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Regioselective synthesis of π-complexes of substituted polycyclic aromatic compounds. Experimental (NMR) and theoretical (DFT) studies of η^6,η^6-haptotropic rearrangements in naphthalenechromiumtricarbonyl complexes[☆]

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Abstract

A new regioselective method for the synthesis of (η^6-naphthalene)chromium tricarbonyl complexes bearing a substituent R in desired positions of either the coordinated or non-coordinated ring was proposed. The kinetics of η^6,η^6-haptotropic rearrangements (IRHR) was investigated by NMR spectroscopy for ten pairs of isomer complexes (R = D, CH_3, Me_3Sn, Me_3Si and Cl in position 1 or 2 of coordinated or non-coordinated rings). The free activation energies $\Delta G^{\#}$ fall into a quite narrow range of 28–31 kcal mol^{-1} and are therefore relatively insensitive to the influence of substituent R whereas equilibrium constants of IRHR change considerably from 0.03 to 17.26 within the compounds investigated. Electron donating (withdrawing) substituents R increase (decrease) the relative thermodynamic stability of the isomers containing a substituent in coordinated rings. The density functional theory method (DFT) with extensive basis set describes quite satisfactory the geometry and the energy of ground states and correctly predict that the least motion route of $Cr(CO)_3$ from one ring to another via the center of the C_{4a}–C_{8a} bond is forbidden. The transition state for the rearrangement of (η^6-naphthalene)chromium tricarbonyl has trimethylenemethane structure of C_{2v}-symmetry in which the $Cr(CO)_3$-group is slightly shifted to the ligand periphery. For the monosubstituted naphthalenechromium tricarbonyls thus, there are two reaction channels of the chromium tricarbonyl group slippage between unsubstituted and substituted rings, one of which is practically unperturbed determining the low sensitivity of the rearrangement rate to the effects of ligand substitution even for 1-R substituted complexes. Calculated activation barriers are in a good accordance with the experimentally determined $\Delta G^{\#}$ values. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Haptotropic rearrangements; Arenechromium tricarbonyl complexes; Kinetics; NMR spectroscopy; Quantum chemical calculations

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1. Introduction

A common property of π-complexes with polycyclic aromatics is their ability to undergo inter-ring haptotropic rearrangements (IRHR) in the course of which

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[☆] Dedicated to Professor Alberto Ceccon on the occasion of his 65th birthday.

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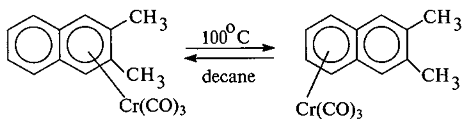
an organometallic group is shifted from one cycle to another along the plane of the π-ligand [1–4]. The first example of such a rearrangement was found by Deubzer [5], who demonstrated that both isomers (η^6-dimethylnaphthalene)chromium tricarbonyl (I) and (II) reversibly rearranged to each other at elevated temperatures (ca. 100°C) in decane (η^6,η^6-IRHR) (Eq. 1).



(I) (II) (1)

Similar rearrangements were found later by other authors for chromium tricarbonyl complexes of other substituted naphthalenes [6–10]. It was shown that in non-polar solvents the rearrangement proceeds intramolecularly with the free activation energies being in the range of 27–30 kcal mol^{-1}. However the number of the investigated complexes was too restricted to allow reliable conclusions concerning substituent effects on the metallotropic equilibrium and activation parameters.

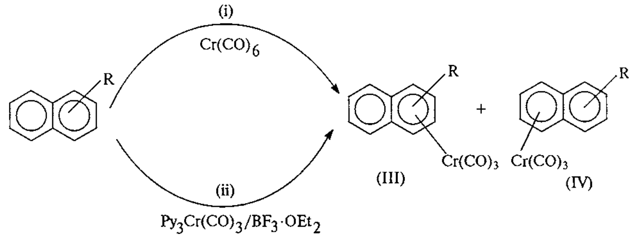
A η^6,η^6-inter-ring haptotropic rearrangement was also found for 2-ethylnaphthalene complexes of iridium [11]. Albright and Hoffmann [12] carried out a theoretical investigations of IRHR of the type (1) using orbital symmetry analysis and EHT for the calculation of the potential energy surface. For the nickel complex (η^2-$C_{10}H_8$)Ni($Pr_2NCH_2CH_2NPr_2$) interesting rearrangements were found in the course of which the metal is shifted both between double bonds inside one aromatic ring and between the two six-membered rings of the ligand (η^2,η^2-rearrangement) [13].

The goal of the present study was to obtain more detailed information about kinetics and mechanism of η^6,η^6-IRHR in chromium tricarbonyl complexes of substituted naphthalenes. In this connection we developed a general method for the target synthesis of such complexes with the desired position of the substituents in coordinated or non-coordinated rings and synthesized ten pairs of isomeric complexes with substituents R = D, CH_3, Me_3Sn, Me_3Si and Cl in 1- and 2-positions of the coordinated and non-coordinated rings. In these complexes we investigated thermally induced η^6,η^6-IRHR both experimentally (NMR) and theoretically by density functional theory method (DFT).

2. Results and discussion

2.1. Synthesis of chromium tricarbonyl complexes of substituted naphthalenes with desired position of substituent in coordinated or non-coordinated rings

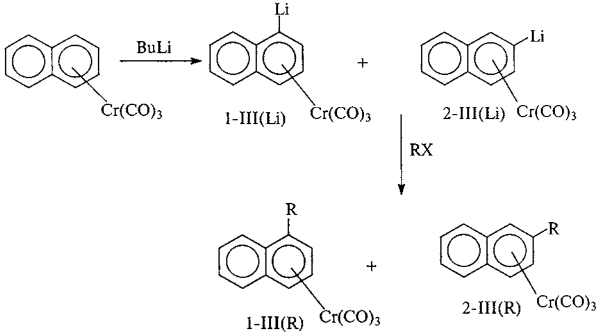
Two methods were used up to now to prepare substituted naphthalene chromium tricarbonyl complexes, involving reactions of substituted naphthalenes with $Cr(CO)_6$ or $Py_3Cr(CO)_3/BF_3 \cdot OEt_2$, respectively (Oefele reaction [14]) (2). The former reaction was carried out under reflux in dibuthyl ether [15] or in decaline in the presence of polar additives [16].



(2)

As a rule (2i) and (2ii) yield mixtures of both possible structural isomers which could be separated either by crystallization [5] or by chromatography [17]. We have early shown that the regioselectivity of the Oefele reaction (2ii) can be considerably increased by using substituted naphthalenes bearing strong electron donor or electron acceptor substituents. Thus, complexes of the type III (R = $SnMe_3$, $SiMe_3$) and IV (R = Br) were isolated as single products of the reaction (2ii) on using (1- or 2-naphthyl)trimethylstannane (silane) or 1- or 2-bromonapthalene as starting materials. At this stage the desired future position of substituent R is determined.

The second way to synthesize (η^6-$C_{10}H_7R$)$Cr(CO)_3$ involves metalation of (η^6-naphthalene)chromium tricarbonyl. The metalation with BuLi in THF at − 70°C, followed by treatment with electrophiles RX, gives, as a rule, the mixture of 1- and 2-isomers complexes of the type III (Scheme 3).



(3)

Thus, the process is not regioselective because metalation proceeds both at the C(1) and C(2) positions. The regioselective metalation at the C(2) was achieved by Kuendig [7], who changed BuLi for sterically demanding TMPLi, making 2-substituted complexes of the type III accessible. However, 1-substituted complexes have remained difficult to synthesize so far. Here we report a general and convenient route to the synthesis of complexes (III) and (IV) via the reaction sequence shown in Scheme 4.

Table 1
NMR-parameters ^{1}H and ^{13}C (δ in ppm, J in Hz) for chromium tricarbonyl complexes of substituted naphthalenes in hexafluorobenzene (C_6F_6)

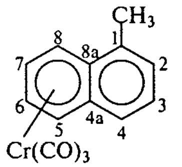
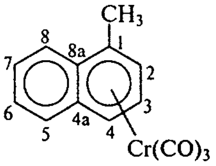
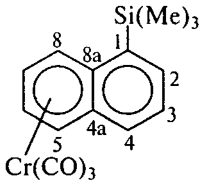
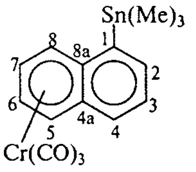
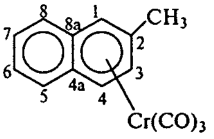
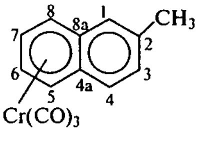
Compound	Coordinated ring	Non-coordinated ring, carbonyls
 VII	H_5: 6.20 (d, $J(5,6) = 6.54$, $J(5,7) = 1.36$); H_6: 5.67 (t, $J(6,7) = 6.10$, $J(6,8) = 1.20$); H_7: 5.62 (t, $J(7,8) = 6.85$, $J(7,5) = 1.36$); H_8: −6.27 (d, $J(8,7) = 6.85$, $J(8,6) = 1.20$) C_5–C_8: 89.25, 93.75, 94.51, 94.99; C_{4a}, C_{8a}: 107.99, 109.13	H_2: 7.38 (d, $J(2,3) = 7.13$); H_3:7.46 (distorted t, $J(3,4) = 7.15$); H_4: 7.49 (distorted d) CH_3: 2.78 (m) C_1: 139.81; CH_3: 20.97; CO: 234.43; C_2–C_4: 129.52, 130.82, 131.44
 XVII	H_2: 5.52 (d, $J(2,3) = 5.80$); H_3: 5.65 (dd, $J(3,4) = 6.67$); H_4: 6.08 (d); CH_3: 2.84 C_2–C_4: 92.07, 95.45, 96.46; C_1, C_{4a}, C_{8a}: 106.10, 109.08, 109.22; CH_3: 20.85	H_6,H_7: 7.63 (m); H_8: 7.68 (m); H_5: −7.92 (m) C_5–C_8: 128.80, 131.54, 131.67, 132.81; CO: 234.94
 IX	H_5: 6.09 (dd, $J(5,6) = 6.60$, $J(5,7) = 1.28$); H_6: 5.52 (dt, $J(6,7) = 6.45$, $J(6,8) = 1.20$); H_7: 5.61 (dt, $J(7,8) = 6.88$, $J(7,5) = 1.28$); H_8: 6.43 (dt, $J(8,7) = 6.88$, $J(8,4) = 0.9$) C_5–C_8: 92.72, 93.64, 94.03, 94.49; C_{4a}, C_{8a}: 107.69, 113.89	H_2: 7.75 (dd, $J(2,3) = 6.67$, $J(2,4) = 1.23$);H_3: 7.42 (dd, $J(3,4) = 8.64$, $J(3,2) = 6.67$); H_4: 7.59 (m, $J(4,3) = 8.64$, $J(4,8) = 0.9$); $Si(CH_3)_3$: 0.65, c, $J(^{29}Si–^{1}H) = 6.4$) C_1:143.50, C_2–C_4, 139.14, 129.75, 133.36; $Si(CH_3)_3$: 1.45; CO: −234.07
 XI	H_5: 6.08 (m, $J(5,6) = 6.40$, $J(5,7) = 1.50$); H_6: 5.50 (m, $J(6,7) = 6.45$, $J(6,8) = 1.20$); H_7: 5.59 (m, $J(7,8) = 6.30$, $J(7,5) = 1.28$); H_8: 6.16 (m, $J(8,7) = 6.30$, $J(8,4) = 0.93$) C_5: 94.23, C_6: 94.47, C_7: 94.52, C_8: 93.40, C_{4a}: 108.62, C_{8a}: 114.70	H_2: 7.67 (dd, $J(2,3) = 6.50$, $J(2,4) = 1.24$); H_3: 7.39 (dd, $J(3,4) = 8.50$, $J(3,2) = 6.50$); H_4: 7.53 (m, $J(4,3) = 8.50$, $J(4,8) = 0.93$); $Sn(CH_3)_3$: 0.63 (s, $J(^{119}Sn–^{1}H) = 55.82$); $J(^{117}Sn–^{1}H) = 53.37$) C_1: 148.81, C_2: 139.14, C_3: 129.74, C_4: 133.36; $Sn(CH_3)_3$: −7.32; CO: 234.14
 XVIII	H_1: 6.00 (s(b)); H_3: 5.47 (d, $J(3,4) = 6.73$); H_4: 6.18 (d); CH_3: 2.52 (s(b)) C_1, C_3, C_4: 90.81, 91.10, 94.06; C_2, C_{8a}, C_{4a}: 103.92, 106.16, 107.46; CH_3: 20.41	H_5: 7.63 (m, $J(5,6) = 8.93$); H_6: 7.50 (m, $J(6,7) = 7.17$); H_7: 7.55 (m, $J(7,6) = 6.50$); H_8: 7.60 (m, $J(8,7) = 8.93$) C_5–C_8: 127.75, 128.53, 128.60, 128.67; CO: 232.88
 VIII	H_5: 6.10 (d, $J(5,6) = 6.68$); H_6: 5.48 (t, $J(6,7) = 6.40$); H_7: 5.52 (t); H_8: −6.05 (d, $J(8,7) = 6.60$) C_5–C_8: 91.83, 92.67, 93.74, 94.64; C_{4a}, C_{8a}: 106.03, 109.42	H_1: 7.39 (s(b)); H_3: 7.40 (d, $J(3,4) = 8.85$); H_4: 7.50 (d, $J(4,3) = 8.85$) C_1, C_3, C_4: 128.96, 131.39, 133.23; C_2: 141.12; CH_3: 23.23; CO: 234.23

Table 1 (*Continued*)

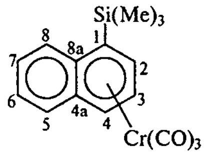
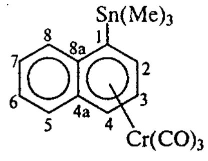
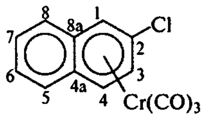
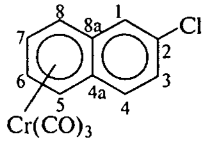
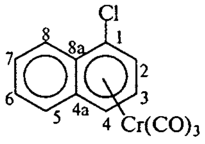
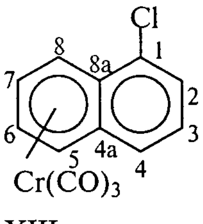
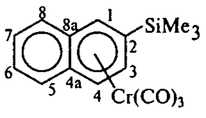
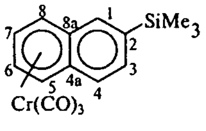
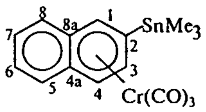
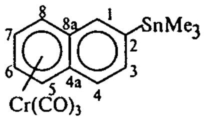
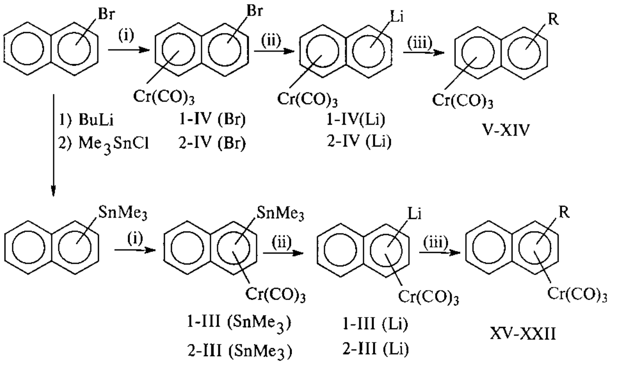
Compound	Coordinated ring	Non-coordinated ring, carbonyls
 XIX	H_2: 5.77 (d, $J(2,3) = 6.20$); H_3: 5.38 (t, $J(4,2) = 1.10$); H_4: -6.33 (d, $J(4,3) = 6.70$); $Si(CH_3)_3$:0.68 (s, $J(^{29}Si–^1H) = 6.7$)	H_5: 7.62 (d, $J(5,6) = 7.40$; H_6: 7.43, (m); H_7: 7.55 (m); H_8: 7.88 (d, $J(7,8) = 7.56$
	C_2, C_3, C_4: 93.15, 95.52, 103.00; C_1: 113.88; C_{4a}, C_{8a}: 106.47, 107.68; $Si(CH_3)_3$:1.85	C_5–C_8: 129.66, 131.36, 131.38, 133.36; CO: 234.40
 1-III($SnMe_3$)	H_2: 5.58 (dd, $J(2,3) = 5.94$, $J(2,4) = 1.19$); H_3: 5.46 (dd, $J(3,4) = 5.92$); H_4: 6.23(dt, $J(4,8) = 1.19$); $SnMe_3$: 0.70	H_5: 7.60 (m); H_6: 7.46 (m); H_7: 7.53 (m); H_8: 7.65 (m)
	C_3, C_4: 94.57, 95.52; C_2: 103.47; C_1: 114.64; C_{4a}, C_{8a}: 108.05, 99.75; $Sn(CH_3)_3$: -6.52	C_5–C_8: 130.07, 131.39, 132.96, 133.19; CO: -234.62
 XXII	H_1: 6.27 (dd, $J(1,3) = 1.74$, $J(1,5) = 0.47$); H_3: 5.73 (dd, $J(3,4) = 6.84$); H_4: 6.31 (dd, $J(4,8) = 0.46$)	H_5: 7.74 (m); H_6: 7.62 (m); H_7: 7.69 (m); H_8: 7.74 (m)
	C_1: 91.71; C_4: 92.45; C_3: 95.14; C_2: 114.13; C_{8a}: 108.66; C_{4a}: 105.96	C_5–C_8: 131.18, 131.37, 131.73, 132.48; CO: 233.56
 XIV	H_5: 6.26 (dt, $J(5,6) = 6.59$, $J(1,5) = 0.72$); H_8: 6.19 (d, $J(8,7) = 6.65$); H_7: 5.74 (dt,$J(7,5) = 1.13$); H_6: 5.69 (dt, $J(6,7) = 6.51$, $J(6,8) = 1.2$)	H_3: 7.47 (dd, $J(3,4) = 9.05$, $J(3,1) = 2.07$); H_1: 7.67 (d); H_4: 7.75 (d)
	C_5–C_8: 91.66, 92.58, 94.60, 95.25; C_{8a}, C_{4a}: 106.14, 109.97	C_1, C_3, C_4: 129.61, 132.67, 134.04; C_2: 138.20; CO: 234.02
 XXII	H_2: 5.79 (dd, $J(2,3) = 6.28$, $J(2,4) = 0.97$); H_3: 5.72 (t); H_4: 6.70 (d, $J(3,4) = 6.61$)	H_5: 7.78 (m); H_6, H_7: 7.72 (m); H_8: 8.13 (m)
	C_2, C_3, C_4: 90.61, 93.82, 94.56; C_{8a}, C_{4a}: 106.70, 108.00; C_1: 111.06	C_5–C_8: 128.76, 131.74, 131.81, 132.17; CO: 233.29
 XIII	H_5: 6.22 (dd, $J(5,6) = 6.42$, $J(5,7) = 1.38$); H_6, H_7: 5.68 (m); H_8: 6.50 (d, $J(7,8) = 6.60$)	H_2: 7.57 (dd, $J(2,3) = 7.31$, $J(2,4) = 1.27$); H_3: 7.52 (t); H_4: 7.67 (d, $J(3,4) = 8.35$)
	C_5–C_8: 88.72, 92.38, 94.50, 94.87; C_{8a}, C_{4a}: 106.18, 109.44	C_2, C_3, C_4: 130.22, 130.56, 130.97; C_1: 136.51; CO: 233.40

Table 1 (*Continued*)

Compound	Coordinated ring	Non-coordinated ring, carbonyls
 XX	H_1: 6.26 (s); H_3: 5.71 (d, $J(3,4) = 7.62$); H_4: 6.08 (d); $SiMe_3$: 0.56, s, $J(^{29}Si–^1H) = 6.70$ C_1, C_3, C_4: 91.63, 99.26, 100.31; C_2: 110.07; C_{8a}, C_{4a}: 103.42, 108.11; $SiMe_3$: 0.11	H_5–H_8: 7.54–7.64 (m) C_5–C_8: 130.86, 131.43, 132.10, 132.34; CO: 234.82
 X	H_5, H_8: 6.19 (m); H_6, H_7: 5.65 (m) C_5–C_8: 92.91, 92.99, 94.84, 95.09; C_{4a}, C_{8a}: 107.89, 108.88	H_1: 7.87 (m, $J(1,5) = 0.85$, $J(1,3) = J(1,4) = J(1,8) = 1.80$); H_3: 7.74 (dd, $J(3,4) = 8.50$); H_4: -7.62 (dt, $J(4,8) = J(1,4) = 0.82$); $SiMe_3$: 0.53, $J(^{29}Si–^1H) = 6.70$ C_1, C_3, C_4: 130.28, 135.36, 137.92; C_2: 146.19; CO: 234.56; $SiMe_3$: -0.18
 2-III($SnMe_3$)	H_1: 6.19 (s); H_3: 5.67 (dd, $J(3,4) = 6.50$, $J(3,1) = 0.70$); H_4: 6.12 (d); $SnMe_3$: 0.61, $J(^{119/117}Sn–^1H) = 55.7/54.3$ C_1, C_3, C_4: 92.61; 101.50, 102.23; C_2: 103.42; C_{8a}, C_{4a}: 109.49, 109.97; $SnMe_3$: -8.09, $J(^{119/117}Sn–^{13}C) = 367.58/356.49$	H_5–H_8: 7.53 (m) C_5–C_8: 130.95, 131.67, 132.04, 132.12; CO: 235.19
 XII	H_5, H_8: 6.20 (d, $J(5,6) = J(7,8) = 6.65$); $H_6(H_7)$: 5.68 (t, $J(5,7) = J(6,8) = 1.22$); $H_7(H_6)$: 5.64 (t) C_5–C_8: 92.83, 93.32, 94.88, 95.33; C_{8a}, C_{4a}: 108.43, 108.76	H_1: 7.84 (s); H_3: 7.59 (d, $J(3,4) = 8.32$); H_4: 7.76 (dd, $J(4,8) = 0.70$); Me_3Sn: s, 0.53, $J(^{119/117}Sn–^1H) = 56.25/53.78$ C_1, C_3, C_4: 130.23, 138.02, 139.94; C_2: 148.77; CO: 234.79; Me_3Sn: -8.87, $J(^{119/117}Sn–^1H) = 361.31/353.25$



(4)

i. $PyCr(CO)_3/Et_2O \cdot BF_3$, ether, 0°C → room temperature;
ii BuLi, ether, −70°C → −50°C;
iii. RX, ether, −50°C → room temperature;
1- or 2-R: D (V, VI); CH_3 (VII, VIII); Me_3Si (IX, X); Me_3Sn (XI, XII); Cl (XIII, XIV); (R in non-coordinating ring);
1- or 2-R: D (XV, XVI); CH3 (XVII, XVIII); Me_3Si (XIX, XX); Cl (XXI, XXII) (R in coordinated ring).

Initially, 1- and 2-bromonaphthalene under the condition of Oefele reaction give complexes 1-IV(Br) and 2-IV(Br), whereas 1- and 2-trimethylstannylnaphthalene give complexes 1-III(Me_3Sn) and 2-III(Me_3Sn), respectively (step 4i) [14].

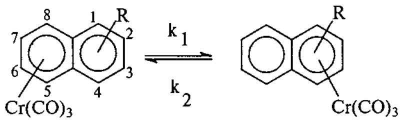
The complexes III(Me_3Sn) and IV(Br), being treated at the second step (4ii) with BuLi in ether at −70°C up to −50°C, undergo Sn/Li- and Br/Li-exchange upon warming, respectively, to give lithium derivatives III(Li) and IV(Li). The latter are stable in ether at −50°C and do not show any Li/H-exchange. This stability is the key element guaranteeing the desired position of substituent R in the complexes V–XIV and XV–XXII to be obtained from the final reaction (4iii) of III(Li) and IV(Li) with electrophiles RX. In contrast, in THF III(Li) and IV(Li) at −50°C undergo intra- and intermolecular

Li/H-exchange, thus making the final reaction (4iii) non-selective.

Complexes V–XXII were characterized by means of ^{1}H- and ^{13}C-NMR spectroscopy. These data are shown in Table 1. The comparison of chemical shifts ^{1}H and ^{13}C for the coordinated and non-coordinated rings proves that the signals of the nuclei coordinated with transition metals are shifted upfield. Corresponding J_{HH} couplings are also reduced which is quite characteristic for the arene complexes of transition metals.

2.2. The study of the kinetics of IRHR in the complexes V–XXII

For all newly synthesized complexes the kinetics of IRHR were investigated in C_6F_6 solution at 85°C by ^{1}H-NMR in 5 mm tubes. The solubilities of the complexes were high enough to determine precisely the concentrations of isomers up to very high degrees of interconversion. Special measures were carried out to purify C_6F_6 and to prepare samples (see Section 4) in order to avoid even traces of oxygen and moisture. For the deuterium containing complexes V, VI, XV and XVI the investigation of kinetics was done by means of ^{2}H-{^{1}H}-NMR and for the remaining complexes by means of ^{1}H-NMR (Eq. 5).



IV III

R=D, Cl, CH_3, $Si(CH_3)_3$, $Sn(CH_3)_3$

(5)

The kinetic parameters are well reproducible for the pairs of complexes differing only by the position of the $Cr(CO)_3$-group notwithstanding what positional isomer was taken at the start. A typical example of kinetic curves is the interconversion of the complexes VIII and XVIII as shown in Fig. 1.

It is noteworthy that we did not observe the appearance of the free ligands in any of the experiments. This proves that the reaction in C_6F_6 at 85°C proceeds intramolecularly. Under these conditions the enantiomers of chromium tricarbonyl complexes of monosubstituted naphthalenes also retain their optical purity in the course of their thermal rearrangements in contrast to toluene where considerable racemization due to intermolecular reactions takes place. Initially enantiomers were separated by HPLC on a Chiracel OD column. These results will be published separately.

The processing of the NMR data was performed using the program KINETICS [18]. In all cases the rearrangements (5) obey the first order reaction reversible model with high precision. The rate and equilibrium constants as well as the free activation energy values are presented in Table 2. The data of Kuendig for the IRHR in chromium tricarbonyl complexes of 2-methylnaphthalene in cyclohexane-d_{12}, data for (η^6-phenalene)chromium tricarbonyl [18] and (η^6-dimethylsilaacenaphthene(DMSA)) chromium tricarbonyl [19] were included in Table 2 for the comparison.

The analysis of the data obtained allows to draw the following conclusions:

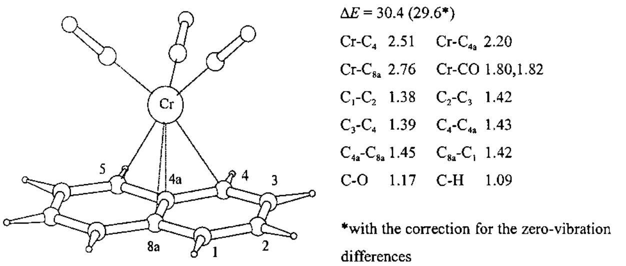
1. In C_6F_6 the solubility of the complexes is higher than in C_6D_{12} and no arene exchange reactions were observed as in benzene and toluene, allowing the determination rate constants of IRHR and $\Delta G^{\#}$ values with high precision.
2. The equilibrium constants obtained are in a good accordance with known literature data. In all cases isomeric complexes bearing donors in the coordinated or acceptors in non-coordinated ring are thermodynamically more stable.
3. The comparison of the data obtained for the complex VIII with the results of Kuendig [7] shows that in C_6F_6 the rate of direct and reverse reactions are expectedly somewhat increased as compared to the C_6D_{12} solution.
4. Generally inter-ring haptotropic rearrangements in 1-substituted chromium tricarbonyl complexes ofnaphthalene proceed slower than in analogous 2-substituted complexes.
5. For monosubstituted complexes the values of free activation energies $\Delta G^{\#}$ only slightly depend on the nature of the substituent R.

2.3. The investigation of the mechanism of η^6,η^6-haptotropic rearrangements in naphthalene chromium tricarbonyls by means of density function theory (DFT)

The rather slight substituent effect on the kinetic parameters of IRHR (5) is quite unexpected, especially when compared with most of the of the other metallotropic rearrangements investigated where these effects are much more pronounced. A reasonable explanation of this result was obtained in the course of the detailed mechanistic investigation of the rearrangement by DFT. Recently, it was shown that this method which requires only very modest calculation expenditures [20] gives results which qualitatively are quite similar to the results of ab initio calculations. In the course of calculations we used a program developed by one of us and extended basis sets as described earlier [21]. In this paper it was demonstrated that calculation results reproduce very well structural parameters in η^6-naphthalene chromium tricarbonyl including such details as differences in Cr–$C_{1(2)}$ and Cr–$C_{4a(8a)}$ bond lengths.

Calculation results are presented in Table 3. On the qualitative level these results are in accordance with those of Albright and Hoffmann [13]. In particular, it is noteworthy that the least motion route of $Cr(CO)_3$ from one ring to another via the center of the C_{4a}–C_{8a} bond is forbidden. The transition state for IRHR in (η^6-naphthalene)chromium tricarbonyl has a trimethylenemethane structure (XXIII) with a C_{2v}-symmetry in which the $Cr(CO)_3$-group is slightly shifted to the ligand periphery. On the potential energy surfacethere is no stationary point (energy minimum) corresponding to the intermediate of the η^3-allyl type which was postulated by Albright and Hoffmann [13].

For the substituted naphthalene chromium tricarbonyls there are two reaction channels for the chromium tricarbonyl group transfer between unsubstituted and substituted rings (Scheme 6) via transition states (XXIV) and (XXV). The calculation reproduces quite well the relative stabilities of isomers differing in the $Cr(CO)_3$-group position with respect to the unsymmetrically substituted naphthalene ligand. Substituent variations most strongly affects the energy of transition state (XXV) for the substituent in the position 2, where it is proximate to the migrating group. The energies of transition states (XXIV) in general change only slightly (± 0.5 kcal mol^{-1}), except for the 2-Me_3Si substituent. The existence of two reaction channels, one of which is practically unperturbed, determines the only slight sensitivity of the rearrangement rate to the effects of ligand substitution. Considering the inherent approximations (approximation of isolated molecule, neglecting the difference of energies of zero vibration) the calculated activation barriers are in a good accordance with the experimentally determined $\Delta G^{\#}$ values.



(XXIII)

3. Conclusions

A general method of synthesis of chromium tricarbonyl complexes of monosubstituted naphthalenes with the desired position of the substituent was developed and the kinetics of the η^6,η^6-inter-ring rearrangement was investigated for a representative set of compounds by means of NMR spectroscopy. Results from DFT calculations suggest plausible reaction pathways allowing conclusions on the mechanism and the influence of the structural factors on their rates and the equilibrium position of IRHR.

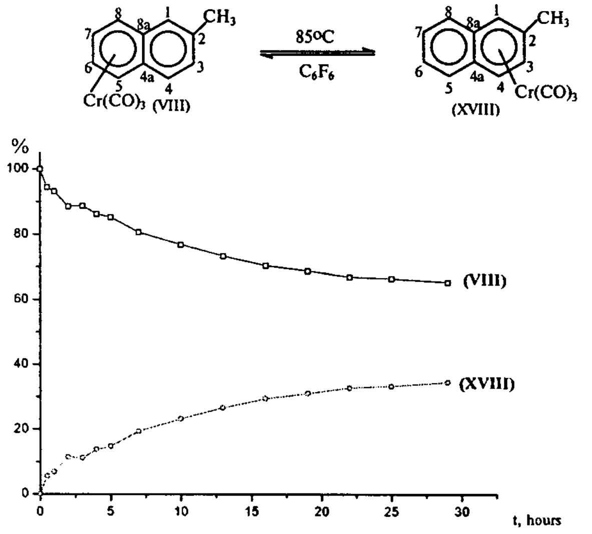


Fig. 1. Kinetic curves of isomerisation of chromium tricarbonyl complexes of methylnaphthalene VIII and XVIII starting from VIII.

4. Experimental

4.1. General procedures

All operations, except thin-layer chromatography, were performed in a purified argon atmosphere. All solvents (ether, decane, THF) were purified by refluxing over K/Na alloy and distilled from it under argon just prior to use. C_6F_6 was freed from water and oxygen by storage on potassium mirror, distillation and three consecutive freeze–pump–thaw cycles at 10^{-5} mm. If not specifically mentioned chromatography was carried out on a silica 40/100 μ Chemapol (Bratislava). IR spectra were recorded on a UR-20 Carl Zeiss spectrometer in

Table 2
Data for the thermal isomerization of substituted (η^6-naphthalene)chromium tricarbonyls in hexafluorobenzene at 85°C

Substituent	$k_1 \cdot 10^{-5}$ (s^{-1})	$k_2 \cdot 10^{-5}$ (s^{-1})	$K_{eq.}$	$\Delta G^{\#}_{358}$ (kcal mol^{-1})
1-CH_3	0.90 ± 0.01	0.51 ± 0.02	1.77	29.4 ± 0.6
2-CH_3[a]	1.82 ± 0.10	1.01 ± 0.10	1.80	29.2
2-CH_3	3.02 ± 0.24	1.45 ± 0.07	2.09	28.5 ± 1.2
1-$Si(CH_3)_3$	2.40 ± 0.02	0.50 ± 0.02	4.80	28.7 ± 0.7
2-$Si(CH_3)_3$	1.93 ± 0.03	0.11 ± 0.01	17.26	29.1 ± 0.6
1-$Sn(CH_3)_3$	0.70 ± 0.01	0.14 ± 0.01	5.00	29.5 ± 0.5
2-$Sn(CH_3)_3$	2.24 ± 0.04	0.17 ± 0.01	13.26	28.8 ± 0.7
1-Cl	0.15 ± 0.01	4.36 ± 0.06	0.034	30.6 ± 0.4
2-Cl	0.40 ± 0.01	3.46 ± 0.06	0.12	30.2 ± 0.8
2-D[b]	0.38 ± 0.02	0.38 ± 0.02	1.00	30.4 ± 0.8
η^6-phenalene $Cr(CO)_3$	0.52 ± 0.03[c]	0.11 ± 0.03[c]	4.73	29.65
η^6-DMSA $Cr(CO)_3$	2.87 ± 0.3[c]	1.61 ± 0.2[c]	1.78	30.89

[a] Calculation based on the data of Kuendig [7].
[b] Data for deuterium complex XVI.
[c] Data for 368 K.

heptane. NMR spectra were recorded on a Varian VXR-400 spectrometer (resonance frequency 400 MHz for ^1H). The assignments of the signals in ^1H-NMR spectra were performed with the help of double resonance (in some cases COSY and NOESY techniques were used) and Overhauser effect measurements by means of the NOEDIF procedure which is included in software of the spectrometer. The assignment of the signals in ^{13}C-NMR spectra were performed with the help of DEPT and by comparison with the spectra of model compounds. In some cases HETCOR and selective INEPT were used for assignment of protonated and quaternary carbons correspondingly.

About 15 mg (0.05 mol l^{-1}) of complexes dissolved in C_6F_6 were heated in a sealed 5 mm or 10 mm o.d. standard sample tube for registration of ^1H- and ^2D-NMR spectra, respectively, at 85°C in a thermostat with the accuracy of temperature maintenance ± 0.5°C. After corresponding time intervals sample tubes were lifted out of thermostat and cooled rapidly to ambient temperature with cold water and then ^1H- and ^2D-NMR spectra were recorded. For the stabilization of the resonance conditions in the course of spectra registration the corresponding signals of deuterium from TMS-d_{12} and fluorine from C_6F_6 were used. A special probe was built by Dr. V.A. Roznyatovsky for the registration of high accuracy ^2D-NMR spectra utilizing ^{19}F lock.

Since a considerable number of the signals with a wide range of intensities are overlapping in the spectra, the conventional procedure of integration does not provide desirable accuracy for the determination of concentrations. In this case, the technique based on the deconvolution of the spectra was used with the help of the PC adopted program developed by Dr. V.A. Roznyatovsky. Complete spectral contour was presented as the sum of Lorenzian lines along with phase correction taking into account magnetic field inhomogeneity.

Determination of kinetic parameters was performed based of published algorithm [24] which has been adopted also for the analysis of complex kinetic equations in [18].

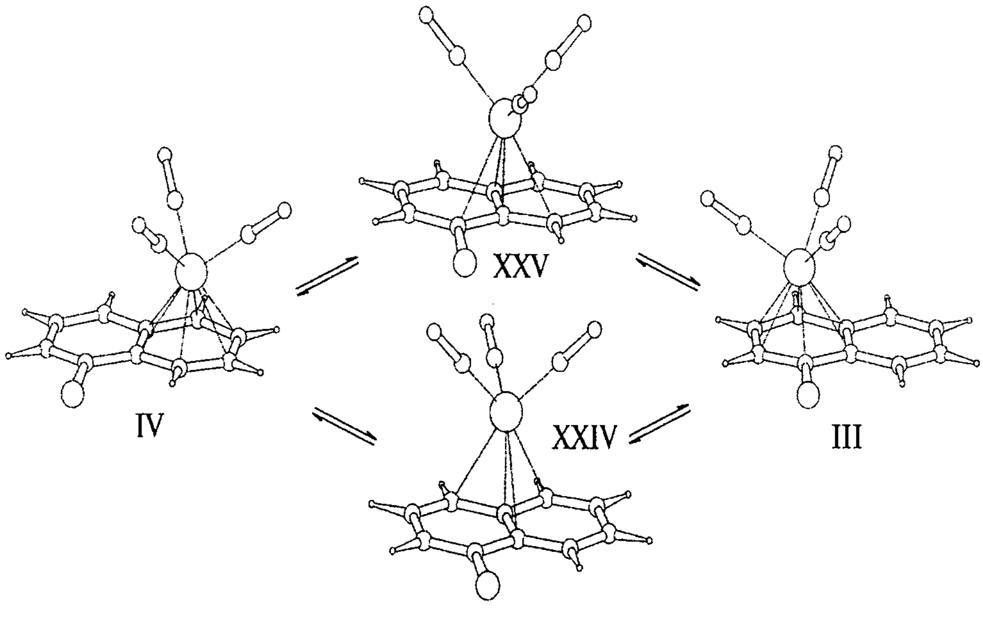
Mass spectra were recorded on a MAT-112S under electron impact of 70 eV.

4.2. General technique for the synthesis of complexes XV–XXII via reaction of Li-salts of the type IVa,b obtained by Me_3Sn, Li-exchange (or transmetallation reaction [23]) with electrophiles

Complexes V–XIV were obtained via reaction of

Table 3
Relative energies of initial (IV) complexes, of the products (III), and of transition states (XXIV) and (XXV), kcal mol^{-1} (see Scheme 6)

	Complexes IV	Complexes III	Transition state XXIV	Transition state XXV
R=H	0	0	30.44	30.44
R=1-Cl	0	2.78	33.93	30.82
R=2-Cl	0	2.22	30.23	30.91
R=1-$SiMe_3$	−1.64	0	29.59	30.63
R=2-$SiMe_3$	−4.47	0	26.41	26.62
R=1-Me	0.52	0	32.18	30.38
R=2-Me	−0.19	0	28.86	29.92



(6)

corresponding Li-salts generated by Br, Li-exchange [22] from chromium tricarbonyl complexes IV and BuLi in ether at −50°C with electrophiles RX (Scheme 4). The general procedure for their synthesis as well as synthesis of III and IV via the Oefele reaction were described earlier [16]. ^{1}H-NMR data of V–XIV are presented in Table 1.

4.2.1. General procedure of synthesis of lithum salts of type (IVLi)

A solution (ca. 5 mM) of trimethylstannylnaphthalene complexes (IIIa) or (IIIb) in ether was treated with a threefold excess of *n*-BuLi in hexane at −78°C. The temperature was increased to −50°C under stirring and the solution turned deep orange. At −50°C stirring was continued for 15 min. The mixture was then treated with excess of electrophile (D_2O, CH_3I, Me_3SiCl, C_2Cl_6) and stirred for the further 30 min. Solvent was distilled off at 0°C in vacuum, and the reaction mixture was chromatographed on SiO_2 column or subjected to TLC. A mixture of hexane and ether (20:1 or 30:1) was used as eluent. The complexes were recrystallized from benzene-heptane mixture.

4.2.2. Reaction of lithum salts of type (IVc,d) with electrophiles

4.2.2.1. Synthesis of complex (XV). From 0.07 g (0.16 mmol) of (IVa) and 1 ml of D_2O as described above 0.03 g (69%) of (XV) was obtained. Mass spectrum (12 eV, 200°C): 265 (70) M$^+$, 237 (52) [M–CO]$^+$, 209 (65) [M–2CO]$^+$, 181 (75) [M–3CO]$^+$, 129 (6) [M–3CO–Cr]$^+$, 52 (100) Cr$^+$.

4.2.2.2. Synthesis of complex (XVI). From 0.09 g (0.21 mmol) of (IIIb) and 1 ml of D_2O as described above 0.04 g (72%) of (XVI) was obtained. Mass spectrum (10 eV, 160°C): 265 (68) M$^+$, 237 (46) [M–CO]$^+$, 209 (56) [M–2CO]$^+$, 181 (70) [M–3CO]$^+$, 129 (10) [M–3CO–Cr]$^+$, 52 (100) Cr$^+$.

4.2.2.3. Synthesis of complex (XVII). From 0.08 g (0.19 mmol) of (IIIa) and 0.5 g of freshly distilled CH_3I as described above 0.045 g (87%) of (XVII) was obtained. Mass spectrum (12 eV, 200°C): 278 (65) M$^+$, 250 (22) [M–CO]$^+$, 222 (26) [M–2CO]$^+$, 194 (5) [M–3CO]$^+$, 142 (6) [M–3CO–Cr]$^+$, 52 (100) Cr$^+$.

4.2.2.4. Synthesis of complex (XVIII). From 0.1 g (0.23 mmol) of (IIIb) and 0.7 g of freshly distilled CH_3I as described above 0.06 g (92%) of (XVIII) was obtained. Mass spectrum (12 eV, 200°C): 278 (58) M$^+$, 250 (31) [M–CO]$^+$, 222 (20) [M–2CO]$^+$, 194 (5) [M–3CO]$^+$, 142 (8) [M–3CO–Cr]$^+$, 52 (100) Cr$^+$.

4.2.2.5. Synthesis of complex (XIX). From 0.24 g (0.57 mmol) of (IIIb) and 1.3 g (12 mmol) of freshly distilled Me_3SiCl as described above 0.1 g (50%) of (XIX) was obtained. Mass spectrum (70 eV, 160°C): 336 (10) M$^+$, 280 (12) [M–CO]$^+$, 252 (70) [M–2CO]$^+$, 224 (6) [M–3CO]$^+$, 172 (8) [M–3CO–Cr]$^+$, 52 (100) Cr$^+$.

4.2.2.6. Synthesis of complex (XX). From 0.16 g (0.38 mmol) of (IIIb) and 0.9 g (8 mmol) of freshly distilled Me_3SiCl as described above 0.09 g (75%) of (XX) was obtained. Mass spectrum (70 eV, 160°C): 336 (6) M$^+$, 280 (14) [M–CO]$^+$, 252 (65) [M–2CO]$^+$, 224 (6) [M–3CO]$^+$, 172 (14) [M–3CO–Cr]$^+$, 52 (100) Cr$^+$.

4.2.2.7. Synthesis of complex (XXI). From 0.13 g (0.30 mmol) of (IIIb) and 0.7 g (3 mmol) of recrystallized C_2Cl_6 as described above 0.03 g (35%) of (XXI) was obtained. Mass spectrum (12 eV, 200°C): 298 (18) M$^+$, 270 (6) [M–CO]$^+$, 242 (26) [M–2CO]$^+$, 214 (35) [M–3CO]$^+$, 162 (100) [M–3CO–Cr]$^+$, 52 (40) Cr$^+$.

4.2.2.8. Synthesis of complex (XXII). From 0.17 g (0.40 mmol) of (IIIb) and 0.9 g (3.8 mmol) of recrystaliized C_2Cl_6 as described above 0.05 g (47%) of (XXII) was obtained. Mass spectrum (12 eV, 200°C): 298 (14) M$^+$, 270 (8) [M–CO]$^+$, 242 (30) [M–2CO]$^+$, 214 (40) [M–3CO]$^+$, 162 (100) [M–3CO–Cr]$^+$, 52 (46) Cr$^+$.

Acknowledgements

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References

[1] B. Mann, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 3, chapter 20, 1982, p. 89.

[2] B Mann, Chem.Soc.Rev. 15 (1986) 167.

[3] N.A. Ustynyuk, Organomet. Chem. USSR 2 (1989) 20.

[4] Yu.A. Ustynyuk, Vest. Mosk. Univ. Ser. Khim. 23 (1982) 605.

[5] B. Deubzer, PhD dissertation, Technische Hochschule Muenchen, 1966.

[6] K.H. Doetz, R Dietz, Chem.Ber. 110 (1977) 1555.

[7] E.P. Kuendig, V. Desorby, C. Grivet, B. Rudolf, S. Spichiger, Organometallics 6 (1987) 1173.

[8] R.U. Kirss, P.M. Treichel Jr, J. Am. Chem. Soc. 108 (1986) 853.

[9] Y.F. Oprunenko, S.G. Malyugina, Yu.A. Ustynyuk, N.A. Ustynyuk, Izv. Akad. Nauk SSSR Ser. Khim. (1984) 2405.

[10] Yu.F. Oprunenko, S.G. Malyugina, Yu.A. Ustynyuk, N.A. Ustynyuk, Izv. Akad. Nauk SSSR Ser. Khim. (1985) 2156.
[11] R. Crabtree, C. Parnell, Organometallics 3 (1984) 1727.
[12] T.A. Albright, P. Hofmann, R. Hoffmann, P. Lillya, P.A. Dobosh, J. Am. Chem. Soc. 105 (1983) 3396.
[13] A. Stanger, H. Weismann, J. Organomet. Chem. 515 (1996) 183.
[14] Yu.F. Oprunenko, S.G. Malyugina, Yu.A. Ustynyuk, N.A. Ustynyuk, D.N. Kravtsov, J. Organomet. Chem. 338 (1988) 357.
[15] E.O. Fischer, H.P. Fritz, J. Organomet. Chem. 7 (1967) 121.
[16] M. Hudechek, S Toma, J. Organomet. Chem. 393 (1990) 115.
[17] Yu.F. Oprunenko, S.G. Malyugina, O.Ya. Babushkina, P.N. Nesterenko, Yu.A. Ustynyuk, Organomet. Chem. USSR 2 (1988) 599.
[18] N.G. Akhmedov, S.G. Malyugina, V.I. Mstislavsky, Yu.F. Oprunenko, V.A. Roznyatovsky, Yu.A. Ustynyuk, Organometallics 17 (1998) 4607.
[19] Yu.F. Oprunenko, S.G. Malyugina, O.K. Sokolikova, O.K. Afanasova, Yu.A. Ustynyuk, N.A. Ustynyuk, Organomet. Chem. USSR 3 (1990) 1396.
[20] T. Ziegler, Chem. Rev. 91 (1991) 651.
[21] D. Laikov, Chem. Phys. Lett. 281 (1997) 151.
[22] Yu.F. Oprunenko, I.A. Shaposhnikova, Yu.A. Ustynyuk, Organomet. Chem. USSR 4 (1991) 684.
[23] M. Wright, Organometallics 8 (1989) 407.
[24] V.G. Gorsky, E.A. Katsman, F.D. Klebanova, A.A. Grigor'ev, Theor. Exp. Chem. (USSR) 2 (1987) 191.