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Inter-ring $\eta^6 \rightleftarrows \eta^6$ haptotropic rearrangements in naphthalenetricarbonylchromium complexes

Yu.F. Oprunenko, S.G. Malugina, Yu.A. Ustynyuk *

M.V. Lomonosov State University, Department of Chemistry, Moscow, 117234 (U.S.S.R.)

N.A. Ustynyuk, D.N. Kravtsov

Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, 117813 Moscow (U.S.S.R.)

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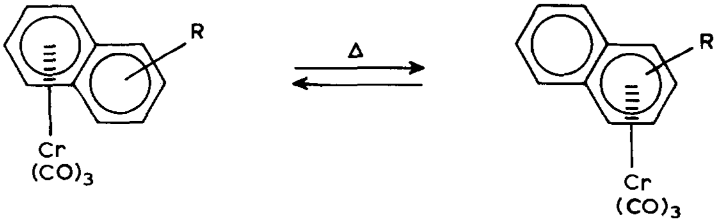
Abstract

Two methods for the controlled introduction of substituents in the coordinated and non-coordinated ring of η^6-naphthalenetricarbonylchromium are proposed. When the selectively substituted naphthalenetricarbonylchromium complexes are heated the tricarbonylchromium groups are redistributed between the substituted and the unsubstituted rings because of inter-ring haptotropic rearrangements. The rate constants of these isomerizations were measured. During rearrangement of individual isomers of (1-methylacenaphthene)tricarbonylchromium the configuration of the methyl group does not change, thus testifying to intramolecular rearrangements.

Introduction

Recently in the chemistry of π-complexes of transition metals with aromatic polycycles inter-ring haptotropic rearrangement, i.e. the transition of metal between the rings along the plane of a ligand, has received ever-growing attention. The reversible and irreversible metal rearrangements between 6- and 5-membered rings have been previously observed in the fluorenyl-anion complexes and related aromatic systems [1,2]. The same processes for naphthalene complexes (eq. 1) have received little attention.



(1)

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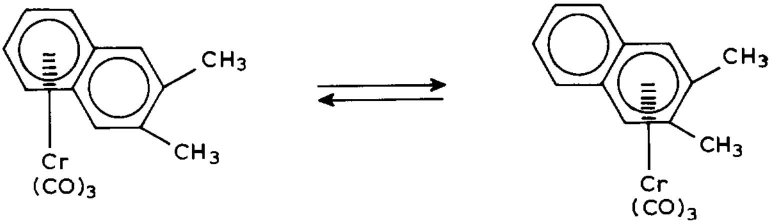
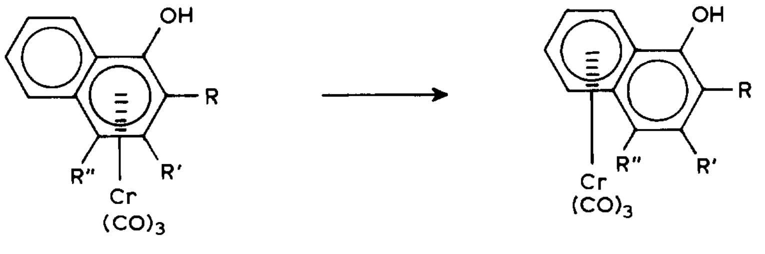
The IR spectra of isomers in the ν(CO) region for both the degenerate (R = H) and the non-degenerate (R ≠ H) processes are very close and almost indistinguishable, which makes the study of these rearrangements (eq. 1) extremely complicated. Dynamic NMR spectroscopy cannot be applied owing to the high activation energy of isomerization (eq. 1). On heating, ^{1}H and ^{13}C NMR spectra the samples of were did not change for the following naphthalene complexes: $[(\eta^6\text{-}C_{10}H_8)Ir(C_5Me_5)]^{2+}$ (PF_6), 70 °C, CF_3COOH, [3]; $(\eta^6\text{-}C_{10}H_8)_2Cr$ (130 °C, C_6D_6) [4]; $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$ (110 °C, Bu_2O or sulfolane) [5].

In order to study the inter-ring rearrangements as in eq. 1, it is necessary to introduce a substituent R into the coordinated or non-coordinated ring of naphthalene. However the absence of suitable techniques hampers systematic study of such processes. In cases when the inter-ring haptotropic shift in naphthalene complexes was established, the controlled introduction of the substituent was accomplished via processes very different from each other. For example, Deubzer obtained a mixture of two isomer complexes by the interaction of 2,3-dimethylnaphthalene with $Cr(CO)_6$ and then separated one isomer by thorough fractional crystallization. This enabled him to detect the isomerization (eq. 2) and hence evaluate the thermodynamic parameters of the process, although equilibrium was not reached [6]. Unfortunately, the results have not been published in journals and have thus not been widely cited.



(2)

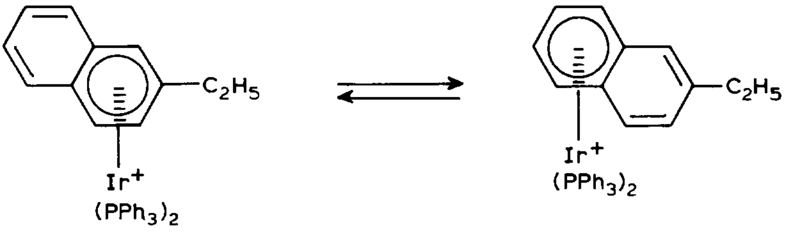
Reaction of $CH_3O(Ph)C{=}Cr(CO)_5$ or $Ph_2C{=}Cr(CO)_5$ with alkyne gives the chromium tricarbonyl complexes of the substituted naphthanols with $Cr(CO)_3$ group bonded to the "naphthol" ring. When heated to 80 °C in dibutyl ether, irreversible migration of chromium tricarbonyl group to the unsubstituted ring occurs (eq. 3) [7].



(3)

R" = OCH3 or Ph
R' = H or CH3
R = CH3 , n-C3H7 , n-C4H9 and Ph.

In the reaction of 2-vinylnaphthalene with $[IrH_2(Me_2CO)_2(PPh_3)_2]^+$, the vinyl group is hydrogenated to the ethyl group and the arene complex with iridium in the "ethylated" ring is formed. This complex is reversibly isomerized (eq. 4) under unusually mild conditions (CH_2Cl_2, +10 °C). At equilibrium the isomer ratio is 1 : 1.



(4)

Although the above examples confirm that processes of the type in eq. 1 occur they cannot serve as a basis for a comprehensive investigation. In order to conduct such an investigation we have developed two methods for the controlled introduction of substituents into the coordinated, or non-coordinated, ring (eq. I) in the η^6-naphthalenetricarbonylchromium system (eq. 1). Consequently, the kinetic and thermodynamic parameters for the processes of type 1 were obtained. These isomerizations are mainly intramolecular, as was confirmed by crossover experiments, and substantiated by the fact that the rearrangements of individual isomers of (1-methyl-acenaphthene)tricarbonylchromium did not effect the configuration of the methyl group. Some of the results discussed below have been published previously [9,10]. Similar $\eta^6 \rightleftarrows \eta^6$ rearrangements for the isomer (1,1-dimethyl-1-silaacenaphthene)tricarbonylchromium complexes have been studied [11]. While this report was being prepared for publication, the article by Kündig et al. [12] appeared in which the haptotropic inter-ring rearrangements of the type (1) in the selectively deuterated tricarbonylchromium complexes were described. However no experimental details were given. Later Kirss and Treichel [13] described isomerization (1) for the selectively deuterated methoxynaphthalenetricarbonylchromium complexes.

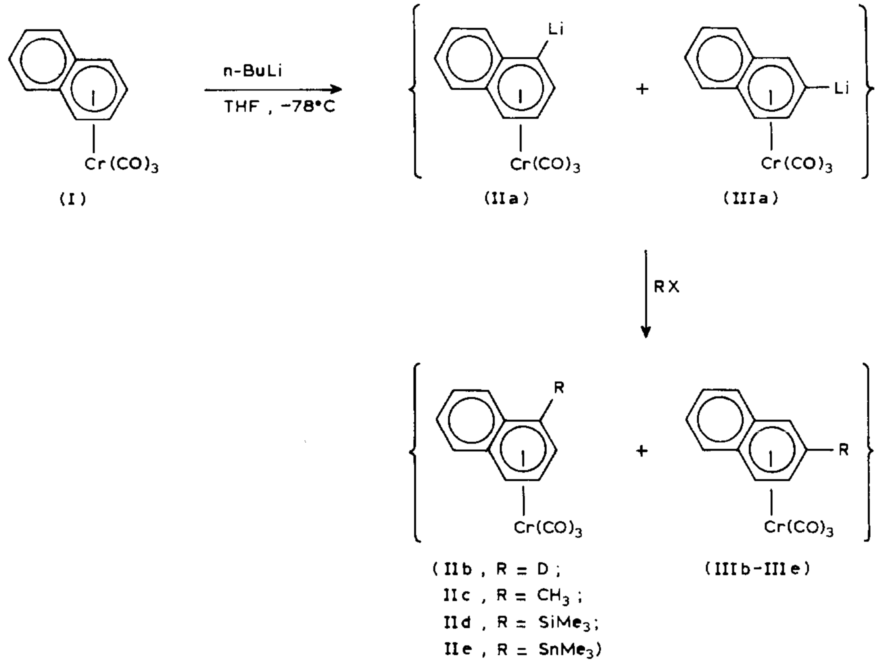
Results and discussion

To introduce the substituent into the coordinated ring (I), complex I was metallated with n-BuLi in THF, with the subsequent treatment of Li-derivatives IIa and IIIa with electrophiles RX (Scheme 1).

The coordination with chromium tricarbonyl group is known to increase arene proton acidity (pK_a values decrease by 6–7 units [14]) and hard nucleophiles (p- and s-BuLi, CH_3Li) metallate the π-ring rather than add to it [15]. The metallation of I with BuLi was carried out in THF at −78 °C. The mixture of α- and β-lithiumnaphthyl chromium tricarbonyl IIa, IIIa that formed under these conditions was treated by electrophile without prior separation and yielded mixtures of α- and β-substituted complexes II and III. No complexes with substituent on the non-coordinated ring were detected. Thus, it may be concluded that the metallation reaction proceeds almost exclusively at the coordinated ring, I.

In all cases initial I was detected among the reaction products and is apparently formed by the protonation of the intermediate lithium naphthyl derivatives Iα, Iβ by acid admixtures in RX or because of the incomplete metallation of I.

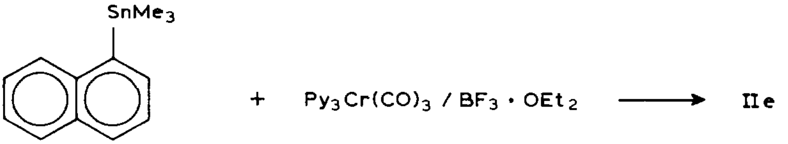
No di-substituted complexes were detected.



Scheme 1

The ratio of α- and β-isomers (II/III) depends on the steric requirements of R group. This may be caused by the IIa ⇄ IIIa equilibrium because of Li,H exchange and different correlations of the interaction rates between IIa, IIIa and RX, on the one hand, and Li,H exchange, on the other. At present an additional study is being conducted to account for the different ratios of α- and β-isomers; the results will be reported in subsequent publications.

Complexes IIe and IIIe were obtained individually from the corresponding naphthyl trimethyl stannanes using the technique suggested by Öfele [16] (eqs. 5 and 6):



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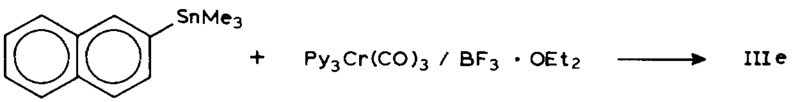
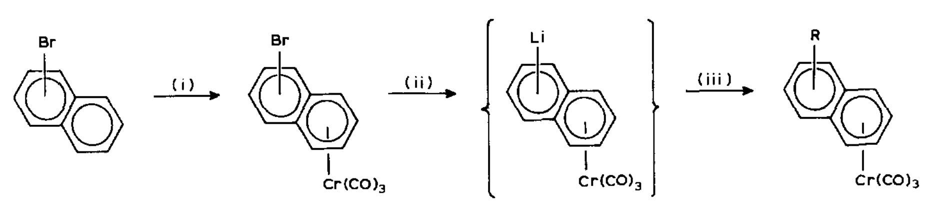
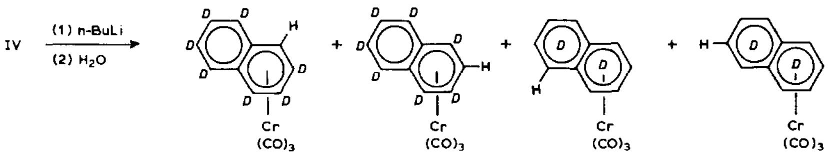


(6)

The approach illustrated in Scheme 1 was used to introduce protium into d_8-naphthalenetricarbonylchromium (IV) (eq. 7).



Scheme 2. VIf, α-Br-isomer; VIa, α-Li-isomer; VIb–VIe, α-isomers; VIIf, β-Br-isomer; VIIa, β-Li-isomer; VIIb–VIIe, β-isomers. (Where: (b R = D, c R = CH_3, d R = $SiMe_3$, e R = $SnMe_3$). (i) $Py_3Cr(CO)_3/3BF_3 \cdot OEt_2$, ether, 0–25 °C; (ii) n-BuLi, ether, −78 → −50 °C; (iii) RX, ether, −50 → 0 °C;



(7)

(IVα) (IVβ) (Vα) (Vβ)

^1H NMR spectroscopy showed that apart from IVα (singlet δ 5.35, C_6D_6) and IVβ (δ 4.72) the isomers with protium in the non-coordinated ring Vα (δ 6.92) and Vβ (δ 6.80) were present among the reaction products (eq. 7). The IVα : IVβ : Vα : Vβ ratio is 35 : 47 : 9 : 9 *.

The selective metallation of the coordinated ring was used by Treichel [13] to introduce deuterium into methoxynaphthalenechromium tricarbonyl complexes.

We used a different approach to introduce the substituent into the non-coordinated ring (cf. Scheme 2).

The interaction of α- or β-bromonaphthalenes with $Py_3Cr(CO)_3/Et_2O \cdot BF_3$ yielded VIf and VIIf, complexes in which chromium atom is bonded to the unsubstituted ring. They were used to produce the corresponding Li derivatives VIa, VIIa by Br,Li exchange. VIa and VIIa (without intermediate separation) were treated with electrophiles RX (D_2O, CH_3I, $ClSiMe_3$, $ClSnMe_3$) to give the complexes VIb–VIe and VIIb–VIIe with the substituent R in the non-coordinated ring. It is essential that the individual isomers and not their mixtures are formed via Scheme 2. The major by-product is naphthalenetricarbonylchromium (1) formed by the protonation of VIa or VIIa. The admixtures in RX may serve as a proton source. An alternative explanation, i.e. the interaction of VIa or VIIb with solvent seems unlikely for the ether.

It is noteworthy that the "smoothest" introduction of substituents (Scheme 2) occurs in ether. Unexpectedly, when the same reactions (Scheme 2) were repeated in THF isomers II and III (in the case of IId, IIe and IIId, IIIe) were detected among the reaction products together with complexes VI and VII. Their origin is being studied at present and will be reported later.

The methods proposed for the introduction of substituents enabled the study of the inter-ring metallotropic rearrangements II ⇄ VI and III ⇄ VII.

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* According to mass-spectroscopic data, a small amount of $C_{10}D_6H_2Cr(CO)_3$ is also formed. This is consistent with ^1H NMR analysis.

Table 1

K_{eq} values for the isomerizations VI ⇄ II and VII ⇄ III

R	$K_{eq} = [II]/[VI]$	$K_{eq} = [III]/[VII]$
D	1	1
CH_3	0.88	1.80
Me_3Si	3.98	6.27
Me_3Sn	$\geqslant 97/\leqslant 3$	$\geqslant 97/\leqslant 3$

Heating of the isomers (VI or VII) or mixtures (II and III) in decane at 130 °C leads to the redistribution of chromium tricarbonyl group between the substituted and unsubstituted rings. The equilibrium (Table 1) is reached in 4–8 h and is independent of what the starting isomer was. The complexes II, III, VI and VII are relatively stable under these conditions.

Only in the case of the stannyl derivatives was the equilibrium shifted completely toward the isomers II and III; in the other cases an equilibrium of the two forms was observed. In benzene and toluene the isomerizations (1) proceed at low temperature, but they are complicated to a certain extent by the substitution of naphthalene ligand by solvent, which is typical of naphthalenetricarbonylchromium complexes [12,17].

The actual rearrangement in the NMR tube was not observed often (Table 2) owing to partial decomposition of samples. To check the degree of isomerization (1) in decane, the mixtures of complexes were isolated from the reaction solution and their ^1H and ^2H NMR spectra were recorded.

The values $K_{IV\beta \to V\beta}$ and $K_{IV\alpha \to V\alpha}$ are equal within ^1H NMR accuracy. For this rearrangement E_A is 28.67 kcal/mol, lg A is 12.82; $S^{\#}$ is 1.64 e.u. The concentration of the complexes was 10^{-1} mmol/l.

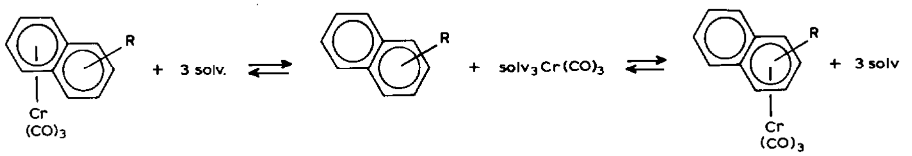
The mechanism of rearrangements (1) is of special importance. The calculations using the EH method [1] and the possibility of producing arenetricarbonylchromium complexes by substituting naphthalene ligand in I [12,17], favour both dissociative intermolecular and intramolecular mechanisms for inter-ring haptotropic rearrangements.

Table 2

Kinetic parameters of isomerizations (type 1) obtained by use of ^1H NMR spectroscopy

Starting complex	Isomerization conditions	Values of K, s^{-1} ($\times 10^5$)
VIc	toluene-d_8, 100 °C	$K_{VIc \to IIc} = 1.0$
		$K_{IIc \to VIc} = 0.9$
VIIc	toluene-d_8, 100 °C	$K_{VIIc \to IIIc} = 2.9$
		$K_{IIIc \to VIIc} = 1.6$
VId	toluene-d_8, 100 °C	$K_{VId \to IId} = 13.76$
		$K_{IId \to VId} = 3.46$
VIId	toluene-d_8, 100 °C	$K_{VIId \to IIId} = 23.86$
		$K_{IIId \to VIId} = 11.14$
VIe	C_6D_6, 75 °C	$K_{VIe \to IIe} = 0.88$
VIIe	C_6D_6, 75 °C	$K_{VIIe \to IIIe} = 1.12$
IVα + IVβ	toluene-d_8, 100 °C	$K_{IV\alpha \to V\alpha} = 11.0$
	toluene-d_8, 114 °C	$K_{IV\alpha \to V\alpha} = 44.5$

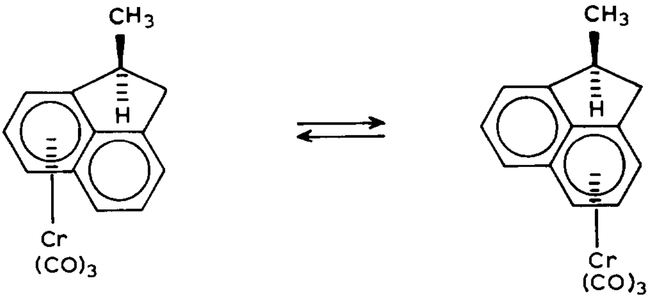
The intramolecular mechanism of such rearrangements presupposes the idea that an organometallic group "slides" along the plane of the π-ligand without breaking the bond connecting it (eq. 1). The dissociative mechanism, on the other hand, is characterised by the dissociation of arene complex formation of a kinetically independent particle with solvent molecules ($solv_3Cr(CO)_3$), which then interacts with another ring of π-ligand (eq. 8).



(8)

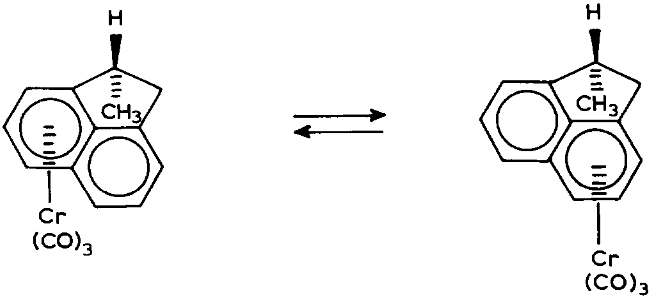
To determine the intra- or intermolecular character of rearrangements (1) the isomerizations IX ⇄ X and XI ⇄ XII were studied (eqs. 9 and 10). A mixture of complexes IX–XII was obtained by the interaction of 1-methylacenaphthene with $Py_3Cr(CO)_3/BF_3 \cdot OEt_2$. The individual *exo*-methyl complexes IX and X and the mixture of *endo*-methyl derivatives XI and XII were separated by HPLC [18]. The individual isomers IX and X when heated only undergo the isomerization IX ⇄ X, without the formation of *endo*-isomers XI and XII, and the reversible rearrangement of XI ⇄ XII is not accompanied by the formation of *exo*-isomers IX and X. Hence, the processes outlined in eqs. 9 and 10 may be said to be intramolecular.

The minor contribution of the intermolecular mechanism (8) is also substantiated by the fact that heating naphthalenetricarbonylchromium complexes under condi-



(IX) (X)

(9)



(XI) (XII)

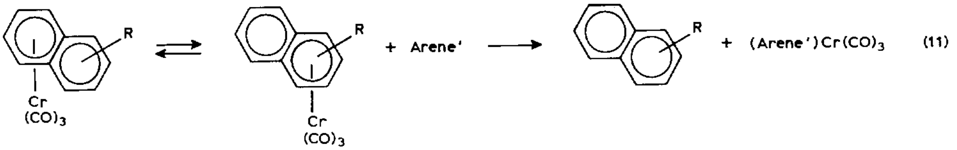
(10)

Table 3

Results of reactions (eq. 10)

Starting complexes	Arene′	Ratio of arene′/ starting complex	Conditions: solvent, temperature (°C), time (h)	Yield of arene′ $Cr(CO)_3$ (approx. (%))
IVα + IVβ	naphthalene-H_8	2 : 1	decane, 120, 6	12
IVα + IVβ	naphthalene-H_8	20 : 1	decane, 120, 6	30
IVα + IVβ	C_6D_6	30 : 1	pure C_6D_6, 100 °C, 6	10
IVα + IVβ	$C_6D_5CD_3$	30 : 1	pure $C_6D_5CD_3$, 115 °C, 6	20

tions of the isomerization (1) (decane, 130 °C, 5–6 h) in an excess of added arene yields the substitution products of naphthalene ligand, i.e. (arene′)$Cr(CO)_3$ in infinitesimal quantities (eq. 11 and Table 3).



(11)

Thus, the rate of rearrangement (1) under these conditions is higher than the substitution rate of naphthalene ligand. The fact that the yield of substitution products may be increased by the increased concentration of arene, higher temperature and the use of coordinating solvents does not contradict the conclusion about the intramolecular nature of the process (1).

Experimental

All operations, except for preparative TLC, were carried out in argon atmosphere. THF and decane were purified by refluxing over K/Na alloy, and ether was purified by refluxing over sodiumbenzophenone ketyl. Solvents were distilled in argon atmosphere immediately before use.

IR spectra were recorded by a UR-20 spectrophotometer, and NMR spectra were recorded by Varian XL-100 and XL-400 spectrometers. Chemical shifts are given in δ scale (m = multiplet, d = doublet, dd = doublet of doublets, s = singlet, t = triplet). A Finnigan-MAT 4600 was used to record the mass spectra at electron impact (10–70 eV); the peak, intensity, and ion are given. The Cr^+ peaks for all complexes were intense only at 70 eV.

1. Synthesis of naphthalenechromium tricarbonyl complexes by the Öffele technique [16]

η^6-Naphthalenetricarbonylchromium (I). To a mixture of 2.24 g (17.5 mmol) of naphthalene and 5 g (13.4 mmol) of $Py_3Cr(CO)_3$ in 75 ml of ether at −10 °C, was added (8.5 g, 60 mmol) of freshly distilled $BF_3 \cdot OEt_2$. The temperature was slowly increased to 25 °C with stirring. After the reaction mixture had been stirred for a further hour it was treated with water. The ether layer was dried over $MgSO_4$ and then the ether was removed under vacuum at 0 °C. The residue was chromato-

graphed on a column with silica gel (3 cm × 40 cm); the orange band of I was eluted by a petroleum ether/benzene mixture, the portion of benzene was increased progressively to 50%. Recrystallization from benzene/heptane mixture yielded 2.37 g (67%) of orange crystals of I, melting point 135–137 °C. ν(CO) (heptane): 1976, 1916, 1902 cm^{-1}. Mass spectrum (12 eV, 200): 264 (68) M^+; 236 (22) $[M-CO]^+$; 208 (80) $[M-200]^+$; 180 (70) $[M-3CO]^+$ 128 (12) $[M-3CO-Cr]^+$; 52 (5) Cr.

(1-Trimethylstannyl-1–4,4a,8a-η-naphthalene)tricarbonylchromium (IIe). The above technique gave 0.25 g (38%) of orange crystals of IIe from 0.45 g (1.55 mmol) of α-naphthyltrimethylstannane [19], 0.81 g (2.16 mmol) of $Py_3Cr(CO)_3$ in 50 ml of ether and 1.38 g (9.75 mmol) of $BF_3 \cdot Et_2O$. Melting point of IIe 110–112 °C. ν(CO) (heptane): 1972, 1911, 1900 cm^{-1}. Found: C, 45.06; H, 3.55; Cr, 11.99; Sn, 27.36. $C_{16}H_{16}O_3CrSn$ calc: C, 45.04; H, 3.8; Cr, 12.19; Sn, 27.81%. ^1H NMR (C_6D_6, 400 MHz): 0.37 ($SnMe_3$; $J(H-^{119}Sn) = 55$ Hz); 4.73t (H(3), $J_{2,3} = J_{3,4} = 6.0$ Hz); 5.06 (H(2)); 5.57 d (H(4)); 6.78t (H(6)), $J_{5,6} = 7.8$ Hz), $J_{6,7} = 7.7$ Hz); 6.88t (H(7) $J_{7,8} = 7.8$ Hz), 6.96d (H(5)); 7.32d (H(8)). Mass spectrum (11 eV, 160 °C): 428(100) M^+; 400 (2) $[M-CO]^+$; 372 (95) $[M-2CO]^+$; 344 (5) $[M-3CO]^+$; 292 (2) $[M-3CO-Cr]^+$.

(2-Trimethylstannyl-1–4,4a,8a-η-naphthalene)tricarbonylchromium (IIIe). The technique described for the synthesis of I was used, and 0.08 g (12%) of orange crystals of IIIe were isolated from 0.45 g (1.55 mmol) of β-naphthalenetrimethylstannane [19], 0.81 g (2.16 mmol) of $Py_3Cr(CO)_3$ in 50 ml of ether and 1.38 g (9.75 mmol) of $BF_3 \cdot OEt_2$. Melting point of I is 119–121 °C, ν(CO) (heptane): 1970, 1911, 1890 cm^{-1}. Found: C, 44.73; H, 3.75; Cr, 12.24; Sn, 27.94. $C_{16}H_{16}O_3CrSn$ calc: C, 45.04; H, 3.8; Cr, 12.19; Sn, 27.81%. ^1H NMR (400 MHz, C_6D_6): 0.30 ($SnMe_3$, $J(H-^{119}Sn) = 56$ Hz); 5.06d (H(3), $J_{3,4} = 6.5$ Hz); 5.5d (H(4)); 5.84s (H(1)); 6.8–7.2m (H(5)–H(8)). Mass spectrum (11 eV, 160 °C): 428 (100) M^+; 400 (2) $[M-CO]^+$; 372 (95) $[M-2CO]^+$; 344 (5) $[M-3CO]^+$; 292 (1) $[M-3CO-Cr]^+$.

(1-Bromo-4a,5–8,8a-η-naphthalene)tricarbonylchromium (VIf). The technique as for the synthesis of I was used and gave 0.92 g of dark-red crystals of VIf from 2.11 g (10.1 mmol) of β-bromonaphthalene, 3.15 g (8.4 mmol) of $Py_3Cr(CO)_3$ in 50 ml of ether and 5.4 g (37.8 mmol) of $BF_3 \cdot OEt_2$. Melting point is 151–153 °C. ν(CO) (heptane): 1981, 1924, 1909 cm^{-1}. Found: C, 45.28; H, 2.23; Cr, 15.79; Br, 22.85. $C_{13}H_7O_3BrCr$ calc: C, 45.51; H, 2.06; Cr, 15.15; Br, 23.29%. ^1H NMR (100 MHz, C_6D_6): 4.81m (H(6), H(7)); 5.00 (H(5)), 5.84m (H(8)); 6.19t (H(3), $J_{3,2} = J_{3,4} = 7.5$ Hz); 6.56d (H(2)); 6.84 (H(4)). Mass spectrum (12 eV, 200 °C, for Br): 344 (52) M^+; 316 (18) $[M-CO]^+$; 288 (68) $[M-2CO]^+$; 260 (100) $[M-3CO]^+$; 208 (52) $[M-3CO-Cr]^+$; 52 (20) Cr^+.

2-Bromo-4a,5–8,8a-η-naphthalene)tricarbonylchromium (VIIf). Similar to the synthesis of VIf, 2.45 g (39%) of dark-red crystals of VIIf were produced from 3.82 g (18.6 mmol) of β-bromonaphthalene, 7.06 g (18.9 mmol) of $Py_3Cr(CO)_3$ in 100 ml of ether and 12.1 g (85.2 mmol) of $BF_3 \cdot OEt_2$. Melting point of VIIf is 144–146 °C, ν(CO) (heptane): 1981, 1922, 1909 cm^{-1}. Found: C, 45.77; H, 2.06; Cr, 15.64; Br, 22.0. $C_{13}H_7O_3BrCr$ calc: C. 45.51; H, 2.06; Cr, 15.15; Br, 23.29%. ^1H NMR (C_6D_6, 100 MHz): 4.55m (H(6), H(7)); 5.1m (H(5), H(8)); 6.54d (H(4), $J_{4,3} = 6.86$ Hz); 6.86d (H(3)); 7.12s (H(1)). Mass spectrum, (12 eV, 200 °C): 344 (60) M^+; 316 (20) $[M-CO]^+$; 288 (75) $[M-2CO]^+$; 260 (72) $[M-3CO]^+$; 208 (35) $[M-3CO-Cr]^+$.

(η^6-Naphthalene-d_8)tricarbonylchromium (IV). Using the technique for the synthesis of I, 0.86 g (43%) of orange crystals of IV were produced from 1.24 g (9.1 mmol) of naphthalene-d_8 (V/O "Isotope"), 2.7 g (7.3 mmol) of $Py_3Cr(CO)_3$ in 50 ml of ether and 4.7 g (33 mmol) of $BF_3 \cdot OEt_2$. ^{2}H NMR (62 MHz, C_6H_6): 4.72s (H(2), H(3)); 5.35s (H(1), H(4)); 6.80s (H(6), H(7)); 6.92s (H(5), H(8)).

2. General technique for producing mixtures of complexes IIb–IIe, IIIb–IIIe

Solution I in THF at −78°C was treated with three-fold excess of n-BuLi solution in hexane. The temperature was increased to −68°C with stirring and the colour of the solution deepened to red. At −68°C the solution was stirred for 15 min, treated with electrophile, and stirred for a further 30 min. Solvent was removed under vacuum at 0°C, the residue was chromatographed on plates with silica gel eluting with a 2 : 1 or 3 : 1 mixture of petroleum ether and benzene. The complexes were recrystallized from benzene-heptane mixture.

Using the above technique, 0.14 g (87%) of a mixture of IIb and IIIb (IIb/IIIb ratio = 0.8) was isolated from a mixture of 0.15 g of I in 30 ml of THF and 1.0 ml of D_2O.

Similarly, 0.07 g (66%) of a mixture of IIc and IIIc (IIc/IIIc ratio = 0.56) was isolated from a mixture of 0.1 g of I in 20 ml of THF and 1.17 g of CH_3I.

0.18 g (74%) of a mixture of IIe and IIIe (IIe/IIIe ratio = 0.44) was isolated from a mixture of 0.15 g of I in 30 ml of THF and 0.56 g of Me_3SnCl.

0.17 g (45%) of a mixture of IId and IIId (IId/IIId ratio is 0.31) was isolated from a mixture of 0.3 g of I and 0.72 g of Me_3SiCl.

0.13 g (43%) of IVα and IVβ, Vα, Vβ in the ratio of 35 : 47 : 9 : 9 was isolated from a mixture of 0.3 g (1.1 mmol) of (naphthalene-d_8)tricarbonylchromium in 30 ml of THF and 1 ml of water.

3. General technique for synthesizing complexes VIb–VIe and VIIb–VIIe

A solution of the bromonaphthalene complexes, VIf and VIIf in ether was treated with a three-fold excess of n-BuLi in hexane at −78°C. The temperature was increased to −50°C with stirring and the solution turned orange. At −50°C stirring was continued for 15 min. The mixture was then treated with electrophile (D_2O, CH_3I, Me_3SnCl, Me_3SiCl) and stirred for a further 30 min. Solvent was distilled off at 0°C, and the reaction mixture was chromatographed on SiO_2 column or subjected to TLC. A mixture of petroleum ether and benzene (2 : 1 or 3 : 1 ratio) was used as eluent. The complexes were recrystallized from benzene-heptane mixture.

α-Substituted complexes VIb–e

(1-Deutero-4a,5–8,8a-η-naphthalene)chromium tricarbonyl (VIb). 0.08 g (67%) of orange crystals of VIb were produced from 0.15 g (0.45 mmol) of VIf in 75 ml of ether and 1 ml of D_2O. Melting point of VIb is 135–137°C, ν(CO) (heptane): 1975, 1915, 1902 cm^{-1}. ^{1}H NMR (100 MHz, C_6D_6); 4.70m (H(1), H(4)); 5.32m (H(2), H(3)); 6.82m (H(5), H(6), H(7)); ^{2}H NMR (62 MHz, C_6H_6); 6.92s (referred to $Si(CD_3)_4$). Mass spectrum (12 eV, 200°C): 265 (76) M^+; 237 (48) $[M-CO]^+$; 209 (65) $[M-2CO]^+$; 181 (70) $[M-3CO]^+$; 129 (4) $[M-3CO-Cr]^+$. The content of I free from deuterium was 20%.

(1-Methyl-4a-5–8,8a-η-naphthalene)tricarbonylchromium (VIc). 0.09 g (54%) of orange crystals of VIf were produced from 0.2 g (0.59 mmol) of VIf in 100 ml of ether and 0.37 g (2.6 mmol) of freshly distilled CH_3I. Melting point of VIf is 120–122 °C. ν(CO) (heptane): 1977, 1916, 1904 cm^{-1}. Found: C, 60.81; H, 3.56; Cr, 18.28. $C_{14}H_{10}O_3Cr$ calc: C, 60.43; H, 3.6; Cr, 18.70%. ^1H NMR (C_6D_6, 100 MHz), 2.12s (CH_3); 5.36m (H(5), H(8)); 4.68m (H(6), H(7)); 6.54–6.90m (H(2)–H(4)). Mass spectrum (12 eV, 200 °C) 278 (65) M^+; 250 (12) $[M-CO]^+$; 232 (17) $[M-2CO]^+$; 204 (3) $[M-3CO]^+$; 152 (15) $[M-3CO-Cr]^+$; 52 (40) Cr^+.

[(1-Trimethylstannyl)-4a,5–8,8a-η-naphthalene]tricarbonylchromium (VIe). 0.09 g (25%) of red crystals of VIe were isolated from a mixture of 0.2 g (0.59 mmol) of VIf in 100 ml of ether and 0.45 g (3.3 mmol) of trimethylchlorostannane. Melting point of VIe is 127–129 °C. ν(CO) (heptane): 1974, 1913, 1900 cm^{-1}. Found: C, 45.36; H, 3.69; Cr, 12.18; Sn, 27.80. $C_{16}H_{16}O_3CrSn$ calc: C, 45.04; H, 3.8; Cr, 12.19; Sn, 27.91%. ^1H NMR (C_6D_6, 100 MHz): 0.33 ($SnMe_3$, $J(H-^{119}Sn) = 54.3$ Hz); 4.68m (H(6), H(7)); 5.36m (H(5)); 5.72m (H(8)); 6.6–7.1 m (H(2)–H(4)). Mass spectrum (70 ev): 428 (100) M^+; 400 (3) $[M-CO]^+$; 372 (85) $[M-2CO]^+$; 344 (16) $[M-3CO]^+$; 292 (5) $[M-3CO-Cr]^+$; 52 (100) Cr^+.

[(1-Trimethylsilyl-4a,5–8,8a-η-naphthalene)tricarbonylchromium (VId). 0.1 g (50%) of red crystals of VId were isolated from a mixture of 0.2 g (0.59 mmol) of VIf in 100 ml of ether and 0.65 g (6 mmol) of trimethylsilyl. Melting point of VId is 130–132 °C. ν(CO) (heptane) 1975, 1913, 1901 cm^{-1}. Found: C, 56.58; H, 5.13; Si, 8.28. $C_{16}H_{16}O_3SiCr$ calc: C, 57.13; H, 4.8; Si, 8.36; Cr, 15.47%. ^1H NMR (C_6D_6, 400 MHz): 0.42 ($SiMe_3$); 4.76t (H(6)), $J_{6,5} = 6.8$ Hz, $J_{6,7} = 6.3$ Hz); 4.86t (H(7), $J_{7,8} = 6.8$ Hz); 5.4d (H(5)); 6.05d (H(8)); 6.90dd (H(3), $J_{3,4} = 7.3$ Hz, $J_{3,2} = 8.2$ Hz); 7.33d (H(4); 7.08d (H(2)). Mass spectrum (70 eV, 160 °C); 336(8) M^+; 280(9) $[M-CO]^+$; 252 (65) $[M-3CO]^+$; 52 (100) Cr^+.

Series of β-substituted complexes VIIb–VIIe.

(2-Deutero-4a,5–8,8a-η-naphthalene)tricarbonylchromium (VIIb). 0.15 g (98%) of VIIb was isolated from a mixture of 0.2 g (0.59 mmol) of VIIf in 100 ml of ether and 1 ml of D_2O. ^1H NMR (100 MHz, C_6D_6): 4.70m (H(1), H(4)); 5.35m (H(2), H(3)); 6.80m (H(5), H(6), H(8)); ^2H NMR (62 MHz, C_6H_6); 6.80s (from $Si(CD_3)_4$). Mass spectrum (10 eV, 160 °C): 265 (76) M^+; 237 (42) $[M-CO]^+$; 209 (54) $[M-2CO]^+$; 181 (75) $[M-3CO]^+$; 129 (12) $[M-3CO-Cr]^+$. The content of I free from deuterium is $\leqslant 15\%$.

(2-Methyl-4a,5–8,8a-η-naphthalene)chromium tricarbonyl (VIIc). A mixture of 0.2 g (0.59 mmol) of VIIf in 100 ml of ether and 0.37 g (2.6 mmol) of CH_3I yielded 0.12 g (72%) of orange crystals of VIIc, melting point 129–131 °C. ν(CO) (heptane): 1977, 1916, 1903 cm^{-1}. ^1H NMR (62 MHz, C_6D_6): 6.66s (H(1) $J_{1,3} = 1.68$ Hz); 6.60d (H(3), $J_{3,4} = 6.9$ Hz); 6.84d (H(4)); 5.28d (H(5), $J_{5,6} = 6.60$ Hz); 4.68t (H(6), $J_{6,7} = 6.60$ Hz; $J_{6,8} = 0.90$ Hz); 4.62t (H(7), $J_{7,8} = 6.60$ Hz); 5.28d (H(8)). ^1H NMR (C_6D_6, 400 MHz); 1.82s (CH_3); 4.18t (H(6), $J_{6,5} = J_{6,7} = 6.6$ Hz); 4.62t (H(7), $J_{7,8} = 6.6$ Hz); 5.28d (H(5), H(8)); 6.60d (H(3), $J_{3,4} = 6.9$ Hz); 6.66s (H(1)); 6.84d (H(4)).

(2-Trimethylstannyl-4a,5–8,8a-η-naphthalene)tricarbonylchromium (VIIe). 0.2 g (0.59 mmol) of VIIf in 100 ml of ether and 0.53 g (3.8 mmol) of trimethylchlorostannane yielded 0.1 g (39%) of orange crystals of VIIe, melting point 116–118 °C. ν(CO) (heptane): 1974, 1913, 1900 cm^{-1}. Found: C, 45.77; H, 4.0. $C_{16}H_{16}O_3CrSn$

calc: C, 45.04; H, 3.8; Cr, 12.19; Sn, 27.81. ^1H NMR (C_6D_6, 100 MHz), 0.16 ($SnMe_3$, $J(H-^{119}Sn) = 61$ Hz); 4.75m (H(6), H(7)); 5.4m (H(5), H(8)); 7.0–7.2m (H(3), H(4)); 7.48s (H(1)). Mass spectrum (11 eV, 160 °C): 428 (100) M^+; 400 (2) $[M-CO]^+$; 372 (95) $[M-2CO]^+$; 344 (5) $[M-3CO]^+$; 292 (1) $[M-3CO-Cr]^+$.

(2-trimethylsilyl-4a,5–8,8a-η-naphthalene)tricarbonylchromium (VIId). 0.2 g (0.59 mmol) of VIIf in 100 ml of ether and 0.7 g (6.4 mmol) of Me_3SiCl yielded 0.11 g (55%) of red crystals of VIId, melting point 105–170 °C. ν(CO) (heptane): 1975, 1913, 1901 cm^{-1}. ^1H NMR ($C_6D_5CD_3$, 100 MHz): 0.13s ($SiMe_3$); 4.6m (H(6), H(7)); 5.22m (H(5), H(8)); 6.8–7.1m (H(3), H(4)); 7.3s (H(1)). Mass spectrum (70 eV, 160 °C): 336 (8) M^+; 280 (9) $[M-2CO]^+$; 252 (65) $[M-3CO]^+$; 52 (100) Cr^+.

Determination of equilibrium constants for the haptotropic rearrangements (1)

A weighed sample of complex VI or VII (120 mg) was heated at 100–130 °C in decane (80 ml) for 4–8 h. 10 ml aliquots were taken each hour, quickly cooled, and then chromatographed on a short column with silica gel 40/100 μ (Chemapol, Chekoslovakia). Complexes were recrystallized from a mixture of heptane and benzene. The solvent was removed under vacuum, the residue was diluted with C_6D_6 and the content of isomers was determined by ^1H NMR spectroscopy.

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