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Transition metal complexes with heterocyclic analogs of fluorene

1. Synthesis, structures, and haptotropic rearrangements of tricarbonylchromium complexes of dibenzothiophene

M. V. Zabalov, ★ ***I. P. Gloriozov, Yu. F. Oprunenko, and D. A. Lemenovskii***

Department of Chemistry, Moscow State University,
Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 932 8846. E-mail: zabalov@org.chem.msu.ru

The complex formation of dibenzothiophene with chromium carbonyl complexes of the general formula $L_3Cr(CO)_3$ (L = Py, NH_3, or CO) afforded η^6-$C_{12}H_8SCr(CO)_3$ (**1**). In the presence of tetramethylethylenediamine, complex **1** was selectively metallated with BuLi at position 4 of the coordinated ring to form η^6-4-$LiC_{12}H_8SCr(CO)_3$ (**2**). In decane, the tricarbonylchromium group is reversibly and intramolecularly migrates from the unsubstituted to substituted ring due to the inter-ring haptotropic rearrangement (IRHR) at 130 °C for 100 h. In decane, the rate constant of IRHR was estimated experimentally by ^1H NMR spectroscopy and theoretically by the density functional theory (DFT).

Key words: tricarbonylchromium complexes, dibenzothiophene, inter-ring haptotropic rearrangement, X-ray diffraction analysis, kinetics, NMR, quantum-chemical calculations.

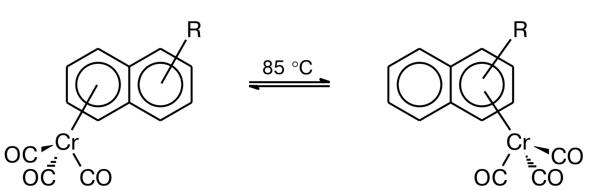
Transition metal complexes with polycyclic aromatic ligands are of considerable interest due to their structural characteristics[1] and dynamical properties.[2] In recent years, the ability of these complexes to catalyze many organic reactions has gained practical importance.[3] Besides, tricarbonylchromium complexes are widely used for the synthesis of difficultly accessible organic compounds.[4,5]

Of molecular dynamics processes, inter-ring haptotropic rearrangements (IRHR) in these compounds have been extensively studied in recent years.[6] These rearrangements involve the intramolecular migration of a transition metal together with its ligand environment along the carbopolycyclic system from one ring to another. Such rearrangements were observed for many transition metals (Cr, Mo, W, Rh, Pd, Ir, Ni, Mn, Fe, *etc.*).[6] However, the kinetics of these reactions was studied in detail by ^1H NMR spectroscopy primarily for tricarbonylchromium complexes of naphthalene,[7—10] biphenyl,[11,12] biphenylene[13,14] (Scheme 1), and some other carbocyclic systems.[6] In particular, inter-ring haptotropic rearrangements were studied in neutral and anionic fluorene complexes.[15,16]

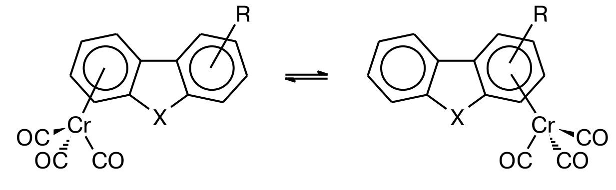
However, there are only a few examples of IRHR in metal complexes with heteropolycyclic aromatic ligands,[17,18] which are of considerable interest for the study of the effect of a heteroatom on IRHR and catalytic activities of these systems. Tricarbonylchromium complexes of heterocyclic analogs of fluorene, *viz.*, of dibenzothiophene, dibenzofuran, and carbazole (η^6-$C_{12}H_8X)Cr(CO)_3$ (X = S, O, or NR, respectively), can be considered as the simplest and synthetically readily accessible models.

The inter-ring migration of the $Cr(CO)_3$ group (Scheme 2) can proceed through the five-membered ring, like in complexes with the fluorenyl anion,[15] to form η^5 complexes (in principle, these complexes are known for pyrrole[19] and thiophene[20]), at the periphery of the ligand,[21] and intermolecularly.[22]

Scheme 1



Scheme 2



X = S, O, NR′

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The aim of the present study was to develop a procedure for the synthesis of difficultly accessible dibenzothiophene complex **1** [23] and methods for the introduction of substituents into the coordinated ring of this complex.

Results and Discussion

We synthesized the tricarbonylchromium complex of dibenzothiophene η^6-$C_{12}H_8SCr(CO)_3$ (**1**) according to four procedures:

1) by the Öfele reaction[24] of $Py_3Cr(CO)_3$ with dibenzothiophene in the presence of BF_3 etherate at −20 °C; the yield was 39%;

2) by the reaction of dibenzothiophene with the $(MeCN)_3Cr(CO)_3$ complex in dioxane at 5—50 °C; the yield was 30%;

3) by the Rausch reaction[25] of dibenzothiophene with $(NH_3)_3Cr(CO)_3$ in boiling dioxane; the yield was 25%;

4) by the Fischer reaction[26] of dibenzothiophene with $Cr(CO)_6$ (and using Toma's modification under the conditions of the Fischer reaction in the presence of THF or ethyl formate as the catalyst[27,28]). In the latter case, we failed to isolate the target complex because it rapidly decomposed at high temperature and in the presence of polar additives.

Earlier,[23] complex **1** has been prepared in lower yield (10%) by the reaction of $(MeCN)_3Cr(CO)_3$ with dibenzothiophene using azeotropic distillation of acetonitrile with dioxane.

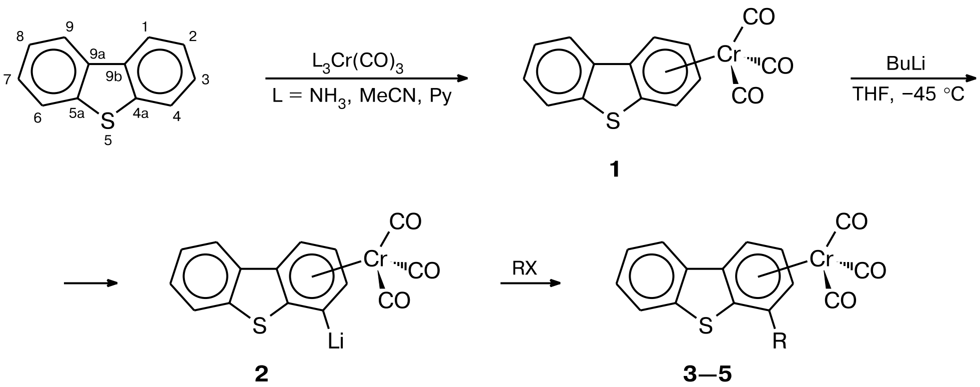
A comparison of our results with the published data[29] shows that the complex formation with heterocyclic ligands, unlike that with polyaromatic carbocycles, gives somewhat lower yields. The complex formation by the Öfele reaction of dibenzothiophene with tricarbonyltris(pyridine)chromium in the presence of BF_3 etherate (Scheme 3) is the procedure of choice.

Complex **1** was functionalized by lithiation. The reaction of complex **1** with Bu^{n}Li in THF in the presence of tetramethylethylenediamine (TMEDA) at temperatures from −78 to −40 °C followed by the kinetically controlled reaction of lithium derivative **2** with electrophiles (MeI, $ClSiMe_3$, or $ClSnMe_3$)[30] proceeded regioselectively to give complexes 4-R-$C_{12}H_8SCr(CO)_3$ **3—5** in 90, 80, and 92% yields, respectively.

Apparently, like other orthometallation reactions, the process under consideration is accompanied by additional coordination of the lithium ion at the lone electron pair of the sulfur atom resulting in the regioselective addition of the substituent at position 4 of the starting complex. Many examples of selective metallation of transition metal complexes with heterocyclic ligands under the conditions of kinetic control have been reported.[30] As an illustration, we refer to complexes with thiophene,[31] benzothiophene,[32] and indole[33] and to functionally substituted benzenetricarbonylchromium complexes.[4,5,34]

However, the rate of metallation of complex **1** is lower compared to those of the reactions of the complexes with thiophene, benzothiophene, indole, and functionally substituted benzene derivatives. In the absence of coordinating agents (TMEDA), a much longer time, an excess of Bu^{n}Li, and a higher temperature are required for the reaction to be brought to completion, *i.e.*, up to the disappearance of an impurity of the unconsumed starting complex **1**, whereas the reactions with the above-mentioned complexes proceeded in good yields even in the absence of TMEDA and an excess of Bu^{n}Li at −78 °C during the same time.[34] When the temperature was increased to −20 °C, an impurity of a 1,4-disubstituted complex was detected (^{1}H NMR spectroscopic data) among the products of the reaction of complex **1** with Bu^{n}Li, which is associated with the formation of dilithium derivative **6**. At temperatures higher than −20 °C, the lithium derivatives began to decompose giving intensely colored products.

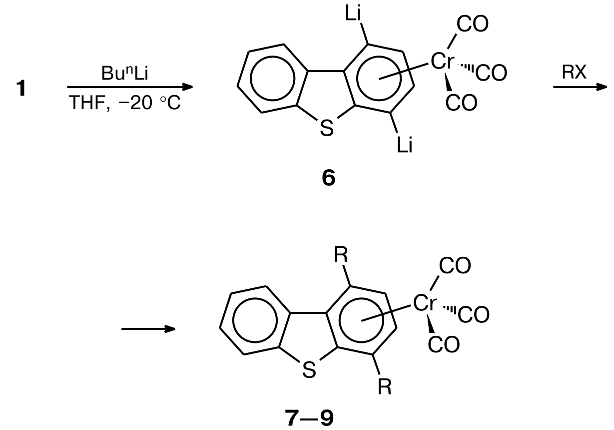
Scheme 3



R = Me (**3**), $SiMe_3$ (**4**), $SnMe_3$ (**5**)

We used the formation of 1,4-disubstituted derivatives for the development of a preparative procedure for the synthesis of such compounds. Complex **1** was efficiently transformed into 1,4-disubstituted derivatives **7—9** (Scheme 4) in 84, 75, and 76% yields, respectively, in the presence of a substantial excess of Bu^{n}Li at a temperature below –50 °C during 4 h followed by the addition of the corresponding electrophilic reagents.

Scheme 4



R = Me (**7**), SiMe$_3$ (**8**), SnMe$_3$ (**9**)

Complexes **1**, **3**, and **7** have very similar mobilities on silica gel and Al_2O_3 and they cannot be separated by TLC or column chromatography. However, small impurities of the starting complex **1** can be easily removed by recrystallization, because the solubility of these complexes in organic solvents increases in the series **7** < **3** < **1**. By contrast, the silyl and stannyl complexes differ sufficiently in mobility to be isolated by column chromatography (Al_2O_3 as sorbent).

The structures of all compounds were established by ^{1}H and ^{13}C NMR spectroscopy. The positions of the substituents in complexes **3—5** and **7—9** were determined by the nuclear Overhauser effect experiments,[35] calculations according to additive schemes taking into account the ring current, as well as by analyzing two types of the vicinal spin-spin coupling constants $^3J_{H,H}$ in the coordinated nucleus and comparing these values with the corresponding constants for naphthalene complexes.[8] The NMR spectroscopic data are given in Table 1. The structures of complexes **3** and **7** were confirmed by X-ray diffraction study of mixed crystals prepared by crystallization of the complexes from the reaction mixture of **3** and **7**. These data will be published elsewhere.

Monomethyl-substituted complex **3** is the model of choice for revealing IRHR in dibenzothiophene complexes and studying its characteristic features. According to the ^{1}H NMR spectroscopic data, heating of complex **3** in decane at 130 °C for 10 h afforded complex **10** due to the intra-ring IRHR **3** $\rightleftharpoons$ **10** ([**3**] : [**10**] ≈ 3 : 1) (Scheme 5).

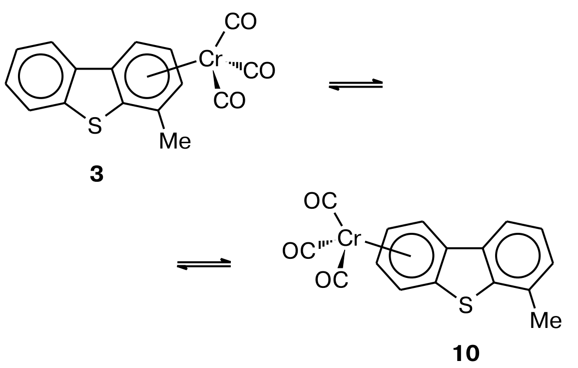
Further heating of a mixture of complexes **3** and **10** at 130 °C for 100 h led to an equilibrium ratio [**3**] : [**10**] ≈ 60 : 40, which remained unchanged upon subsequent heating. This made it possible to estimate the rate constant of IRHR $k_{obs} = (2.85\pm0.04) \cdot 10^{-5}\ s^{-1}$ and the free activation energy $\Delta G^{\#} = 32.24\ kcal\ mol^{-1}$. The latter value is only 1 kcal mol^{-1} lower than those for tricarbonylchromium complexes of acetylfluorene.[16]

The mechanism of the inter-ring haptotropic migration of the metal-containing group was theoretically stud-

Table 1. ^{1}H NMR spectra of complexes **1**, **3—5**, and **7—9**

Complex	δ (J/Hz)							
	H(1)	H(2)	H(3)	H(4)	H(6)	H(7)	H(8)	H(9)
1	5.58 (d, J = 6.5)	4.44 (t, J = 6.2)	4.64 (t, J = 6.3)	5.24 (d, J = 6.4)	7.18 (d, J = 7.7)	7.12 (t, J = 7.4)	7.02 (distort.t, J = 7.7, J = 7.4)	7.50 (d, J = 7.4)
3	5.46 (d, J = 6.1)	4.61 (m, 2 H)		—	7.22 (d, J = 6.8)	7.16 (t, J = 7.7)	7.05 (t, J = 7.7)	7.55 (d, J = 7.7)
4	5.97 (d, J = 6.5)	5.04 (m, 2 H)		—	7.28 (d, J = 7.5)	7.12 (t, J = 7.9)	7.06 (t, J = 7.9)	7.52 (d, J = 7.4)
5	5.93 (d, J = 6.6)	4.57 (t, J = 6.2)	5.09 (d, J = 5.9)	—	7.32 (t, J = 7.7)	7.15 (t, J = 7.9)	7.07 (t, J = 7.9)	7.55 (d, J = 8.1)
7	—	4.39 (d, J = 6.2)	4.75 (d, J = 6.0)	—	7.28 (d, J = 8.0)	7.14 (t, J = 7.8)	7.06 (t, J = 7.6)	7.94 (d, J = 8.3)
8	—	5.61 (d, J = 6.3)	5.74 (d, J = 6.3)	—	7.31 (d, J = 7.2)	7.15 (t, J = 7.5)	7.08 (t, J = 7.5)	7.73 (d, J = 7.3)
9	—	5.04 (d, J = 5.7)	5.70 (d, J = 5.7)	—	7.27 (d, J = 7.2)	7.14 (t, J = 8.2, J = 7.2)	7.04 (t, J = 8.2, J = 7.2)	8.03 (d, J = 8.2)

Scheme 5



ied for the starting symmetrical complex **1** by the density functional theory (DFT)^{36} using the *ab initio* generalized gradient approximation and the PBE functional (Perdew—Burke—Ernzerhof). The one-electron wave functions were expanded in the extended TZ2P atomic basis sets of the contracted Gaussians {311/1}, {6,11111/411/11}, {611111111/5111111/11}, and (61111111111/511111111/5111} for the H, C, S, and Cr atoms, respectively.

A quantum-chemical study of the potential energy surface (PES) of the degenerate haptotropic rearrangement $Cr(CO)_3$ from the basic state (**Pr**) (Fig. 1), *i.e.*, from one benzene ring to another, demonstrated that the reaction proceeds through an intermediate (**Im**) (Fig. 2), which corresponds to a structure in which the $Cr(CO)_3$ group is coordinated to four peripheral carbon atoms, *i.e.*, to a structure of the pseudodiene complex. The reaction path links the product with an intermediate through a transition state (**TS**) (Fig. 3). The structure of the latter corresponds to the structure of a distorted trimethylenemethane complex. The interatomic distances in the basic state, intermediate, and transition state are given in Table 2. The calculated reaction coordinate in mass-weighted Cartesian coordinates is shown in Fig. 4. Taking into account the zero-point energy, the barrier is 31.2 kcal mol^{-1}. The relative energy of the intermediate is 27.3 kcal mol^{-1}.

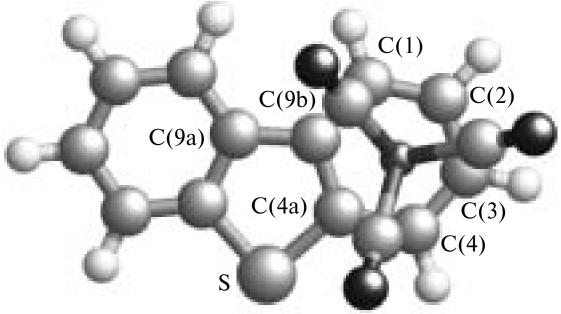


Fig. 1. Structure of the basic state. $E = -2243.896954$ a.u., $\Delta E = 0$ kcal mol^{-1}, ZPVE = 115.1 kcal mol^{-1}, $\Delta E^0 = 0.0$ kcal mol^{-1}.

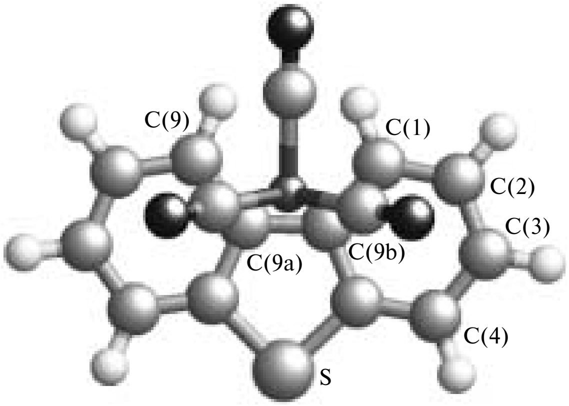


Fig. 2. Structure of the intermediate. $E = -2243.852321$ a.u., $\Delta E = 28.0$ kcal mol^{-1}, ZPVE = 114.4 kcal mol^{-1}, $\Delta E^0 = 27.3$ kcal mol^{-1}.

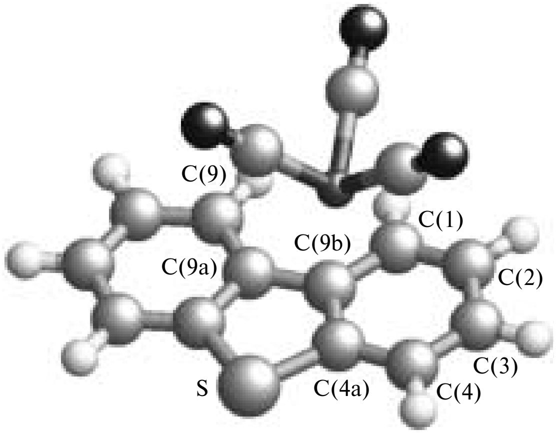


Fig. 3. Structure of the transition state. $E = -2243.847205$ a.u., $\Delta E = 31.2$ kcal mol^{-1}, ZPVE = 114.1 kcal mol^{-1}, $\Delta E^0 = 30.2$ kcal mol^{-1}.

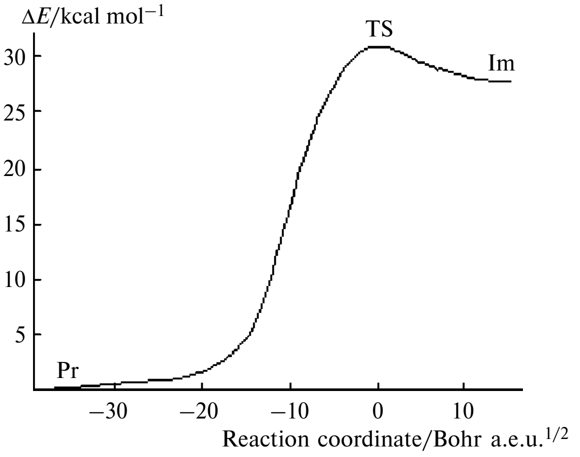


Fig. 4. Calculated reaction coordinate of the metallotropic rearrangement in mass-weighted Cartesian coordinates.

Table 2. Interatomic distances in the basic state (**Pr**), intermediate (**Im**), and transition state (**TS**)

Distance	r/Å		
	Pr	**Im**	**TS**
Cr—C(1)	2.213	2.612	2.379
Cr—C(2)	2.213	3.551	2.961
Cr—C(3)	2.205	4.085	3.416
Cr—C(4)	2.230	3.886	3.343
Cr—C(4a)	2.292	3.029	2.748
Cr—C(9)	4.400	2.604	3.355
Cr—C(9a)	3.436	2.260	2.711
Cr—C(9b)	2.298	2.262	2.216
Cr—CO	1.847	1.822, 1.822, 1.806	1.812
Cr—S	3.718	3.727	3.750
C—O	1.166	1.172	1.172

Experimental

All reactions were carried out under argon. Anhdyrous THF, dioxane (purified by Na—benzophenone), hexane (distilled over Na), and acetonitrile (distilled over CaH_2) were used as solvents. Trimethylchlorosilane was purified by refluxing over magnesium chips. Trimethylchlorostannane and a Bu^nLi solution (Aldrich) were used without additional purification; $Cr(CO)_6$ was purified by sublimation at 0.1 Torr and 45 °C. The complexes $Cr(NH_3)_3(CO)_3$,[25,37] $Cr(MeCN)_3(CO)_3$, and $Cr(Py)_3(CO)_3$ [37] were synthesized according to known procedures.

The NMR spectra were recorded on a Varian-400 instrument in C_6D_6. Elemental analysis was carried out by the Group of Microanalysis at the Department of Chemistry of the Moscow State University.

Synthesis of dibenzothiophenetricarbonylchromium 1. ***A.*** A solution of $BF_3 \cdot Et_2O$ (5.56 mL, 45 mmol) in Et_2O (15 mL) was slowly added to a mixture of dibenzothiophene (3.68 g, 20 mmol) and $(Py)_3Cr(CO)_3$ (3.73 g, 10 mmol) in Et_2O (100 mL) cooled to −20 °C. The reaction mixture was stirred at −20 °C for 15 min, slowly warmed to ~20 °C, stirred at ~20 °C for 2 h, and cooled to 0 °C. Then deaerated water (100 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3×30 mL). The combined ethereal extracts were passed through a layer of Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in a minimum amount of benzene and transferred to a chromatographic column. The excess unconsumed dibenzothiophene was eluted with hexane and then the target product was eluted with benzene. Complex **1** was obtained in a yield of 1.23 g (39% with respect to $(Py)_3Cr(CO)_3$) as yellow-orange crystals. The ^1H NMR spectroscopic data are given in Table 1. $^{13}C\{^1H\}$ NMR, δ: 91.2 (C(1)); 85.8 (C(2)); 86.3 (C(3)); 88.4 (C(4)); 125.4 (C(6)); 123.0 (C(7)); 121.4 (C(8)); 128.2 (C(9)); 134.0 (C(9a)); 104.0 (C(9b)); 115.7 (C(4a)); 139.4 (C(5a)); 232.8 (CO). IR (CH_2Cl_2), ν/cm^{-1}: 1966, 1892 (C=O).

B. A solution of dibenzothiophene (7.36 g, 40 mmol) in dioxane (30 mL) was added to a suspension of $(MeCN)_3Cr(CO)_3$ (5.18 g, 20 mmol) in dioxane (60 mL) cooled to 5 °C. The reaction mixture was slowly warmed to ~20 °C, stirred for 1 h, heated to 50 °C, and again stirred for 30 min. The resulting red solution was filtered through a glass filter and concentrated *in vacuo*. The residue was heated in hexane (150 mL). Then the hexane was removed by decantation. The residue was dried *in vacuo* and dissolved in a minimum amount of benzene. The reaction solution was transferred to a column with Al_2O_3. The excess unconsumed dibenzothiophene was eluted with hexane and the target product was eluted with benzene. The yield was 1.92 g (30%).

C. A mixture of $(NH_3)_3Cr(CO)_3$ (1.87 g, 10 mmol) and dibenzothiophene (3.68 g, 20 mmol) in dioxane (100 mL) was refluxed for 3 h. The reaction solution was filtered through a glass filter and concentrated *in vacuo*. The residue was dissolved in a minimum amount of benzene. The solution was transferred to a column with Al_2O_3. The excess unconsumed dibenzothiophene was eluted with hexane and the target product was eluted with benzene. The yield was 0.64 g (25%).

Metallation of complex 1 and the reactions with electrophiles (general procedure). A solution of Bu^nLi in hexane (0.3 mL, 1.2 mmol, 3.9 mol L^{-1}) was added to a solution of complex **1** (0.32 g, 1 mmol) and TMEDA (0.15 mL, 2 mmol) in THF (20 mL) cooled to −78 °C. The reaction mixture was slowly warmed to −45 °C, stirred at this temperature for 2.5 h, and cooled to −78 °C. Then the corresponding electrophile (6.4 mmol) was added. The reaction mixture was slowly heated to ~20 °C and stirred for 8 h. Deaerated MeOH (1 mL) was added and the solvent was concentrated *in vacuo*. The residue was dissolved in a minimum amount of benzene and the solution was transferred to a column with Al_2O_3. The organic impurities were eluted with hexane and the target product was eluted with benzene.

Tricarbonyl(4-methylbenzothiophene)chromium (3). The yield was 0.30 g (90%), yellow-orange crystals. Found (%): C, 57.20; H, 3.01. $C_{16}H_{13}CrO_3S$. Calculated (%): C, 57.48; H, 3.01. IR (CH_2Cl_2), ν/cm^{-1}: 1964, 1889 (C=O).

Tricarbonyl(4-trimethylsilylbenzothiophene)chromium (4). The yield was 0.31 g (80%), yellow-orange crystals. Found (%): C, 55.11; H, 4.10. $C_{18}H_{19}CrO_3SSi$. Calculated (%): C, 55.09; H, 4.11. IR (CH_2Cl_2), ν/cm^{-1}: 1965, 1889 (C=O).

Tricarbonyl(4-trimethylstannylbenzothiophene)chromium (5). The yield was 0.44 г (92%), yellow-orange crystals. Found (%): C, 44.79; H, 3.36. $C_{18}H_{19}CrO_3SSn$. Calculated (%): C, 44.76; H, 3.34. IR (CH_2Cl_2), ν/cm^{-1}: 1962, 1888 (C=O).

The ^1H NMR spectroscopic data are given in Table 1.

Dimetallation of complex 1 and the reactions with electrophiles (general procedure). A solution of Bu^nLi in hexane (1.3 mL, 5 mmol, 3.9 mol L^{-1}) was added to a solution of complex **1** (0.32 g, 1 mmol) and TMEDA (0.45 mL, 6 mmol) in THF (20 mL) cooled to −78 °C. The reaction mixture was slowly cooled to −20 °C, stirred for 4 h, and cooled to − 78 °C. Then the corresponding electrophile (22 mmol) was added. The reaction was slowly warmed to ~20 °C and stirred for 8 h. Then deaerated MeOH (2 mL) was added and the solvent was removed *in vacuo*. The residue was dissolved in a minimum amount of benzene and the solution was transferred to a column with Al_2O_3. The organic impurities were eluted with hexane and the target product was eluted with benzene.

Tricarbonyl(1,4-dimethyldibenzothiophene)chromium (7). The yield was 0.29 g (84%), yellow crystals. Found (%): C, 58.65; H, 3.49. $C_{17}H_{15}CrO_3S$. Calculated (%): C, 58.62; H, 3.47. $^{13}C\{^1H\}$ NMR, δ: 103.3 (C(1)); 92.1 (C(2)); 92.5 (C(3)); 100.0 (C(4)); 125.4 (C(6)); 124.8 (C(7)); 123.3 (C(8)); 136.0 (C(9)); 233.7 (CO). IR (CH_2Cl_2), ν/cm^{-1}: 1963, 1887 (C=O).

Tricarbonyl[1,4-di(trimethylsilyl)dibenzothiophene]chromium (8). The yield was 0.35 g (75%), yellow-orange crystals. Found (%): C, 54.32; H, 5.19. $C_{21}H_{27}CrO_3SSi_2$. Calculated (%): C, 54.28; H, 5.21. IR (CH_2Cl_2), ν/cm^{-1}: 1966, 1889 (C=O).

Tricarbonyl[1,4-di(trimethylstannyl)dibenzothiophene]chromium (9). The yield was 0.49 g (76%), yellow-orange crystals. Found (%): C, 39.22; H, 3.74. $C_{21}H_{27}CrO_3SSn_2$. Calculated (%): C, 39.06; H, 3.75. IR (CH_2Cl_2), ν/cm^{-1}: 1960, 1887 (C=O).

The ^{1}H NMR spectroscopic data are given in Table 1.

Thermal rearrangement of complex 3. A solution of complex **3** (1 mmol) in decane (50 mL) was placed in a tube. The tube was heated on an oil bath at 130 °C for 100 h after which the complex was completely dissolved. Heating was terminated at intervals, the reaction mixture was rapidly cooled with ice water, and an aliquot (1/10) was withdrawn. Then the tube was again sealed and heated. A mixture of complexes in decane was transferred to a column with Al_2O_3 and the decane was eluted with hexane. A mixture of isomeric complexes formed as a result of IRHR was eluted with benzene and the solvent was evaporated *in vacuo*. The residue was dissolved in C_6D_6 and the ^{1}H NMR spectrum was recorded.

Calculations of the IRHR kinetics. The relative concentrations were determined by repeated integration of well-resolved signals of the methyl groups in the ^{1}H NMR spectra followed by averaging. The dependence of the growing concentration of an isomer was calculated according to the formula for a reversible first-order reaction

$$\ln[(A_0 - A_e)/A_t - A_e)] = (k_1 + k_2)\Delta t,$$

where A_0, A_e, and A_t are the initial, equilibrium, and running concentrations of complex **3**, respectively. The corresponding linear kinetic equation was processed by the least-squares method.

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