 97 mmol) was added to a mixture of phenalene (5.7 g, 21.4 mmol) and $Cr(CO)_3Py_3$ (8 g, 21.4 mmol) in ether (75 mL) at $-10^\circ C$. The reaction mixture was stirred at $25^\circ C$ for 1 h and then washed with water three times. The ethereal layer was dried over $MgSO_4$. The ether was removed *in vacuo*. The residue was chromatographed on a 3×40 cm column with silica gel (a benzene—petroleum ether mixture was used as the eluent). After recrystallization of the red zone from a heptane—benzene mixture, a mixture of complexes 1 and 2 was obtained in a ratio of 40 : 60 (accord-

ing to the data of 1H NMR spectroscopy) in a yield of 3.8 g (44%). More mobile complex 1 was completely separated from 2 by TLC on silica gel (a 10 : 1 hexane—ether mixture was used as the eluent). Compound 1 was crystallized from heptane as red prisms, m.p. $168-170^\circ C$. Literature data:¹⁴ m.p. $116-118^\circ C$. MS: m/z (I_{rel} (%)): 302 $[M]^+$ (20.47), 246 $[M-2CO]$ (12.32), 218 $[M-3CO]$ (70.13), 165 $[M-HCr(CO)_3]$ (52.46), 52 $[Cr]$ (100). IR, $\nu(CO)/cm^{-1}$: 1904, 1918, 1976. The parameters of the 1H and ^{13}C NMR spectra are given in Tables 1, 2, and 3.

Lithium salt 9. A mixture of complexes 1 and 2 in THF was treated with a solution of Bu^tLi in hexane (the molar ratio $(1+2)/Bu^tLi = 1 : 3$) at $-70^\circ C$. The reaction mixture was stirred at $-70^\circ C$ for 15 min. The solution turned dark-red. The parameters of the 1H NMR spectra are given in Table 4.

Synthesis of complexes 3, 4, 5, and 1 from lithium salt 9. Water (0.1 mL) in THF (5 mL) was added to a solution of salt 9, which was obtained from a mixture of compounds 1 and 2 (0.2 g, 0.49 mmol) in THF (30 mL), at $-70^\circ C$. The reaction mixture was heated to $-20^\circ C$. The solvent was removed *in vacuo*. The residue was chromatographed on plates with silica gel (a 10 : 1 hexane—ether mixture was used as the eluent). Complex 1 was obtained in a yield of 0.18 g (90%).

Analogously, complex 5 was obtained from a mixture of compounds 1 and 2 (0.16 g, 0.4 mmol) and D_2O (0.1 mL) in a yield of 0.15 g (93%). Complex 3 was obtained from a mixture of 1 and 2 (0.17 g, 0.42 mmol) and MeI (1.2 g) followed by TLC in a yield of 0.1 g (57%).

The reaction of salt 9, which was prepared from a mixture of complexes 1 and 2 (0.20 g, 0.5 mmol), with butyl iodide (0.18 g, 1 mmol), which was stored over copper chips and freshly distilled over Na_2CO_3 , gave complex 4 in a yield of 0.20 g (70%).

Mass spectrum of compound 5, m/z (I_{rel} (%)): 303 $[M]^+$ (17.13), 247 $[M-2CO]$ (13.29), 220 $[M+1-3CO]$ (22.79), 219 $[M-3CO]$ (52.39), 218 $[M-1-3CO]$ (14.54), 166 $[M-HCr(CO)_3]$ (31.48), 165 $[M-1-HCr(CO)_3]$ (18.48), 52 $[Cr]$ (100). IR, $\nu(CO)/cm^{-1}$: 1905, 1918, 1977.

Compound 3 was crystallized from hexane as red platelets, m.p. $153-154^\circ C$. MS, m/z (I_{rel} (%)): 316 $[M]^+$ (24.1), 260 $[M-2CO]$ (18.8), 246 $[M-CO-CH_2-CO]$ (11.65), 233 $[M-2CO-C_2H_5]$ (31.44), 232 $[M-3CO]$ (89.56), 230 $[M-3CO-2H]$ (25.3), 217 $[M-3CO-CH_3]$ (16.5), 180 $[M-Cr(CO)_3]$ (12.61), 179 $[M-HCr(CO)_3]$ (55.29), 178 $[M-H_2Cr(CO)_3]$ (10.32), 165 $[M-CH_3Cr(CO)_3]$ (56.68), 52 $[Cr]$ (100). IR, $\nu(CO)/cm^{-1}$: 1905, 1918, 1977. The parameters of the 1H and ^{13}C NMR spectra are given in Tables 5 and 3.

Synthesis of anion 10 by deprotonation of 1-*exo*-methylphenalene complex 3. Complex 10 was synthesized analogously to anion 9 by treating a solution of compound 3 (0.3—0.5 mmol) in THF (15—20 mL) with a solution of Bu^tLi in hexane (a threefold excess with respect to 3). The mixture was stirred at $-40^\circ C$ for 15 min (the mixture turned dark-red), and complex 10 formed.

Protonation and methylation of complex 10. Protonation and methylation of compound 10 was carried out as described above for anion 9.

Complex 12 was obtained from compound 10 (0.12 g, 0.29 mmol) and H_2O (0.1 mL) in a yield of 0.09 g (75%). IR, $\nu(CO)/cm^{-1}$: 1906, 1918, 1978. The parameters of the 1H and ^{13}C NMR spectra are given in Tables 5 and 3.

Analogously, complex 11 was obtained from complex 3 (0.2 g, 0.48 mmol) and CH_3I (1.4 g) as red needles in a yield of 0.18 g (87%), m.p. $120-122^\circ C$ (from pentane). MS, m/z (I_{rel} (%)): 330 $[M]^+$ (14.24), 274 $[M-2CO]$ (14.26), 247 $[M-2CO-C_2H_5]$ (11.7), 246 $[M-3CO]$ (87.8), 244

[M-3CO-2H] (28.2), 231 [M-3CO-CH₃] (12.94), 230 [M-3CO-CH₂] (12.56), 194 [M-Cr(CO)] (12.7), 193 [M-HCr(CO)] (59.13), 179 [M-CH₃Cr(CO)₃] (100), 178 [M-HCr(CO)₃-CH₃] (30.06), 165 [M-CH₃Cr(CO)₃-CH₂] (5.36), 152 [M-Cr(CO)₃-C₃H₅] (7.88), 52 [Cr] (79.11). IR, $\nu(\text{CO})/\text{cm}^{-1}$: 1905, 1914, 1975. The parameters of the ¹H and ¹³C NMR spectra are given in Tables 5 and 3.

Complex 14. Deprotonation of complex 11 and quenching of the resulting anion 13 with water were carried out using the procedure described above for complexes 1 and 12. Complex 14 was obtained from compound 11 (0.15 g, 0.35 mmol) in a yield of 0.12 g (80%). Chromatographic separation was carried out on plates with silica gel (a 20 : 1 hexane-ether mixture was used as the eluent) and then on a column with Silpearl silica gel (100 : 1 and 50 : 1 hexane-ether mixtures as the eluent). IR, $\nu(\text{CO})/\text{cm}^{-1}$: 1904, 1917, 1978. The parameters of the ¹H NMR spectra are given in Table 5.

Thermal isomerization of complexes 5 and 3 in C₆F₆ and toluene. A solution of complex 5 or 3 (12 mg) in C₆F₆ (in some cases, toluene was added to hexafluorobenzene, which enhanced the solubility of the complex, increased noticeably the difference in the chemical shifts, and therefore, simplified the precision integration of the spectra) was heated in a 5 or 10 mm-diameter sealed standard tube (when the ¹H or ²D NMR spectra, respectively, were recorded) in the temperature range from 80 to 120 °C in a thermostat (the temperature was maintained within ± 0.5 °C). At certain intervals, the tube was taken out, cooled rapidly to ~ 20 °C with cold water, and the ¹H and ²D NMR spectra were recorded. The resonance conditions were stabilized using the signals of deuterium from SiMe₄-d₁₂ and the signals of fluorine from C₆F₆, respectively. The high-precision ²H NMR spectra of the complexes were recorded with stabilization of the resonance conditions on the fluorine nuclei with the use of a special detector constructed by us. For complex 3, the change in the concentration in the course of measurements in deuterotoluene was monitored by ¹H NMR spectroscopy with stabilization using the signals of deuterium from the solvent. All other operation were carried out analogously to those described above.

Thermal isomerization of complexes 5 and 3 in decane. Decane was added to complex 5 or 3 (100 mg) at 50 °C until the complex dissolved completely. The solution was heated at a fixed temperature during certain intervals. Then the solution was filtered through a small column with silica gel replacing decane by hexane and eluting the complex with benzene. After recrystallization from a benzene-heptane mixture, the crystals obtained were washed with pentane and dried *in vacuo*. The composition of the isomerization products was determined by ¹H and ²D NMR spectroscopy.

Thermal isomerization of complex 16. A solution of compound 16 (0.1 g) in decane (20 mL) was heated at 80 °C for 18 h. Trituration of the reaction mixture was carried out using the procedure described above. The residue was chromatographed on a column with Silpearl silica gel eluting with a hexane-ether mixture with a gradual increase in the concentration of ether from 1 to 2%. Complex 15 was obtained in a yield of 0.01 g (10%). The sample of complex 15 obtained was heated in decane at 140 °C for 18 h. The complexes were freed from decane and chromatographed on Silufol plates in a 30 : 1 hexane-ether mixture. Three dark-red zones were obtained. The two upper zones contained (according to the ¹H NMR spectra) complexes 15 and 17, respectively. The lower zone contained a mixture of complexes 11, 14, and 16. The parameters of the ¹H and ¹³C NMR spectra of the complexes are given in Tables 5 and 3.

X-ray structural analysis of complex 3. X-ray diffraction study was performed on an automated four-circle Hilger &

Table 12. Atomic coordinates ($\times 10^4$; for Cr, $\times 10^5$) and isotropic equivalent thermal parameters (B_{eq}) in the structure of 3

Atom	x	y	z	$U_{\text{eq}}/\text{\AA}^2$
Cr	22189(8)	24466(14)	2169(6)	3.20(2)
O(11)	1589(4)	9(5)	-1333(3)	5.6(2)
O(12)	282(4)	4241(5)	-933(3)	5.9(2)
O(13)	3643(4)	4100(5)	-1000(3)	6.3(2)
C(1)	1560(5)	-983(7)	1269(4)	4.0(2)
C(2)	2313(6)	-2141(6)	908(4)	4.7(2)
C(3)	3389(6)	-1987(7)	901(5)	4.5(2)
C(3a)	3938(5)	-446(7)	1167(4)	3.4(2)
C(4)	5060(6)	-227(8)	1196(4)	4.3(2)
C(5)	5554(5)	1268(10)	1395(4)	4.6(2)
C(6)	4929(5)	2489(10)	1525(4)	4.3(2)
C(6a)	3752(5)	2336(9)	1521(3)	3.5(2)
C(7)	3033(7)	3605(7)	1630(4)	4.1(2)
C(8)	1900(6)	3380(9)	1632(5)	4.2(3)
C(9)	1421(6)	1900(9)	1501(5)	3.7(2)
C(9a)	2073(5)	628(7)	1347(4)	3.3(2)
C(9b)	3244(5)	826(7)	1354(4)	2.7(2)
C(10)	1355(6)	-1468(8)	2291(5)	5.7(2)
C(11)	1855(5)	956(7)	-739(4)	3.6(2)
C(12)	1021(5)	3548(7)	-466(4)	3.7(2)
C(13)	3089(5)	3448(7)	-527(4)	4.0(2)

Watts diffractometer at 20 °C (Mo-K α radiation). All calculations were carried out on an Eclipse S/200 computer using the INEXTL program.⁴⁵ Crystallographic data are as follows: crystals of C₁₇H₁₂CrO₃ are monoclinic, $a = 12.059(1)$ Å, $b = 8.665(1)$ Å, $c = 13.711(1)$ Å, $\beta = 101.48(1)^\circ$, $V = 1404.0(2)$ Å³, space group $P2_1/c$, $Z = 4$, $d_{\text{calc}} = 1.50$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 8.6$ cm⁻¹. Intensities of 902 independent reflections with $I > 2\sigma(I)$ were measured using the $\theta/2\theta$ scanning technique ($2\theta < 50^\circ$). The structure was solved by the heavy-atom method. All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method (H atoms were included in the refinement in calculated positions), $R = 0.032$, $R_w = 0.029$; weighting scheme $W = (\sigma_F^2 + 10^{-4}F_{\text{obs}}^2)^{-1}$, figure of merit $S = 1.28$. Atomic coordinates and equivalent isotropic thermal parameters $U_{\text{eq}} = 1/3 \sum_{ij} U_{ij} a_i^* a_j^* (a_i a_j)$ are given in Table 12.

Procedure for determination of kinetic parameters. Let us consider briefly a number of analytic equations, which form the basis for the algorithm.³⁰ The smooth dependence of the responses (x) of the current concentrations on the desired parameters (k) makes it possible to determine the numerical Jacobian matrix $\bar{X}(k)$ of dimension (N, s) (N is the total number of responses, and s is the number of the desired parameters):

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

In this case, the Fisher information matrix takes the form

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

where \bar{D} is the dispersion matrix of responses. In the general case, the rank of the $\bar{X}(k)$ matrix, v , meets the condition $v \leq s$.

In the case of local nonidentifiability, $v < s$, the $\bar{M}(k)$ matrix is degenerate, and the vector of the desired parameters is not uniquely determined. It is possible to perform numerical

reparametrization of the model with respect to a new set of parameters, θ , to which a new Fisher matrix corresponds:

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

The relation between the matrices takes the form

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

where the \bar{B}^- matrix performs a transformation inverse to that (\bar{B}) which brings the Jacobian matrix $\bar{X}(k)$ to a form such that the first v columns are basic: $\bar{B} = b_j/b_k \cdot \partial\theta/\partial k$. The calculation procedure gave the values of the \bar{B} matrix. The form of the matrix was indicative of the identifiability of the model. In the case of the desired parameter, which was uniquely identified, the corresponding column and row of the \bar{B} matrix contain only one initial element (unity). For new parameters, this condition is not fulfilled, and they have derivatives with respect to more than one desired parameter.

We thank N. S. Kulikov for measuring the mass spectra of the complexes, V. V. Simonyan for performing quantum-chemical calculations by the PM3 method, and M. M. Shtern for help in preparation of the samples for NMR spectroscopy. We thank Varian for supplying a VXR-400 spectrometer within the framework of the Scientific and Technical Collaboration and the Alexander von Humboldt Foundation for supplying an Alpha Digital workstation.

This work was supported by the Russian Foundation for Basic Research (Project No. 96-03-3241a) and the INTAS (Grant 94-2921).

References

1. B. Mann, *Comprehensive Organometallic Chemistry*, Eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, 1982, 3, 1988, 89.
2. B. Mann, *Chem. Soc. Rev.*, 1986, 15, 167.
3. J.-Y. Saillard and R. Hoffmann, *J. Am. Chem. Soc.*, 1984, 106, 2006.
4. T. A. Albright, P. Hofmann, R. Hoffmann, P. Lillya, and P. A. Dobosh, *J. Am. Chem. Soc.*, 1983, 105, 3396.
5. H. A. Ustynyuk, *Metallorg. Khim.*, 1989, 2, 43 [*Organomet. Chem. USSR*, 1989, 2 (Engl. Transl.)].
6. Yu. N. Ustynyuk, *Vestn. Mosk. Univ., Ser. 2: Khimiya*, 1982, 23, 605 (in Russian).
7. M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, 250, 395.
8. T. A. Albright, *Tetrahedron*, 1982, 32, 1339.
9. O. I. Trifonova, Yu. F. Oprunenko, V. I. Mstislavsky, I. P. Gloriov, N. A. Ustynyuk, and Yu. A. Ustynyuk, *Organometallics*, 1990, 9, 1707.
10. K. Nakasuj, M. Yamaguchi, and I. Murata, *J. Am. Chem. Soc.*, 1986, 108, 325.
11. A. Stanger and H. Weismann, *J. Organomet. Chem.*, 1996, 515, 183.
12. A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, Yu. A. Ustynyuk, L. N. Novikova, and Yu. N. Luzikov, *J. Organomet. Chem.*, 1978, 154, 45.
13. A. N. Nesmeyanov, L. N. Novikova, N. A. Ustynyuk, V. G. Andrianov, Yu. F. Oprunenko, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1982, 226, 239.
14. S. Lin and P. Boudjouk, *J. Organomet. Chem.*, 1980, 187, C11.
15. K. Öfele, *Chem. Ber.*, 1966, 99, 1752.
16. N. A. Ustynyuk, L. N. Novikova, V. K. Bel'skii, Yu. F. Oprunenko, S. G. Maiyugina, O. I. Trifonova, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1985, 294, 31.
17. W. J. Bland, R. Davis, and J. L. A. Durrant, *J. Organomet. Chem.*, 1982, 234, C20.
18. V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.*, 1950, 72, 1240.
19. U. Edlund, *Org. Mag. Reson.*, 1979, 12, 661.
20. V. Kunz and W. Nowacki, *Helv. Chim. Acta*, 1967, 50, 1052.
21. B. Rees and P. Coopens, *Acta Crystallogr., B*, 1973, B 29, 2515.
22. J. M. Guss and R. J. Mason, *J. Chem. Soc., Dalton Trans.*, 1973, 1834.
23. K. H. Dötz, R. Dietz, A. von Imhof, and G. Huther, *Chem. Ber.*, 1976, 109, 2033.
24. J. W. Hull, Jr. and W. L. Gladfelter, *Organometallics*, 1982, 1, 264.
25. R. H. Crabtree, E. M. Holt, M. Lavin, and S. M. Morehouse, *Inorg. Chem.*, 1985, 24, 1986.
26. M. Brookhart, W. Lamanna, and M. B. Humphrey, *J. Am. Chem. Soc.*, 1982, 104, 2117.
27. Yu. F. Oprunenko, S. G. Malyugina, O. Ya. Babushkina, Yu. A. Ustynyuk, and N. A. Ustynyuk, *Metallorg. Khim.*, 1989, 2, 599 [*Organomet. Chem. USSR*, 1989, 2 (Engl. Transl.)].
28. K. G. Traylor and K. J. Stewart, *J. Am. Chem. Soc.*, 1986, 108, 6977.
29. V. Freudenberger, H. Prinsbach, and U. Schneidenger, *Helv. Chim. Acta*, 1967, 50, 1087.
30. V. G. Gorskii, E. A. Katsman, F. D. Klebanova, and A. A. Grigor'ev, *Teor. Eksp. Khim.*, 1987, 2, 191 [*Theor. Exp. Chem.*, 1987, 2 (Engl. Transl.)].
31. A. D. Hunter, V. Mozol, and S. D. Tsai, *Organometallics*, 1992, 11, 2251.
32. J. L. Fletcher and M. J. McGlinchey, *Can. J. Chem.*, 1975, 53, 1525.
33. P. G. Gassman and P. A. Deck, *Organometallics*, 1994, 13, 1934.
34. B. Deubzer, H. P. Fitz, C. G. Kreiter, and K. Öfele, *J. Organomet. Chem.*, 1987, 7, 289.
35. R. M. Pagni, M. N. Burnett, and H. M. Hassaneen, *Tetrahedron*, 1982, 38, 843.
36. J. A. Butcher and R. M. Pagni, *J. Am. Chem. Soc.*, 1979, 101, 3997.
37. N. M. Sergeyev, Yu. N. Luzikov, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 1974, 65, 303.
38. C. G. Kreiter, *Adv. Organomet. Chem.*, 1986, 26, 297.
39. J. Müller, M. Menig, and P. V. Rinze, *J. Organomet. Chem.*, 1979, 181, 387.
40. B. D. Johnson, J. Lewis, and D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 1972, 19, 395.
41. M. J. Foreman, P. L. Pauson, G. R. Knox, K. H. Todd, and W. E. Watts, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1141.
42. A. P. ter Borg and H. Kloosterziel, *Rec. Trav. Chim. Pays-Bas*, 1963, 82, 717.
43. S. G. Davies, S. J. Simpson, and Fileebeen-Khan, *Organometallics*, 1983, 2, 539.
44. C. G. Kreiter et al., *J. Organomet. Chem.*, 1988, 355, 149.
45. R. G. Gerd, A. I. Yanovskii, and Yu. T. Struchkov, *Kristallografiya*, 1983, 28, 1029 [*Sov. Phys.-Crystallogr.*, 1983, 28 (Engl. Transl.)].

Received February 28, 1997