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Reaction of complex ligands: Part 95. Chromium tricarbonyl complexes of polysubstituted naphthohydroquinones: regioselective synthesis via [3+2+1]-benzannulation and haptotropic rearrangement☆

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Dedicated to Professor Gottfried Huttner

Abstract

A series of polysubstituted naphthohydroquinoid tricarbonyl chromium complexes were prepared by chromium mediated [3+2+1]-benzannulation of Fischer-type carbene complexes with alkynes. The kinetics and the thermodynamic data of the η^6-η^6-haptotropic rearrangements were investigated by in-situ NMR spectroscopy. The free activation energies $\Delta G^{\#}$ range from 23 to 26 kcal mol^{-1} and only slightly depend on the bulk and the donor/acceptor properties of the substituents. Equilibrium of metal migration was observed for naphthohydroquinone complexes bearing methoxy substituents at the non-hyroquinoid ring (ring A). In complexes bearing methyl groups or only hydrogen substituents at ring A the haptotropic rearrangement is irreversible. An NMR study suggests that the rearrangements of menthyloxy substituted tricarbonyl chromium complexes in hexafluorobenzene occurs intramolecularly. The two diastereomers of complex **19** show different rate constants for the metal shift which is the first example of kinetic data differing for the rearrangement of a ML_n-fragment in two diastereomeric compounds.

Keywords: Arene complexes; Benzannulation; Carbene complexes; Chromium; Haptotropic rearrangement

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1. Introduction

A characteristic property of transition metal π-complexes with polycyclic aromatic ligands is their ability to undergo haptotropic rearrangements (HR) in which the organometallic fragment migrates along the π-system of the arene ligand (Scheme 1).

A large body of experimental information exists for processes of this type in simple cyclic polyenes [2]. First, Deubzer and Öfele reported on the reversible rearrangement of both isomers of (η^6-2,3-dimethylnaphthalene)tricarbonylchromium (η^6-η^6-HR) [3]. Comparable subsequent studies referred to the migration of chromium tricarbonyl fragments in naphthalene [4–9], phenalene, acenaphtene, acenaphthylene, biphenylene and biphenyl ligands (η^6-η^6-HR) as well as for anionic fluorenyl and indenyl π-complexes (η^6-η^5-HR) and their heteroanalogues [10]. Ustynyuk and co-workers monitored the rearrangements of monosubstituted naphthalene complexes by in-situ NMR spectroscopy and determined both kinetic and thermodynamic data for the metal migration [11,12]. The reversible rearrangement of the manganese tricarbonyl fragment along the indeno[1,2-a]indene ligand (η^5-η^5-HR) was described [10] as well as the migration of the PdL_2-fragment along

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☆ For Part 94, see: Ref. [1].

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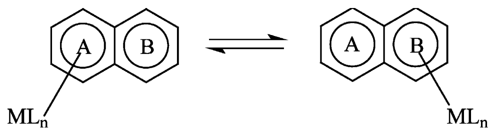


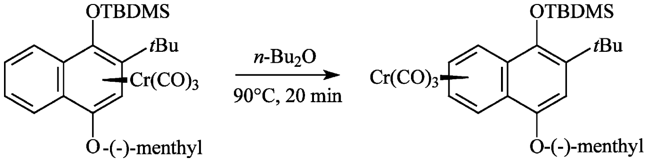
Scheme 1. Haptotropic metal migration in fused arenes.

the η^3-phenalenyl ligand periphery (η^3-η^3-HR) [13] or the shift of $Ni(PR_3)_2$ groups in η^2-anthracenes [14].

The mechanism of the haptotropic rearrangement depends on the nature of the solvent. Non-coordinating solvents (heptane, hexafluorobenzene) favour an intramolecular process [13]. Theoretical studies of haptotropic rearrangements on the basis of orbital symmetry analysis and EHT [15] proposed a pathway along the π-periphery via a trimethylene methane-like intermediate. The calculated activation barrier of about 30 kcal mol^{-1} is in agreement with experimental data (27–30 kcal mol^{-1}). Coordinating solvents (THF, benzene, toluene) have been reported to favour an intermolecular metal migration [12] which is better described as a ligand exchange reaction and which is considerably slower than the intramolecular process.

Most haptotropic rearrangements of chromium tricarbonyl complexes of mono- or disubstituted naphthalenes reported so far are reversible. In contrast, the chromium tricarbonyl fragment coordinated to alkyl- or aryl-substituted hydroquinone rings migrates irreversibly to the unsubstituted naphthalene ring upon warming. The thermal rearrangement of diastereopure *R*,*S*-tricarbonyl[1-4:9,10-η^6-1-*tert*-butyldimethylsiloxy-2-*tert*-butyl-4-(1*R*,2*S*,5*R*)-(−)-menthyloxynaphthalene]-chromium—even when carried out in the coordinating solvent di-*n*-butyl ether—was found to occur with retention of the configuration supporting an intramolecular haptotropic metal shift along the same face of the π-system [8] (Scheme 2).

In order to evaluate the effects of polysubstitution on the metal migration along the naphthalene π-system we prepared a number of densely functionalized naphthohydroquinone complexes by [3+2+1]-benzannulation of chromium methoxy(aryl)carbenes with alkynes. The rearrangement reactions were carried out in hexafluorobenzene and observed by in-situ NMR spectroscopy. Synthetic, kinetic and thermodynamic aspects of these reactions are presented in this paper.



Scheme 2. Thermal rearrangement of *R*,*S*-tricarbonyl[1-4:9,10-η^6-1-*tert*-butyldimethylsiloxy-2-*tert*-butyl-4-(1*R*,2*S*,5*R*)-(−)-menthyloxy-naphthalene]chromium.

2. Results and discussion

2.1. Synthesis of the carbene complexes

The methoxy carbene complexes **2**–**6** were synthesized by the established Fischer method [16]. Addition of an organolithium nucleophile to chromium hexacarbonyl gave the acyl metalate which underwent subsequent *O*-alkylation by trimethyloxonium tetrafluoroborate. The organolithium compounds were prepared in-situ by (i) direct metalation of the methoxy arenes by *n*-butyllithium in the presence of *N*,*N*,*N′*,*N′*-tetramethylethylene diamine in diethyl ether at room temperature or (ii) by treating the bromo arenes with *n*-butyllithium in diethyl ether at −78 °C (Scheme 3). In the case of the *ortho*-methoxy substituted carbene complexes remarkable amounts of the tetracarbonyl chelate complexes were formed during the time of reaction [17].

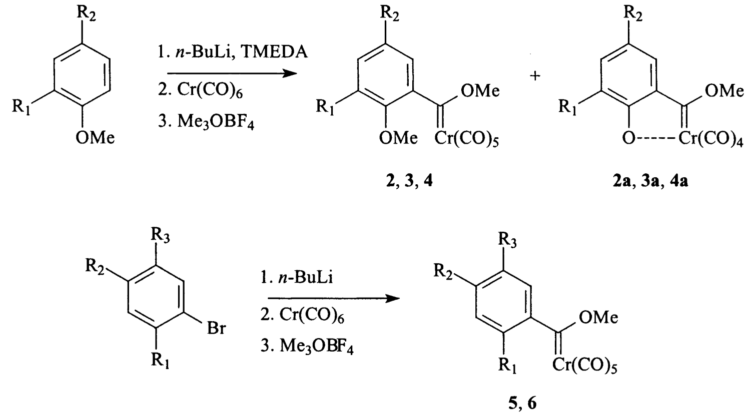
The molecular structure of dimethoxybenzylidene complex **5** was established by X-ray analysis (Fig. 1). It reveals a slight shortening of the *trans*-CO bond (2.6 pm) due to the donor ability of the dimethoxyphenyl substituent. The $Cr-C_C-O_C$ and $Cr-C_B-O_B$-angles deviate from linear which may be caused by steric interactions with the *meta*-methoxy substituent. The pentacarbonyl fragment and the carbene methoxy group show a staggered conformation typical for alkoxy carbene complexes (C1C–CR1–C1–O1 = 37.3°). All other bond lengths and bond angles are in agreement with comparable compounds [18].

The optically active carbene complexes **7**–**9a** were synthesized via an acylation/alcoholysis sequence [20] starting from the tetramethylammonium pentacarbonyl benzoylchromates **10**–**12** (Scheme 4). These milder conditions resulted in smaller amounts of the tetracarbonyl carbene chelate complexes.

2.2. [3+2+1]-Benzannulation

The tricarbonyl chromium complexes **13**–**18** were prepared by [3+2+1]-benzannulation [19] of the carbene complexes **1**–**6** with 3-hexyne and protection of the naphthol intermediates with *tert*-butyldimethylsilyl chloride in the presence of triethylamine (Scheme 5).

The molecular structures of **16** and **18** were established by single crystal X-ray analysis (Fig. 2). In contrast to the vast majority of naphthalene tricarbonylchromium complexes the $Cr(CO)_3$ fragment adopts an eclipsed conformation which presumably results from steric interactions with the ethyl-group attached to C2. In contrast to complexes **23** and **24** the sterically more demanding TBDMS-protecting group forces the ethyl group to the same side of the π-system as the chromium tricarbonyl. In complex **18** considerable steric interactions of the methyl groups attached to the non-hydroquinoid ring with the methoxy and the TBDMS-



	R_1	R_2	R_3	yield (%)
2[16]	H	H	-	63
2a[16]	H	H	-	21
3[17]	H	OMe	-	59
3a[17]	H	OMe	-	29
4[18]	OMe	H	-	65
4a	OMe	H	-	13
5	H	OMe	OMe	55
6	Me	H	Me	92

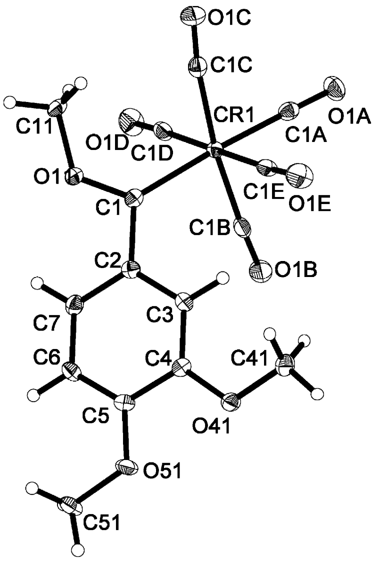
Scheme 3. Synthesis of carbene complexes **2**–**6**.

protecting groups lead to a twist between the two aromatic rings amounting to a dihedral angle C1–C10–C5–C6 of about 16°.

Being interested in (a) the effect of the more bulky menthyloxy substituent on the kinetics and b) the mechanism of the haptotropic rearrangement complexes **19**–**21** were prepared by means of the benzannulation reaction [4,8,19] (Scheme 6). Complex **8** did not react with 3-hexyne under standard conditions probably due to the sterical interactions of the menthyloxy substituent with the ethyl group in position 3 and the methoxy group in *ipso*-position. The reaction of complex **9** resulted in a slow thermal decomposition occurring above 30 °C in solution.

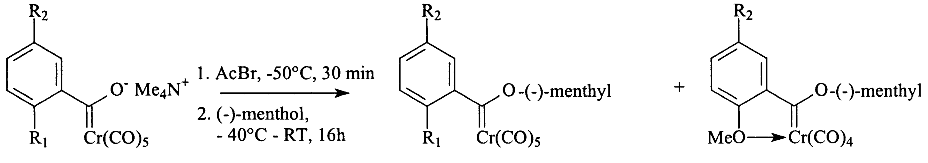
In order to investigate the effect of the bulky TBDMS-protecting group on the thermal rearrangements of the tricarbonyl chromium complexes we isolated the unprotected complex **22** [21] and applied several other protecting groups. Acylation with AcBr and camphanic acid chloride in the presence of Et_3N occurred smoothly to give **24** in 96% and **25** in 79% yield, respectively. The established methods in organic synthesis for protecting phenols as methyl ethers failed in the case of complex **22** and only led to decomplexation. Reaction of complex **22** with MeOTf in the presence of 2,6-lutidine at 0 °C for 3 h finally resulted in the formation of complex **23** in 48% yield (Scheme 7).

The molecular structures of **23** and **24** were established by single crystal X-ray analyses (Fig. 3). In contrast to **16** and **18** complexes **23** and **24** show both



5

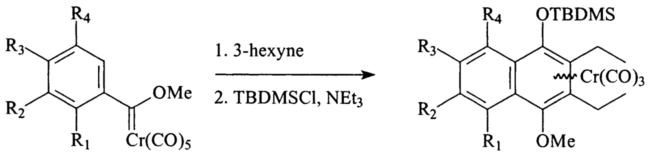
Fig. 1. Molecular structure of **5**. Vibrational ellipsoids are scaled to enclose 50% of the electron density. Selected bond lengths (Å): Cr(1)–C(1A), 1.8800(17); Cr(1)–C(1B), 1.9026(18); Cr(1)–C(1C), 1.9059(18); Cr(1)–C(1D), 1.9042(18); Cr(1)–C(1E), 1.9126(18); Cr(1)–C(1), 2.0761(16); C(1)–O(11), 1.318(2); C(1)–C(2), 1.490(2). Selected bond angles (°): C(1A)–Cr(1)–C(1), 174.63(6); C(1B)–Cr(1)–C(1) 89.37(6); C(1D)–Cr(1)–C(1) 85.54(6); C(1C)–Cr(1)–C(1) 97.70(7); C(1E)–Cr(1)–C(1) 94.16(6); O(1B)–C(1B)–Cr(1), 175.00(14); O(1C)–C(1C)–Cr(1), 173.64(14); O(1D)–C(1D)–Cr(1), 177.84(15); O(1E)–C(1E)–Cr(1), 176.73(14); O(11)–C(1)–Cr(1) 128.87(11); C(2)–C(1)–Cr(1) 124.52(11).



7, 8, 9 **8a, 9a**

	R_1	R_2	yield (%)
7[7]	H	H	71
8	OMe	H	44
8a	OMe	H	7
9	OMe	OMe	54
9a	OMe	OMe	5

Scheme 4. Synthesis of optically active carbene complexes.



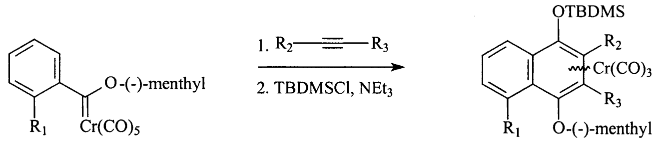
	R_1	R_2	R_3	R_4	yield (%)
13	H	H	H	H	94
14	OMe	H	H	H	63
15	OMe	H	H	OMe	67
16	H	OMe	OMe	H	73
17	OMe	OMe	H	H	70
18	Me	H	H	Me	92

Scheme 5. [3+2+1]-Benzannulation of chromium carbene complexes with 3-hexyne.

the energetically favoured staggered conformation of the chromium tricarbonyl.

Trimethylsilyl substituted complex **26** was prepared by reacting carbene complex **1** with ethynyltrimethylsilane. The air-sensitive hydroquinone complex was protected as *tert*-butyldimethylsilyl ether (Scheme 8). After chromatographic workup we isolated pure **26** in 92% chemical yield as a single regioisomer. The regiochemistry of the reaction was established by X-ray analysis (Fig. 4). Complex **26** reveals the favoured staggered conformation of the chromium tricarbonyl; interactions of the bulky TMS group with the chromium tricarbonyl fragment results in a bending of one of the Cr–C–O axes from linearity.

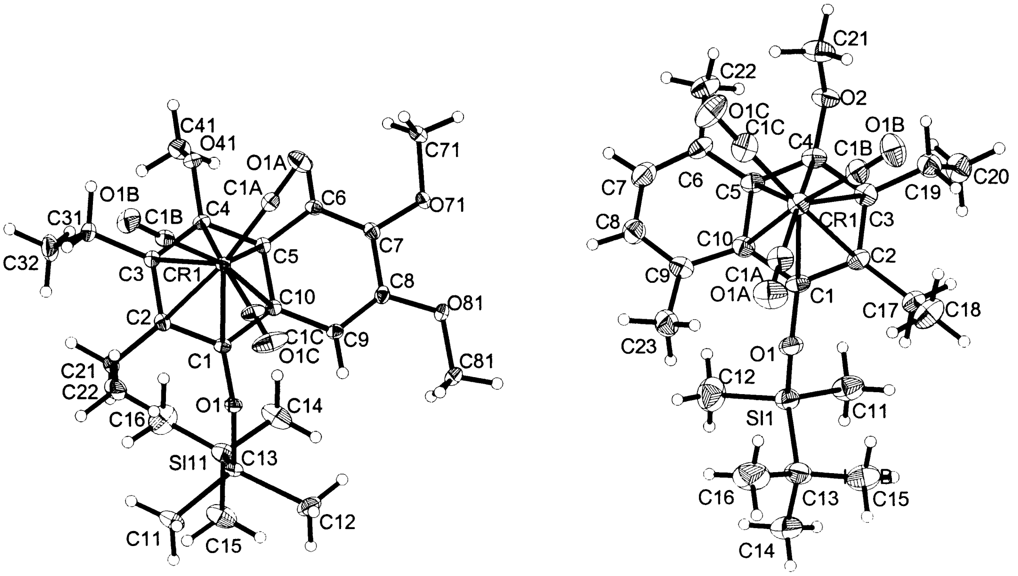
Reaction of ethynyltributylstannane with complex **1** followed by protection with TBDMSCl led to the formation of the isomeric complexes **27** and **28** in a 7:1 ratio (regarding the position of the tributylstannyl group in position 3 or 2) in 51% chemical yield; in addition, unprotected complex **29** was obtained in 15% yield (Scheme 8). The regioselectivity of the annulation reaction was determined by NOE–NMR spectroscopy.



19, 20, 21

	R_1	R_2	R_3	t_R (min)	yield	d.e. (%)
19	H	Et	Et	240	44%	85
20[7]	H	*t*-Bu	H	60	59%	82
21	OMe	*t*-Bu	H	480	48%	81

Scheme 6. Diastereosective benzannulation of optically active carbene complexes with alkynes.



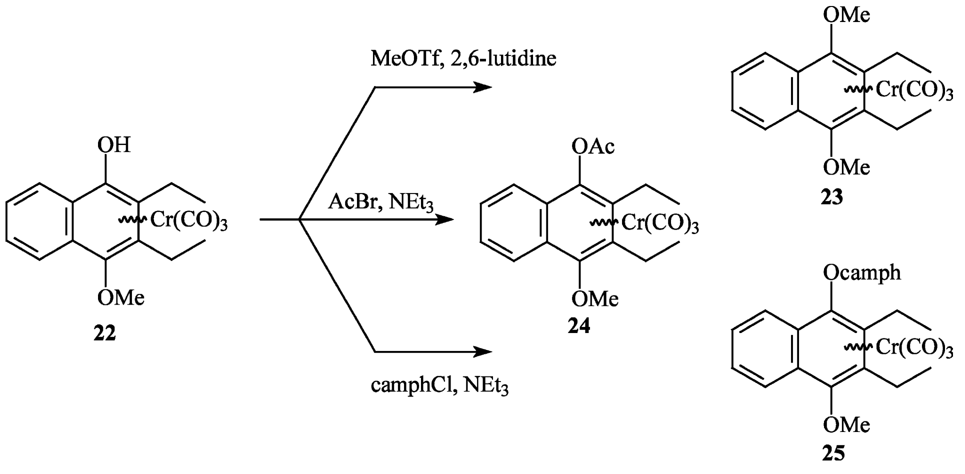
16 **18**

Fig. 2. Molecular structures of **16** and **18**. Vibrational ellipsoids are scaled to enclose 50% of the electron density. **16**: Selected bond lengths (Å): Cr(1)–C(1A), 1.8299(15); Cr(1)–C(1B), 1.8250(15); Cr(1)–C(1C), 1.8350(16); Cr(1)–C(3), 2.2231(14) Cr(1)–C(4), 2.2324(13); Cr(1)–C(2), 2.2568(14) Cr(1)–C(5), 2.2817(13); Cr(1)–C(10), 2.3062(13); Cr(1)–C(1), 2.3067(13); Cr(1)–Z(Ar), 1.763(1). Selected bond angles (°): C(1B)–Cr(1)–C(1A), 6.38(6); C(1B)–Cr(1)–C(1C), 87.38(6); C(1A)–Cr(1)–C(1C), 89.10(6). **18**: Selected bond lengths (Å): Cr(1)–C(1B), 1.829(6); Cr(1)–C(1C), 1.836(6); Cr(1)–C(1A), 1.836(6); Cr(1)–C(3), 2.217(5); Cr(1)–C(10), 2.236(5); Cr(1)–C(4), 2.255(5); Cr(1)–C(2), 2.282(5); Cr(1)–C(1), 2.287(5); Cr(1)–C(5), 2.365(5); Cr(1)–Z(Ar), 1.769(3). Selected bond angles (°): C(1B)–Cr(1)–C(1C), 86.7(2); C(1B)–Cr(1)–C(1A), 86.9(2); C(1C)–Cr(1)–C(1A), 89.9(3). Selected torsion angles (°): C(6)–C(5)–C(10)–C(1), 164.2(5); C(4)–C(5)–C(10)–C(9), 164.6(5); C(6)–C(5)–C(10)–C(9), –15.6(7).

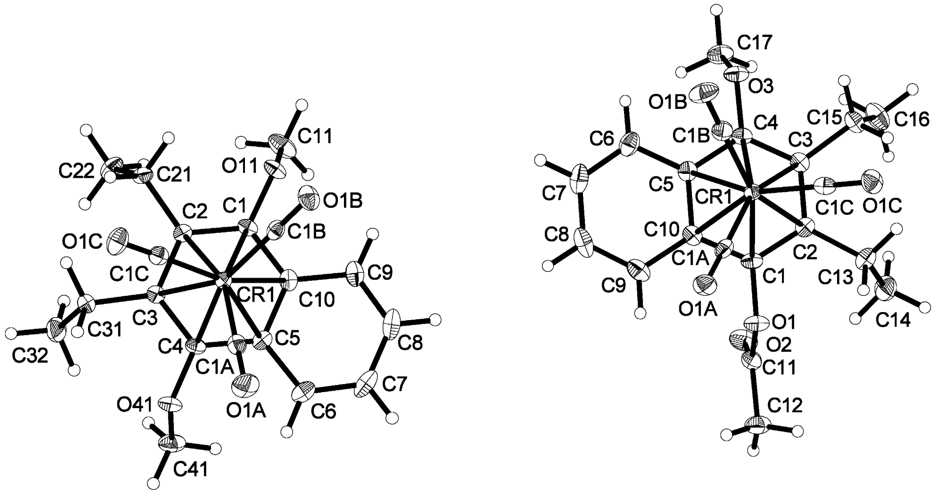
2.3. Haptotropic rearrangement

The kinetics of the haptotropic rearrangement of the tricarbonyl chromium complexes were studied by in–situ ^{1}H-NMR spectroscopy in hexafluorobenzene using benzene-d_6 as external standard. The concentration of the solutions was 0.5 mol l^{-1}. Complexes **13**–**18**, **26** were investigated at 70 °C while complexes **19**–**21**, **24** were studied at 60 °C due to their fast rearrangements at higher temperature. The rearrangements of **22**, **25** and **29** could not be investigated due to their thermal lability (**22**, **29**) or their insolubility in C_6F_6 (**25**). The results are presented in Table 1.

The chromium tricarbonyl complexes **19**–**21** retain their optical purity which is suggestive for an intramolecular mechanism in hexafluorobenzene. No signals of uncoordinated ligands were observed during the rearrangements excluding that ligand exchange reactions occurred. To insure that signals of the free ligands were not isochronous with those of their complexes all free



Scheme 7. Protection of hydroquinone complex **22**.



23 **24**

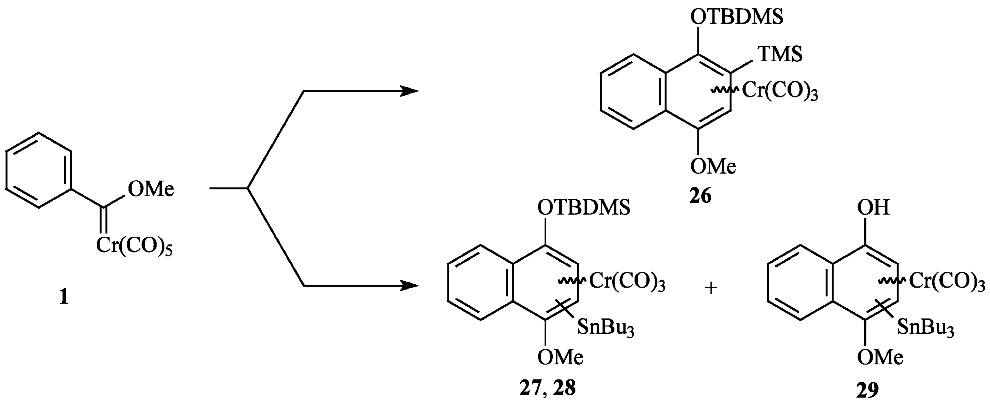
Fig. 3. Molecular structures of **23** and **24**. Vibrational ellipsoids are scaled to enclose 50% of the electron density. **23**: Selected bond lengths (Å): Cr(1)–C(1B), 1.834(2); Cr(1)–C(1C), 1.838(2); Cr(1)–C(1A), 1.841(2); Cr(1)–C(3), 2.2447(18); Cr(1)–C(10), 2.2896(18); Cr(1)–C(4), 2.2293(18); Cr(1)–C(2), 2.2344(17); Cr(1)–C(1), 2.2210(17); Cr(1)–C(5), 2.2640(18); Cr(1)–Z(Ar), 1.737(1). Selected bond angles (°): C(1B)–Cr(1)–C(1C), 89.40(8); C(1B)–Cr(1)–C(1A), 90.78(8); C(1C)–Cr(1)–C(1A), 88.00(8). **24**: Selected bond lengths (Å): Cr(1)–C(1C), 1.8345(15); Cr(1)–C(1A), 1.8468(15); Cr(1)–C(1B), 1.8478(15); Cr(1)–C(1), 2.2062(13); Cr(1)–C(2), 2.2150(14); Cr(1)–C(4), 2.2220(13); Cr(1)–C(3), 2.2356(13); Cr(1)–C(5), 2.2612(14); Cr(1)–C(10), 2.2959(14); Cr(1)–Z(Ar), 1.727(1). Selected bond angles (°): C(1C)–Cr(1)–C(1A), 92.03(6); C(1C)–Cr(1)–C(1B), 89.09(6); C(1A)–Cr(1)–C(1B), 90.09(6).

ligands were prepared by treating a solution of the tricarbonyl chromium complexes with acetonitrile in methylene chloride. After chromatographic workup the free ligands could be obtained in chemical yields of about 90%. Typical examples of ^{1}H-NMR spectra indicating the thermal metal migrations and the concentration–time plots are shown in Fig. 5.

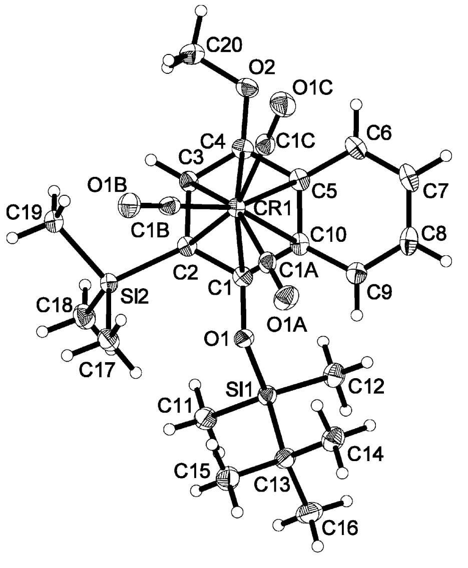
For complexes **15** and **16** the weak intensities of the product signals (less than 10% of rearranged product) did not allow to obtain reliable kinetic data. In all cases the rearrangements obey a first order reaction model with high precision.

The results allow the following conclusions:

1) In cases in which the non-hydroquinoid ring is unsubstituted or only bears methyl substituents the metal migration proceeds irreversibly.
2) Substitution with methoxy groups results in an equilibrium involving two haptotropic isomers. The equilibrium constant of the rearrangement depends on the number and position of the methoxy substituents.
3) The rate constants depend strongly on the size of the substituents. The sterically more demanding menthyloxy substituents accelerate the $Cr(CO)_3$ migration (in comparison to their methoxy analogues). A similar correlation is observed for the



Scheme 8. Reaction of carbene complex **1** with ethynyltrimethylsilane and ethynyltributylstannane.



26

Fig. 4. Molecular structure of **26**. Vibrational ellipsoids are scaled to enclose 50% of the electron density. Selected bond lengths (Å): Cr(1)–C(1B), 1.828(2); Cr(1)–C(1C), 1.833(2); Cr(1)–C(1A), 1.832(3); Cr(1)–C(3), 2.240(2); Cr(1)–C(10), 2.278(2); Cr(1)–C(4), 2.303(2); Cr(1)–C(2), 2.249(2); Cr(1)–C(1), 2.279(2); Cr(1)–C(5), 2.305(2); Cr(1)–Z(Ar), 1.776(1). Selected bond angles (°): C(1B)–Cr(1)–C(1C), 85.95(10); C(1B)–Cr(1)–C(1A), 86.36(10); C(1C)–Cr(1)–C(1A), 90.89(10); O(1B)–C(1B)–Cr(1), 175.8.

bulky *tert*-butyl and trimethylsilyl substituents versus the ethyl substituents. The substitution of the TBDMS protecting group by methyl considerably slows down the metal shift.

4) Substitution with electron-withdrawing groups such as acetoxy accelerates the metal migration whereas tributylstannyl slows down the process.
5) The free activation energies range from 23 to 26 kcal mol^{-1} and, thus, are about 4 kcal mol^{-1} lower than those reported in the literature regarding mono- or disubstituted tricarbonyl chromium complexes of naphthalenes.
6) The rearrangement of **19a** (major diastereomer) and **19b** (minor diastereomer) exhibits the first example of kinetic parameters differing for the intramolecular shift of ML_n in two diastereomeric compounds.

3. Experimental

3.1. General reaction conditions

All reactions were carried out under argon by using Schlenk techniques. The solvents used for the reactions and chromatography were dried by refluxing over lithium aluminium hydride (diethyl ether, *tert*-butyl methyl ether, petroleum ether, methylene chloride) and saturated with argon. Column chromatography was performed with argon saturated silica gel (Machery Nagel type MN 60, 0.01–0.025 mm) at −5 °C under inert gas conditions. Hexafluorobenzene used for the haptotropic rearrangements was used as obtained (NMR grade) from ACROS Organics without further purification. All other organic compounds were used as obtained by commercial suppliers. D.e. values were determined by ^{1}H-NMR spectroscopy.

3.2. Instrumentation

IR: Nicolet Magna 550 FT-IR. NMR: Bruker DRX 500 and AM-400. EIMS: Kratos MS-50

3.3. X-ray crystallographic studies

Crystallisation from n-hexane/methylene chloride at 4 °C provided red crystals of **5**, **16**, **18**, **23**, **24** and **26** which were subjected to single-crystal X-ray analysis. Data were collected on a Nonius κCCD at 123 K. The

Table 1
Kinetic data for the haptotropic rearrangements of naphthohydroquinoid complexes **13**–**27** in hexafluorobenzene

	T (°C)	$k_1 \times 10^{-4}$ (s^{-1})	$k_2 \times 10^{-4}$ (s^{-1})	κ_{eq}	$\Delta G^{\#}_{\mathrm{T}}$ (kcal mol^{-1})
13	70	5.31	–	–	25.31
14	70	7.01	2.09	3.35	25.12
15	70	–	–	0.02	–
16	70	–	–	0.08	–
17	70	12.6	5.41	2.33	24.72
18	70	6.31	–	–	25.19
19a	60	8.98	–	–	24.31
19b	60	15.5	–	–	23.85
20	60	8.46	–	–	24.41
21	60	30.4	1.60	19.0	23.40
23	75	1.38	–	–	24.03
24	60	11.8	–	–	26.62
26	70	1.59	–	–	26.14
27	70	7.35	–	–	26.53

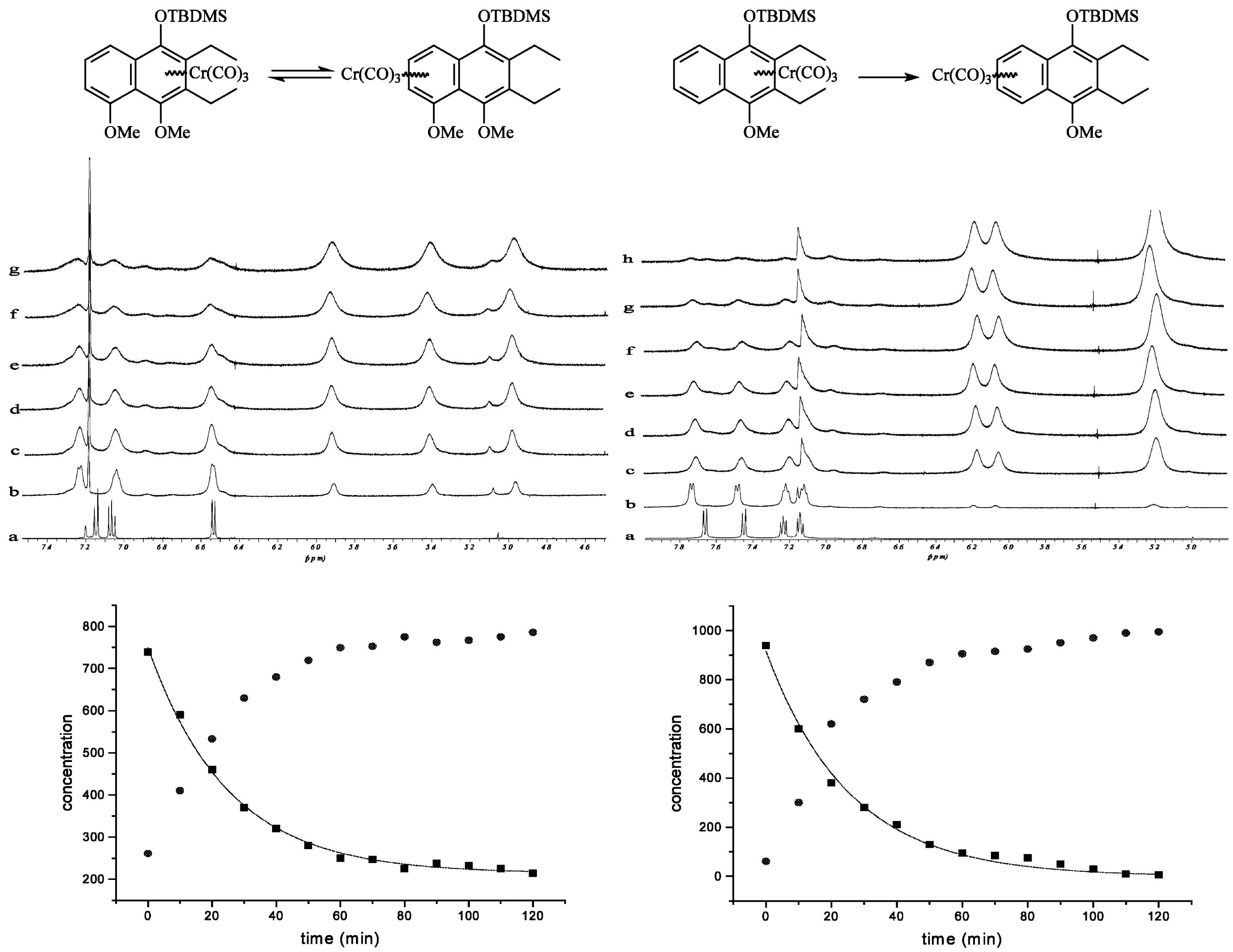


Fig. 5. Examples of sequence of ^{1}H-NMR spectra and the concentration–time-plots of haptotropic rearrangements of **14** (left) and **13** (right) at 70 °C in C_6F_6. During heating the aromatic protons are characteristically shifted upfield due to coordination of the metal fragment to the non quinoid ring. Broadening of the signals is caused by dynamical effects and is not observed for menthyloxy substituted complexes **19**–**21** and **25**. Shifts of H-5 and H-8 signals to lower field at higher temperature is due to stronger rotation of the methoxy or TBDMS-substituents in *ipso* position (*a* = 10 min; *b* = 20 min; *c* = 30 min etc.). The rearrangement of complex **13** has been studied in different concentrations to verify the first order reaction model.

structures were solved by direct methods (**5**, **16**, **18**, **24**, **26**) and Patterson methods (**23**) [22]. The non-hydrogen atoms were refined anisotropically on F^2 [23]. H atoms were refined isotropically using riding model. An empirical absorption correction ($T_{\mathrm{max/min}} = 0.8384/0.7718$) for **5** and an extinction correction for **18** were applied. Further details are given in Tables 5 and 9. Atomic coordinates and equivalent isotropic displacement parameters are given in Tables 2–4, 6–8.

3.4. Reagents

3.4.1. Synthesis of the carbene complexes

*3.4.1.1. Carbene complexes **2**–**4a**.*

3.4.1.1.1. General procedure. At −78 °C 18.75 ml (30 mmol) of *n*-butyl lithium (1.6 M in hexane) in 40 ml of diethyl ether was added slowly to a solution of 30 mmol of anisole (3.24 g), veratrole (4.15 g) or hydroquinone dimethylether (4.15 g) and 0.17 g (1.5 mmol) *N*,*N*,*N′*,*N′*-tetramethylethylenediamine in 100 ml of diethyl ether. After stirring for 60 min at this temperature and a further 90 min at 0 °C 11.0 g (50 mmol) of hexacarbonylchromium was added to the yellow solution. After 120 min at room temperature (r.t.) 7.40 g (50 mmol) of trimethyloxonium tetrafluoroborate were added, and the suspension was stirred for 16 h. The solvent was removed and the dark brown residue was dissolved in petroleum ether and filtered over silica gel. Evaporation and chromatographic purification with petroleum ether–CH_2Cl_2 (5:1) afforded the pentacarbo-

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **5**

	x	y	z	U_{eq} [a]
Cr(1)	2457(1)	7614(1)	1357(1)	13(1)
C(1A)	2481(2)	8469(2)	−440(2)	17(1)
O(1A)	2520(2)	8972(2)	−1541(1)	25(1)
C(1B)	3332(2)	5460(2)	1165(2)	18(1)
O(1B)	3809(2)	4219(2)	968(1)	29(1)
C(1C)	1596(2)	9882(2)	1324(2)	17(1)
O(1C)	1129(2)	11285(2)	1186(1)	25(1)
C(1D)	394(2)	7387(2)	1572(2)	17(1)
O(1D)	−823(2)	7200(2)	1724(1)	28(1)
C(1E)	4521(2)	7856(2)	1152(2)	18(1)
O(1E)	5732(2)	8066(2)	979(1)	30(1)
C(1)	2409(2)	6469(2)	3335(2)	14(1)
C(2)	3516(2)	4799(2)	3995(2)	14(1)
C(3)	5132(2)	4332(2)	3521(2)	15(1)
C(4)	6196(2)	2828(2)	4149(2)	14(1)
C(5)	5640(2)	1708(2)	5275(2)	15(1)
C(6)	4035(2)	2133(2)	5735(2)	17(1)
C(7)	2987(2)	3678(2)	5111(2)	17(1)
O(11)	1329(1)	6908(1)	4241(1)	17(1)
C(11)	93(2)	8520(2)	4005(2)	19(1)
O(41)	7788(1)	2309(1)	3764(1)	18(1)
C(41)	8410(2)	3527(2)	2750(2)	22(1)
O(51)	6784(1)	258(1)	5820(1)	19(1)
C(51)	6271(2)	−961(2)	6929(2)	20(1)

[a] U_{eq} is defiened as one-third of the trace of the orthogonalized U_{ij} tensor.

nyl carbene complexes as red solids (6.52 g, 19.1 mmol, 63% of **2**; 6.58 g, 17.7 mmol, 59% of **3** and 7.25 g, 19.5 mmol, 65% of **4**) and the tetracarbonyl carbene complexes as brown solids (2.02 g, 6.42 mmol, 21% of **2a**; 3.04 g, 8.82 mmol, 29% of **3a** and 1.36 g, 3.95 mmol, 13% of **4a**).

*3.4.1.1.2. Tetracarbonyl[methoxy(2,3-dimethoxybenzylidene)(O,Cr)]chromium (**4a**).* ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 3.01$ (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 4.55 (s, 3H, OCH_3), 6.29 (dd, $^3J_{HH} = 7.1$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, ArH), 6.70 (t, $^3J_{HH} = 8.0$ Hz, 1H, ArH), 7.04 (dd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, ArH) ppm. ^{13}C-NMR (125 MHz, C_6D_6): $\delta = 55.1$ (OCH_3), 55.2 (OCH_3), 71.8 (OCH_3), 109.4, 113.9, 116.8, 124.1 125.0, 152.3 (6 ArC), 215.5 (*cis*-CO), 232.3 (*trans*-CO), 337.2 (Cr=C) ppm. EIMS (70 eV): m/z (%) = 344 (2) [M^+], 316 (8) [$M^+ - CO$], 288 (8) [$M^+ - 2CO$], 260 (17) [$M^+ - 3CO$], 232 (100) [$M^+ - 4CO$], 189 (43) [$M^+ - 4CO - C_3H_8$], 52 (22) [$C_4H_4^+$]. IR (petroleum ether): $\nu_{C=O} = 2021$ (m, A_1^1), 1947 (sh, A_1^2), 1925 (vs, B_1), 1871 (s, B_2) cm^{-1}.

*3.4.1.2. Carbene complexes **5** and **6**.*

3.4.1.2.1. General procedure. At −78 °C 12.5 ml (20 mmol) of *n*-butyllithium (1.6 M in hexane) in 40 ml of diethyl ether was added slowly to a solution of 20 mmol 4-bromoveratrol (4.36 g) or 2-bromo-*p*-xylol (3.72 g) in 100 ml of diethyl ether. After stirring for 30 min at this temperature 4.40 g (30 mmol) of hexacarbonylchromium were added to the yellow suspension. After stirring for 30 min at this temperature and further 120 min at r.t. 4.44 g (30 mmol) of trimethyloxonium tetrafluoroborate were added, and the suspension was stirred for 16 h. The solvent was removed and the dark brown residue was dissolved in petroleum ether and filtered over silica gel. Evaporation and chromatographic purification with petroleum ether–CH_2Cl_2 afforded the products as red solids (4.11 g, 11.0 mmol, 55% of **5** and 6.62 g, 18.4 mmol, 92% of **6**).

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **16**

	x	y	z	U_{eq} [a]
Cr(1)	2580(1)	6139(1)	6439(1)	11(1)
C(1A)	3480(1)	6196(1)	5321(1)	16(1)
O(1A)	4025(1)	6230(1)	4601(1)	27(1)
C(1B)	1310(1)	6027(1)	5594(1)	17(1)
O(1B)	524(1)	5954(1)	5035(1)	28(1)
C(1C)	2329(1)	7147(1)	6359(1)	21(1)
O(1C)	2130(1)	7774(1)	6278(1)	38(1)
C(1)	2650(1)	6212(1)	8154(1)	12(1)
C(2)	1723(1)	5736(1)	7846(1)	14(1)
C(3)	1998(1)	5114(1)	7215(1)	13(1)
C(4)	3171(1)	5005(1)	6906(1)	12(1)
C(5)	4105(1)	5506(1)	7184(1)	12(1)
C(6)	5290(1)	5412(1)	6837(1)	13(1)
C(7)	6155(1)	5899(1)	7120(1)	14(1)
C(8)	5890(1)	6514(1)	7778(1)	14(1)
C(9)	4769(1)	6625(1)	8093(1)	14(1)
C(10)	3838(1)	6124(1)	7809(1)	12(1)
O(11)	2426(1)	6792(1)	8768(1)	14(1)
Si(11)	2427(1)	6920(1)	10009(1)	14(1)
C(11)	881(1)	7146(1)	10369(1)	25(1)
C(12)	3362(2)	7755(1)	10226(1)	27(1)
C(13)	3013(1)	6086(1)	10722(1)	21(1)
C(14)	4327(2)	5932(1)	10516(1)	32(1)
C(15)	2904(2)	6281(1)	11836(1)	32(1)
C(16)	2297(2)	5376(1)	10514(1)	36(1)
C(21)	478(1)	5883(1)	8214(1)	19(1)
C(22)	−101(1)	6594(1)	7815(1)	26(1)
C(31)	1048(1)	4563(1)	6899(1)	18(1)
C(32)	767(2)	4009(1)	7730(1)	29(1)
O(41)	3451(1)	4415(1)	6296(1)	14(1)
C(41)	3803(1)	3761(1)	6846(1)	21(1)
O(71)	7301(1)	5874(1)	6842(1)	18(1)
C(71)	7607(1)	5335(1)	6099(1)	19(1)
O(81)	6842(1)	6946(1)	8010(1)	20(1)
C(81)	6679(1)	7499(1)	8762(1)	24(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

*3.4.1.2.2. Pentacarbonyl[methoxy(3,4-dimethoxybenzylidene)]chromium (**5**).* ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 3.26$ (s, 3H, OCH_3), 3.48 (s, 3H, OCH_3), 4.17 (s, 3H, OCH_3), 6.35 (d, $^3J_{HH} = 8.7$ Hz, 1H, ArH), 7.25 (d, $^4J_{HH} = 2.2$ Hz, 1H, ArH), 7.50 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.2$ Hz, 1H, ArH) ppm. ^{13}C-

Table 4
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **18**

	x	y	z	U_{eq} [a]
Cr(1)	5053(1)	2581(1)	6400(1)	22(1)
C(1A)	4544(6)	1341(4)	6401(3)	31(1)
O(1A)	4251(5)	547(3)	6393(2)	43(1)
C(1B)	6937(6)	2195(4)	6669(3)	29(1)
O(1B)	8127(4)	1961(3)	6862(2)	40(1)
C(1C)	5024(6)	2660(4)	7301(3)	32(1)
O(1C)	5024(5)	2721(3)	7874(2)	48(1)
C(1)	3501(5)	2717(3)	5371(2)	21(1)
C(2)	4921(6)	2896(4)	5286(2)	23(1)
C(3)	5767(6)	3590(4)	5707(3)	24(1)
C(4)	5129(6)	4115(3)	6151(3)	23(1)
C(5)	3672(6)	3974(3)	6228(3)	22(1)
C(6)	2936(6)	4584(4)	6617(3)	27(1)
C(7)	1617(6)	4301(4)	6711(3)	32(1)
C(8)	998(6)	3432(4)	6487(3)	29(1)
C(9)	1589(6)	2857(4)	6083(3)	28(1)
C(10)	2899(5)	3161(4)	5886(3)	23(1)
O(1)	2674(4)	2095(2)	4951(2)	26(1)
Si(1)	1486(2)	2322(1)	4216(1)	27(1)
C(11)	2249(7)	3135(4)	3669(3)	39(2)
C(12)	−184(7)	2890(5)	4383(4)	51(2)
C(13)	1145(6)	1128(4)	3831(3)	35(1)
C(14)	−75(7)	1182(6)	3212(3)	53(2)
C(15)	2503(7)	737(4)	3638(3)	42(2)
C(16)	685(9)	459(5)	4338(4)	58(2)
C(17)	5512(6)	2352(4)	4750(3)	28(1)
C(18)	6190(7)	1420(5)	4972(3)	44(2)
C(19)	7284(6)	3818(4)	5635(3)	28(1)
C(20)	7264(7)	4587(4)	5103(3)	34(1)
O(2)	5921(4)	4862(2)	6468(2)	28(1)
C(21)	6744(7)	4689(4)	7147(3)	37(1)
C(22)	3492(7)	5527(4)	6883(3)	34(1)
C(23)	954(6)	1891(4)	5934(3)	35(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

NMR (62.5 MHz, C_6D_6): $\delta = 57.5$ (OCH_3), 61.9 (OCH_3), 67.1 (OCH_3), 110.6, 118.8, 123.1, 123.9, 146.2, 149.2 (6ArC), 217.9 (*cis*-CO), 235.7 (*trans*-CO), 340.0 (Cr=C) ppm. EIMS (70 eV): *m/z* (%) = 372 (2) [M^+], 344 (5) [M^+ −CO], 316 (19) [M^+ −2CO], 288 (10) [M^+ −3CO], 260 (36) [M^+ −4CO], 202 (100) [M^+ −5CO], 189 (60) [M^+ −5CO−CH], 52 (77) [$C_4H_4^+$]. IR (petroleum ether): $\nu_{C=O} = 2058$ (m, A_1^1), 1980 (w, B), 1953 (vs, E), 1942 (vs, A_1^2) cm^{-1}.

*3.4.1.2.3. Pentacarbonyl[methoxy(2,5-dimethylbenzylidene)]chromium (**6**).* ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 1.91$ (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 3.2–3.6 (s, br, 3H, OCH_3), 6.54 (s, br, 1H, ArH), 6.80 (s, 2H, ArH) ppm. ^{13}C-NMR (62.5 MHz, C_6D_6): $\delta = 18.1$ (CH_3), 20.9 (CH_3), 65.0 (OCH_3), 120.7, 123.0, 127.4, 129.2, 130.9, 135.8 (6ArC), 216.6 (*cis*-CO), 224.9 (*trans*-CO), 359.7 (Cr=C) ppm. EIMS (70 eV): *m/z* (%) = 340 (8) [M^+], 312 (14) [M^+ −CO], 284 (12) [M^+ −2CO], 256 (10) [M^+ −3CO], 228 (21) [M^+ −4CO], 200 (100) [M^+ −5CO], 170 (60) [M^+ −5CO−2CH$_3$], 157 (43) [M^+ −5CO−2CH$_3$−CH], 52 (77) [$C_4H_4^+$]. IR (petroleum ether): $\nu_{C=O} = 2065$ (m, A_1^1), 1988 (w, B), 1967 (vs, E), 1949 (vs, A_1^2) cm^{-1}.

*3.4.1.3. Carbene complexes **7**–**9a**.*

3.4.1.3.1. General procedure. At −50 °C 0.9 ml (10 mmol) of acetyl bromide was added to a solution of 10 mmol tetramethylamonium pentacarbonyl(benzoyl)chromate **10** (3.87 g), **11** (4.01 g), **12** (4.31 g) in 20 ml of methylene chloride. After stirring for 30 min at this temperature a solution of 12 mmol of (−)-menthol in 50 ml methylene chloride was added dropwise to the dark red solution at −40 °C. The reaction mixture was stirred for 18 h and allowed to reach r.t. The solvent was removed and the brown residue was dissolved in petroleum ether and filtered over silica gel. Evaporation and chromatographic purification with petroleum ether–CH_2Cl_2 afforded the pentacarbonyl carbene complexes as red oils (3.10 g, 7.1 mmol, 71% of **7**; 2.10 g, 4.4 mmol, 44% of **8** and 2.70 g, 5.4 mmol, 54% of **9**) and the tetracarbonyl carbene complexes as brown oils (0.30 g, 0.7 mmol, 7% of **8a**; 0.20 g, 0.5 mmol, 5% of **9a**).

*3.4.1.3.2. Pentacarbonyl[(1R,2S,5R)-(−)-menthyloxy-2-methoxybenzylidene)]chromium (**8**).* ^{1}H-NMR (500 MHz, $CDCl_3$): $E/Z = 1{:}\ 1.3$; $\delta = 0.51$, 0.63 (s und d, $^3J_{HH} = 7.0$ Hz, 6H, 2CH$_3$), 0.85, 0.90 (d, $^3J_{HH} = 7.0$ Hz, 6H, 2CH$_3$), 0.97, 0.98 (d, $^3J_{HH} = 7.0$ Hz, 6H, 2CH$_3$), 1.20–2.20 (m, 18H, 6CH$_2$, 6CH), 3.77, 3.81 (s, 6H, 2OCH$_3$), 4.27, 5.42 (m, 2H, 2HCO), 6.70 (d, $^3J_{HH} = 6.3$ Hz, 2H, ArCH), 6.89 (d, $^3J_{HH} = 8.6$ Hz, 2H, ArCH), 7.00 (m, 2H, ArH), 7.21 (m, 2H, ArH) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$) *E*- and *Z*-isomers: $\delta = 16.1$, 16.3 (2CH$_3$), 21.1, 21.2 (2CH$_3$), 21.9, 22.0 (2CH$_3$), 22.6, 22.8 (2CH$_2$), 25.6, 25.8 (2CH), 31.2, 31.3 (2CH), 33.7 (2CH$_2$), 40.8, 41.3 (2CH$_2$), 47.7, 47.9 (2CH), 64.7, 65.8 (2OCH$_3$), 91.9, 92.2 (2HCO), 110.7 (2ArC), 120.1, 120.2 (2ArC), 121.4, 122.0 (2ArC), 129.2, 129.3 (2ArC), 132.7, 133.7 (2ArC), 140.8, 148.9 (2*ipso*-ArC), 216.2, 216.4 (2CO), 225.1 (2CO), 349.5, 351.1 (Cr=C) ppm. EIMS (70 eV): *m/z* (%) = 466 (3) [M^+], 438 (6) [M^+ −CO], 410 (8) [M^+ −2CO], 382 (9) [M^+ −3CO], 354 (29) [M^+ −4CO], 326 (100) [M^+ −5CO], 311 (11) [M^+ −5CO−CH$_3$], 188 (61) [M^+ −5CO−$C_{10}H_{18}$], 52 (34) [$C_4H_4^+$]. IR (petroleum ether): $\nu_{C=O} = 2062$ (m, A_1^1), 1985 (w, B), 1959 (s, E), 1945 (vs, A_1^2), 1926 (m) cm^{-1}.

*3.4.1.3.3. Tetracarbonyl[(1R,2S,5R)-(−)-menthyloxy(2-methoxybenzylidene)(O,Cr)]chromium (**8a**).* ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 0.79$, 0.90, 0.99 (d, $^3J_{HH} = 7.0$ Hz, 9H, 3CH$_3$), 1.20–2.10 (m, 8H, 3CH$_2$, 2CH), 2.53 (m, 1H, CH), 4.26 (s, 3H, OCH$_3$), 5.42 (m, H, HCO), 7.01 (d, $^3J_{HH} = 8{,}4$ Hz, 2H, ArH), 7.06 (td, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, ArH), 7.44 (td, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.8$ Hz, 1H, ArH,), 7.54 (dd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.8$ Hz, 1H, ArH) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$) $\delta = 16.6$ (CH_3), 20.9 (CH_3), 22.2 (CH_3), 23.6 (CH), 26.7 (CH_2), 31.2 (CH_2), 34.2

Table 5
Crystallographic data, data collection and refinement of **5**, **16** and **18**

	5	**16**	**18**
Formula	$C_{15}H_{12}CrO_8$	$C_{26}H_{36}CrO_7Si$	$C_{26}H_{36}CrO_5Si$
M_r	372.25	540.64	508.64
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
Unit cell dimensions			
a (Å)	9.0579(2)	11.2905(1)	9.4349(1)
b (Å)	9.0916(2)	17.9720(1)	14.2908(3)
c (Å)	11.3567(3)	13.4315(1)	20.2833(4)
α (°)	67.215(2)	90	90
β (°)	76.546(2)	90.972(1)	102.352(1)
γ (°)	68.430(2)	90	90
V (A^3)	797.41(3)	2725.03(3)	2671.51(8)
Z	2	4	4
Crystal size (mm^3)	0.45 × 0.30 × 0.25	0.60 × 0.60 × 0.60	0.40 × 0.20 × 0.08
ρ_{calc} (g cm^{-3})	1.550	1.318	1.265
μ (mm^{-1})	0.757	0.505	0.505
$F(000)$	380	1144	1080
Diffractometer	Nonius κCCD	Nonius κCCD	Nonius κCCD
Radiation	Mo–K_α	Mo–K_α	Mo–K_α
λ (Å)	0.71073	0.71073	0.71073
T (K)	123(2)	123(2)	123(2)
Max. 2Θ (°)	50	50	50
Index range	$-10 \le h \le 10$, $-10 \le k \le 10$, $-13 \le l \le 13$	$-13 \le h \le 13$, $-21 \le k \le 21$, $-15 \le l \le 15$	$-11 \le h \le 11$, $-16 \le k \le 16$, $-23 \le l \le 24$
No. of data	6916	50738	37990
No. of unique data	2794	4791	4681
Parameters	217	316	301
$R(F)$ for $I > 2\sigma > (I)$	0.0247	0.0259	0.0648
$wR_2(F^2)$ for all data	0.0678	0.0718	0.1961
Goodness-of-fit on F^2	1.069	1.051	1.120

(CH_2), 41.2 (CH), 46.1 (CH), 63.9 (OCH_3), 91.9 (HCO), 110.7, 116.6, 122.0, 129.3, 133.6, 165.2 (6ArC), 21.5, 214.8, 231.0, 231.5 (4CO), 329.1 (Cr=C) ppm. EIMS (70 eV): m/z (%) = 438 (10) [M^+], 410 (5) [$M^+ -CO$], 382 (2) [$M^+ -2CO$], 354 (18) [$M^+ -3CO$], 326 (68) [$M^+ -4CO$], 188 (90) [$M^+ -4CO–C_{10}H_{18}$], 52 (100) [$C_4H_4^+$]. IR (petroleum ether): $\nu_{C=O} = 2018$ (m, A_1^1), 1935 (sh, A_2^1), 1927 (vs, B_1), 1862 (s, B_2) cm^{-1}.

*3.4.1.3.4. Pentacarbonyl[(1R,2S,5R)-(−)-menthyloxy(2,5-dimethoxybenzylidene)]chromium(0) (**9**).* ^{1}H-NMR (250 MHz, C_6D_6): $E/Z = 10$: 1; $\delta = 0.55$ (d, $^3J_{HH} = 6.7$ Hz, 3H, CH_3), 0.64 (s, br, 3H, CH_3), 0.77 (s, 3H, CH_3), 0.89–1.02 (m, 2H, CH_2), 1.30 (d, $^3J_{HH} = 11.5$ Hz, 2H, CH_2), 1.38 (d, $^3J_{HH} = 10.7$ Hz, 2H, CH_2), 1.72 (m, 1H, CH), 2.06 (m, 1H, CH), 3.34, 3.41 (s, 6H, $2OCH_3$), 4.36 (m, 1H, HCO), 6.42 (d, $^3J_{HH} = 8.9$ Hz, 1H, ArH), 6.56–6.63 (m, 1H, ArH) ppm. ^{13}C-NMR (62,5 MHz, C_6D_6): $\delta = 16.3$ ($2CH_3$), 21.2 ($2CH_3$), 22.0 ($2CH_3$), 22.8 ($2CH_2$), 25.8 (2CH), 31.2 (2CH), 33.7 ($2CH_2$), 41.3 ($2CH_2$), 47.9 (2CH), 55.2 ($4OCH_3$), 92.2 (2HCO), 110.7 (2ArC), 120.1, 120.2 (2ArC), 121.4, 122.0 (2ArC), 129.2, 129.3 (2ArC), 132.7, 133.7 (2ArC), 153.7 (2ArC), 217.1 (*cis*-CO), 225.1 (*trans*-CO), (Cr=C not observed) ppm. EIMS (70 eV): m/z (%) = 496 (5) [M^+], 468 (11) [$M^+ -CO$], 440 (9) [$M^+ -2CO$], 412 (6) [$M^+ -3CO$], 384 (38) [$M^+ -4CO$], 356 (100) [$M^+ -5CO$], 260 (27) [$M^+ -5CO–C_7H_{12}$], 218 (34) [$M^+ -5CO–C_{10}H_{20}$], 203 (77) [$M^+ -5CO–C_{11}H_{23}$], 190 (91) [$M^+ -5CO–C_{12}H_{24}$]. IR (petroleum ether): $\nu_{C=O} = 2062$ (m, A_1^1), 1957 (s, E), 1946 (vs, A_1^2), 1925 (m) cm^{-1}.

*3.4.1.3.5. Tetracarbonyl[(1R,2S,5R)-(−)-menthyloxy(2,5-dimethoxybenzylidene)(O,Cr)]-chromium (**9a**).* ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 0.96$, 1.01, 1.05 (d, $^3J_{HH} = 7.0$ Hz, 9H, $3CH_3$), 1.20–2.10 (m, 7H, $3CH_2$, CH), 2.91 (d, $^3J_{HH} = 12.2$ Hz, 1H, CH), 3.31 (s, 3H, OCH_3), 3.34 (s, 3H, OCH_3), 5.78 (td, $^3J_{HH} = 10.6$ Hz, $^4J_{HH} = 4.4$ Hz, 1H, HCO), 6.04 (d, $^3J_{HH} = 9.0$ Hz, H, ArH), 6.64 (dd, $^3J_{HH} = 9.0$ Hz, $^4J_{HH} = 3.0$ Hz, 1H, ArH), 7.24 (d, $^4J_{HH} = 2{,}93$ Hz, 1H, ArH,) ppm. ^{13}C-NMR (62.5 MHz, C_6D_6): $\delta = 1.2$ (CH_3), 20.9 (CH_3), 22.3 (CH_3), 24.2 (CH), 27.3 (CH_2), 31.4 (CH_2), 34.4 (CH_2), 41.7 (CH), 48.4 (CH), 55.3 (OCH_3), 64.8 (OCH_3), 92.3 (HCO), 102.0, 111.6, 119.4, 133.8, 155.1, 160.3 (6ArC), 215.6, 231.7, 231.8 (4CO), 329.2 (Cr=C) ppm. EIMS (70 eV): m/z (%) = 468 (10) [M^+], 440 (8) [$M^+ -CO$], 412 (3) [$M^+ -2CO$], 384 (26) [$M^+ -3CO$], 356 (100) [$M^+ -4CO$], 260 (54) [$M^+ -4CO–C_7H_{12}$], 218 (68) [$M^+ -4CO–C_{10}H_{20}$], 203 (61) [$M^+ -4CO–$

Table 6
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **23**

	x	y	z	U_{eq} [a]
Cr(1)	6593(1)	2155(1)	2546(1)	13(1)
C(1A)	8860(3)	478(2)	2636(1)	18(1)
O(1A)	10278(2)	−593(2)	2690(1)	31(1)
C(1B)	7731(3)	3437(2)	1870(1)	17(1)
O(1B)	8430(2)	4259(2)	1438(1)	26(1)
C(1C)	6693(2)	3096(2)	3694(1)	18(1)
O(1C)	6774(2)	3657(2)	4422(1)	28(1)
C(1)	4188(2)	3354(2)	1781(1)	14(1)
C(2)	3501(2)	3390(2)	2780(1)	14(1)
C(3)	4022(2)	1827(2)	3280(1)	14(1)
C(4)	5224(2)	323(2)	2755(1)	15(1)
C(5)	5930(2)	282(2)	1731(1)	16(1)
C(6)	7261(3)	−1217(3)	1200(2)	22(1)
C(7)	7895(3)	−1177(3)	237(2)	27(1)
C(8)	7264(3)	329(3)	−265(2)	28(1)
C(9)	6050(3)	1794(3)	209(1)	22(1)
C(10)	5360(2)	1818(2)	1230(1)	16(1)
O(11)	3787(2)	4837(2)	1289(1)	19(1)
C(11)	2080(3)	5331(3)	907(2)	29(1)
C(21)	2209(3)	5056(2)	3300(1)	17(1)
C(22)	181(3)	5227(3)	3509(2)	24(1)
C(31)	3377(3)	1790(2)	4363(1)	19(1)
C(32)	1883(3)	1065(3)	4618(2)	28(1)
O(41)	5805(2)	−1157(2)	3246(1)	20(1)
C(41)	4968(3)	−2310(2)	3048(2)	27(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 7
Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **24**

	x	y	z	U_{eq} [a]
Cr(1)	1344(1)	2400(1)	6644(1)	14(1)
C(1A)	1146(1)	3040(1)	7967(1)	18(1)
O(1A)	990(1)	3417(1)	8809(1)	25(1)
C(1B)	658(2)	3223(1)	5688(1)	21(1)
O(1B)	244(1)	3744(1)	5095(1)	33(1)
C(1C)	3019(2)	2796(1)	6436(1)	19(1)
O(1C)	4096(1)	3006(1)	6284(1)	27(1)
C(1)	1309(1)	1308(1)	7773(1)	17(1)
C(2)	2302(1)	1205(1)	6959(1)	17(1)
C(3)	1928(1)	1270(1)	5707(1)	17(1)
C(4)	603(1)	1459(1)	5368(1)	17(1)
C(5)	−407(1)	1575(1)	6213(1)	18(1)
C(6)	−1724(2)	1831(1)	5870(1)	24(1)
C(7)	−2647(2)	1933(1)	6699(2)	30(1)
C(8)	−2315(2)	1797(1)	7914(2)	32(1)
C(9)	−1059(2)	1584(1)	8285(1)	25(1)
C(10)	−58(1)	1471(1)	7444(1)	18(1)
O(1)	1675(1)	1301(1)	8989(1)	22(1)
C(11)	1507(1)	575(1)	9566(1)	21(1)
O(2)	1077(1)	−13(1)	9068(1)	29(1)
C(12)	1948(2)	658(1)	10844(1)	28(1)
C(13)	3725(2)	1059(1)	7407(1)	23(1)
C(14)	4031(2)	187(1)	7751(2)	30(1)
C(15)	2930(2)	1167(1)	4758(1)	23(1)
C(16)	3148(2)	286(1)	4408(2)	33(1)
O(3)	239(1)	1552(1)	4183(1)	22(1)
C(17)	−401(2)	839(1)	3677(1)	26(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$C_{11}H_{23}$], 190 (50) [$M^+ - 4CO - C_{12}H_{24}$]. IR (petroleum ether) $\nu_{C=O} = 2019$ (m, A_1^1), 1936 (sh, A_1^2), 1927 (vs, B_1), 1861 (s, B_2) cm^{-1}.

3.4.2. [3+2+1]-Benzannulation

3.4.2.1. Benzannulation of carbene complexes 1–6 with 3-hexyne and protection as tert-butyl dimethyl silyl ether.

3.4.2.1.1. General procedure. A solution of 2 mmol carbene complex **1**–**6** and 1 ml (8 mmol) alkyne in 5 ml *tert*-BuOMe were degassed in three cycles and warmed at 55 °C for 60 min. After cooling to r.t. 1.6 g (8 mmol) TBDMSCl and 1.1 ml (8 mmol) Et_3N were added and the solution was stirred at r.t. for 3 h. The solvent was removed under reduced pressure and chromatographic purification with petroleum ether–CH_2Cl_2 afforded the products as red solids (0.90 g, 1.9 mmol, 94% of **13**; 0.64 g, 1.3 mmol, 63% of **14**, 0.72 g, 1.3 mmol, 67% of **15**, 0.79 g, 1.5 mmol, 73% of **16**; 0.76 g, 1.4 mmol, 70% of **17** and 0.94 g, 1.8 mmol, 92% of **18**).

*3.4.2.1.2. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2,3-diethyl-4-methoxynaphthalene]-chromium (**13**).* ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 0.20$ (s, 3H, CH_3), 0.24 (s, 3H, CH_3), 0.92 (s, 9H, $3CH_3$), 1.10 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3), 1.13 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3), 2.40–2.65 (m, $^3J_{HH} = 7.1$ Hz, 4H, $2CH_2$), 3.83 (s, 3H, OCH_3), 7.14 (t, $^3J_{HH} = 9.0$ Hz, 1H, ArH), 7.24 (t, $^3J_{HH} = 6.6$ Hz, 1H, ArH), 7.45 (d, $^3J_{HH} = 6.6$ Hz, 1H, ArH), 7.66 (d, $^3J_{HH} = 9.0$ Hz, 1H, ArH) ppm. ^{13}C-NMR (125 MHz, C_6D_6): $\delta = -4.9$ (CH_3), -3.9 (CH_3), 13.61(CH_3), 15.1 (CH_3), 18.1 (CH_2), 20.0 (CH_2), 24.5 ($C(CH_3)_3$), 64.4 (OCH_3), 97.9, 101.8, 103.5, 108.6 (4ArCH), 123.1, 125.4, 125.6, 127.2 (4ArCH), 137.1, 139.1 (2ArC), 232.7 ($Cr(CO)_3$) ppm. EIMS (70 eV): m/z (%) = 480 (6) [M^+], 452 (4) [$M^+ - CO$], 424 (5) [$M^+ - 2CO$], 396 (14) [$M^+ - 3CO$], 366 (12) [$M^+ - 3CO - 2CH_3$], 344 (81) [$M^+ - Cr(CO)_3$], 329 (26) [$M^+ - Cr(CO)_3 - CH_3$], 73 (100) [$C_3H_9Si^+$]. IR (petroleum ether): $\nu_{C=O} = 1959$ (s, A_1), 1894, 1882 (s, E) cm^{-1}.

*3.4.2.1.3. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2,3-diethyl-4,5-dimethoxy-naphthalene]chromium (**14**).* ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 0.25$ (s, 3H, CH_3), 0.27 (s, 3H, CH_3), 0.92 (s, 9H, $3CH_3$), 1.13 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3), 1.16 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3), 2.23–2.58 (m, $^3J_{HH} = 7.1$ Hz, 4H, $2CH_2$), 3.83 (s, 3H, OCH_3), 6.53 (d, $^3J_{HH} = 7.5$ Hz, 1H, ArH), 7.07 (t, $^3J_{HH} = 9.2$ Hz, 1H, ArH), 7.11 (d, $^3J_{HH} = 9.0$ Hz, 1H, ArH) ppm. ^{13}C-NMR (62.5 MHz, $CDCl_3$): $\delta = -2.8$ (CH_3), -1.9 (CH_3), 15.6 (CH_3), 16.6 (CH_3), 20.4 (CH_2), 21.0 (CH_2), 26.0 ($C(CH_3)_3$), 56.4 (OCH_3), 66.5 (OCH_3), 104.9, 116.5, 126.9, 156.8

Table 8
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **26**

	x	y	z	U_{eq} [a]
Cr(1)	5075(1)	4259(1)	2256(1)	18(1)
C(1A)	3067(3)	3423(2)	2593(1)	20(1)
O(1A)	1799(2)	2878(1)	2795(1)	31(1)
C(1B)	3441(3)	4107(2)	1137(2)	21(1)
O(1B)	2304(2)	4010(1)	450(1)	31(1)
C(1C)	4037(3)	5534(2)	2551(2)	22(1)
O(1C)	3379(3)	6346(1)	2729(1)	34(1)
C(1)	7088(3)	2963(2)	2565(1)	19(1)
C(2)	7334(3)	3319(2)	1742(1)	18(1)
C(3)	7903(3)	4487(2)	1764(2)	19(1)
C(4)	8173(3)	5259(2)	2558(2)	20(1)
C(5)	7816(3)	4902(2)	3390(2)	20(1)
C(6)	8003(3)	5676(2)	4216(2)	23(1)
C(7)	7628(3)	5319(2)	4990(2)	27(1)
C(8)	6989(3)	4186(2)	4988(2)	27(1)
C(9)	6777(3)	3423(2)	4217(2)	22(1)
C(10)	7248(3)	3751(2)	3396(1)	19(1)
O(1)	6566(2)	1857(1)	2589(1)	20(1)
Si(1)	7672(1)	867(1)	3062(1)	19(1)
C(11)	9112(4)	190(2)	2285(2)	27(1)
C(12)	9381(3)	1416(2)	4175(2)	26(1)
C(13)	5587(3)	−162(2)	3207(2)	23(1)
C(14)	4289(4)	391(2)	3795(2)	29(1)
C(15)	4307(4)	−691(2)	2269(2)	31(1)
C(16)	6441(4)	−1097(2)	3676(2)	33(1)
Si(2)	6838(1)	2391(1)	575(1)	20(1)
C(17)	4518(3)	1423(2)	419(2)	26(1)
C(18)	8936(4)	1636(2)	403(2)	30(1)
C(19)	6628(4)	3331(2)	−306(2)	28(1)
O(2)	8746(2)	6370(1)	2625(1)	25(1)
C(20)	8945(4)	6789(2)	1800(2)	32(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(10ArC), 234.1 (Cr(CO)$_3$) ppm. EIMS (70 eV): m/z (%) = 510 (5) [M$^+$], 454 (5) [M$^+$ −2CO], 426 (20) [M$^+$ −3CO], 396 (12) [M$^+$ −3CO–2CH$_3$], 374 (80) [M$^+$ −Cr(CO)$_3$], 359 (43) [M$^+$ −Cr(CO)$_3$–CH$_3$], 73 (100) [C$_3$H$_9$Si$^+$]. IR (petroleum ether): $\nu_{C=O}$ = 1959 (s, A$_1$), 1893, 1882 (s, E) cm^{-1}.

*3.4.2.1.4. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2,3-diethyl-4,5,8-trimethoxy-naphthalene]chromium(0) (**15**).* ^{1}H-NMR (500 MHz, C$_6$D$_6$): δ = −0.05 (s, 3H, CH$_3$), −0.01 (s, 3H, CH$_3$), 0.91 (s, 9H, 3CH$_3$), 1.09 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH$_3$), 1.12 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_3$), 2.16–2.67 (m, $^3J_{HH}$ = 7.1 Hz, 4H, 2CH$_2$), 3.58 (s, 3H, OCH$_3$), 3.75 (s, 3H, OCH$_3$), 3.79 (s, 3H, OCH$_3$), 6.20 (d, $^3J_{HH}$ = 8.5 Hz, 1H, ArH), 6.47 (d, $^3J_{HH}$ = 8.5 Hz, 1H, ArH) ppm. ^{13}C-NMR (125 MHz, C$_6$D$_6$): δ = −5.3 (CH$_3$), −5.0 (CH$_3$), 13.0 (CH$_3$), 16.7 (CH$_3$), 19.3 (CH$_2$), 21.5 (CH$_2$), 24.6 (C(CH$_3$)$_3$), 54.1 (OCH$_3$), 55.2 (OCH$_3$), 66.3 (OCH$_3$), 100.5, 104.1, 106.2, 111.7 (4ArC), 129.8, 137.0, 139.3, 147.5, 152.4 (6ArC), 233.4 (Cr(CO)$_3$) ppm. EIMS (70 eV): m/z (%) = 540 (10) [M$^+$], 484 (12) [M$^+$ −2CO], 456 (5) [M$^+$ −3CO], 426 (18) [M$^+$ −3CO–2CH$_3$], 404 (100) [M$^+$ −3CO–Cr], 389 (43) [M$^+$ −3CO–Cr–CH$_3$], 73 (70) [C$_3$H$_9$Si$^+$]. IR (petroleum ether): $\nu_{C=O}$ = 1959 (s, A$_1$), 1894, 1880 (s, E) cm^{-1}.

*3.4.2.1.5. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2,3-diethyl-4,6,7-trimethoxy-naphthalene]chromium (**16**).* ^{1}H-NMR (500 MHz, C$_6$D$_6$): δ = 0.38 (s, 3H, CH$_3$), 0.41 (s, 3H, CH$_3$), 1.07 (s, 9H, 3CH$_3$), 1.25 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_3$), 1.29 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_3$), 2.49–2.66 (m, $^3J_{HH}$ = 7.1 Hz, 4H, 2CH$_2$), 3.38 (s, 3H, OCH$_3$), 3.49 (s, 3H, OCH$_3$), 3.74 (s, 3H, OCH$_3$), 6.87 (s, 1H, ArH), 7.03 (s, 1H, ArH) ppm. ^{13}C-NMR (62,5 MHz, C$_6$D$_6$): δ = −2.6 (CH$_3$), −1.5 (CH$_3$), 15.9 (CH$_3$), 16.8 (CH$_3$), 19.1 (*C*(CH$_3$)$_3$), 20.8 (CH$_2$), 21.6 (CH$_2$), 26.1 (C(*C*H$_3$)$_3$), 55.5 (OCH$_3$), 55.6 (OCH$_3$), 65.0 (OCH$_3$), 100.0, 102.4 (2ArC), 97.0, 101.2, 102.8, 108.0, 129.7, 131.3, 152.1, 153.5 (8ArC), 235.6 (Cr(CO)$_3$) ppm. EIMS (70 eV): m/z (%) = 540 (3) [M$^+$], 484 (5) [M$^+$ −2CO], 456 (18) [M$^+$ −3CO], 426 (13) [M$^+$ −3CO–2CH$_3$], 404 (75) [M$^+$ −Cr(CO)$_3$], 389 (23) [M$^+$ −Cr(CO)$_3$–CH$_3$], 73 (100) [C$_3$H$_9$Si$^+$]. IR (petroleum ether): $\nu_{C=O}$ = 1950 (s, A$_1$), 1876 1862 (s, E) cm^{-1}.

*3.4.2.1.6. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2,3-diethyl-4,5,6-trimethoxy-naphthalene]chromium (**17**).* ^{1}H-NMR (250 MHz, C$_6$D$_6$): δ = 0.28 (s, 3H, CH$_3$), 0.31 (s, 3H, CH$_3$), 1.11 (s, 9H, 3CH$_3$), 1.24 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_3$), 1.33 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_3$), 2.47–2.91 (m, $^3J_{HH}$ = 7.5 Hz, 4H, 2CH$_2$), 3.37 (s, 3H, OCH$_3$), 3.87 (s, 3H, OCH$_3$), 3.92 (s, 3H, OCH$_3$), 6.76 (d, $^3J_{HH}$ = 9.7 Hz, 1H, ArH), 7.77 (d, $^3J_{HH}$ = 9.7 Hz, 1H, ArH) ppm. ^{13}C-NMR (62.5 MHz, C$_6$D$_6$): δ = −2.7 (CH$_3$), −2.2 (CH$_3$), 15.6 (CH$_3$), 17.1 (CH$_3$), 19.0 (*C*(CH$_3$)$_3$), 20.7 (CH$_2$), 21.7 (CH$_2$), 26.1 (C(*C*H$_3$)$_3$), 56.6 (OCH$_3$), 61.5 (OCH$_3$), 67.1 (OCH$_3$), 102.8, 111.3, 117.2, 123.7 (4ArC), 130.8, 132.2, 135.3, 144.4, 147.2, 151.7 (6ArC), 234.7 (Cr(CO)$_3$) ppm. EIMS (70 eV): m/z (%) = 540 (7) [M$^+$], 484 (5) [M$^+$ −2CO], 456 (23) [M$^+$ −3CO], 441 (11) [M$^+$ −3CO–CH$_3$], 424 (9) [M$^+$ −3CO–2CH$_3$], 404 (36) [M$^+$ −Cr(CO)$_3$], 389 (26) [M$^+$ −Cr(CO)$_3$–CH$_3$], 149 (100) [C$_9$H$_9$O$_2^+$], 73 (21) [C$_3$H$_9$Si$^+$]. IR (petroleum ether): $\nu_{C=O}$ = 1957 (s, A$_1$), 1891, 1880 (s, E) cm^{-1}.

*3.4.2.1.7. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2,3-diethyl-5,8-dimethyl-4-methoxy-naphthalene]chromium (**18**).* ^{1}H-NMR (250 MHz, C$_6$D$_6$): δ = −0.31 (s, 3H, CH$_3$), −0.11 (s, 3H, CH$_3$), 0.97 (s, 9H, 3CH$_3$), 1.18 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_3$), 1.44 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_3$), 2.43 (q, $^3J_{HH}$ = 7.1 Hz, 4H, 2CH$_2$), 2.60 (s, 3H, CH$_3$), 2.73 (s, 3H, CH$_3$), 3.60 (s, 3H, OCH$_3$), 6.46 (d, $^3J_{HH}$ = 6.1 Hz, 1H, ArH), 6.90 (d, $^3J_{HH}$ = 6.1 Hz, 1H, ArH) ppm. ^{13}C-NMR (62.5 MHz, C$_6$D$_6$): δ = −4.2 (CH$_3$), −3.0 (CH$_3$), 14.8 (CH$_3$), 18.8 (CH$_3$), 19.8 (CH$_2$), 21.7 (CH$_3$), 22.8 (CH$_2$), 24.2 (*C*(CH$_3$)$_3$), 25.8 (C(*C*H$_3$)$_3$), 46.7 (CH$_3$) 68.2 (OCH$_3$), 103.5, 113.0 (4ArC), 126.5, 128.9, 130.4, 133.5, 138.4, 141.0 (6ArC), 234.8 (Cr(CO)$_3$) ppm. EIMS (70 eV): m/z

Table 9
Crystallographic data, data collection and refinement of **23**, **24** and **26**

	23	**24**	**26**
Formula	$C_{19}H_{20}CrO_5$	$C_{20}H_{20}CrO_6$	$C_{23}H_{32}CrO_5Si_2$
M_r	380.35	408.36	496.67
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
Unit cell dimensions			
a (A)	7.9444(1)	10.0671(1)	7.0046(2)
b (A)	8.6182(2)	16.4862(2)	12.2544(3)
c (A)	13.9213(3)	11.2950(2)	15.0444(4)
α (°)	88.505(1)	90	97.673(2)
β (°)	80.434(1)	92.697(1)	100.567(2)
γ (°)	67.110(1)	90	96.553(2)
V (A^3)	865.10(3)	1872.53(4)	1245.30(6)
Z	2	4	2
Crystal size (mm^3)	0.25 × 0.08 × 0.06	0.40 × 0.30 × 0.20	0.30 × 0.20 × 0.15
ρ_{calc} (g cm^{-3})	1.460	1.449	1.325
μ (mm^{-1})	0.687	0.645	0.586
$F(000)$	396	848	524
Diffractometer	Nonius κCCD	Nonius κCCD	Nonius κCCD
Radiation	Mo–K_α	Mo–K_α	Mo–K_α
λ (Å)	0.71073	0.71073	0.71073
T (K)	123(2)	123(2)	123(2)
Max. 2Θ (°)	50	50	50
Index range	$-9 \le h \le 9$, $-10 \le k \le 10$, $-16 \le l \le 16$	$-11 \le h \le 11$, $-19 \le k \le 19$, $-13 \le l \le 13$	$-8 \le h \le 8$, $-14 \le k \le 14$, $-17 \le l \le 17$
No. of data	18190	38835	25823
No. of unique data	3050	3276	4385
Parameters	226	245	280
$R(F)$ for $I > 2\sigma > (I)$	0.0280	0.0237	0.0328
$wR_2(F^2)$ for all data	0.0777	0.0675	0.0825
Goodness-of-fit on F^2	1.060	1.060	0.972

(%) = 508 (9) [M^+], 452 (2) [$M^+ - 2CO$], 424 (100) [$M^+ - 3CO$], 368 (37) [$M^+ - 3CO - C_4H_6$], 404 (75) [$M^+ - Cr(CO)_3$], 126 (23) [$C_8H_{14}O^+$], 73 (56) [$C_3H_9Si^+$]. IR (petroleum ether): $\nu_{C=O}$ = 1955 (s, A_1), 1889, 1876 (s, E) cm^{-1}.

3.4.2.2. Benzannulation of carbene complex **7** *with 3-hexyne and protection as tert-butyldimethylsilyl ether.* A solution of 0.87 g (2 mmol) carbene complex **7** and 1 ml (8 mmol) alkyne in 5 ml *tert*-BuOMe were degassed in three cycles and warmed at 55 °C for 4 h. After cooling to r.t. 1.6 g (8 mmol) TBDMSCl and 1.1 ml mmol (8 mmol) Et_3N were added and the solution was stirred at r.t. for 3 h. The solvent was removed under reduced pressure, and chromatographic purification with petroleum ether–CH_2Cl_2 (5:1) afforded 0.53 g of complex **19** as a red solid (0.9 mmol, 44%).

*3.4.2.2.1. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2,3-diethyl-4-(1R,2S,5R)-(−)-menthyloxynaphthalene]chromium (**19**).* ^{1}H-NMR (400 MHz, C_6D_6): δ = 0.49 (d, $^3J_{HH}$ = 11.9 Hz, 1H, CH), 0.58 (s, 6H, $2CH_3$), 0.90 (m, 5H, CH_3, CH_2), 1.07 (s, 9H, $C(CH_3)_3$), 1.06–1.15 (m, 9H, $3CH_3$), 1.27 (m, 2H, CH_2), 1.49 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3), 1.60 (m, 1H, CH_2), 2.43–2.98 (m, $^3J_{HH}$ = 7.6 Hz, 4H, $2CH_2$), 4.27 (m, 1H, HCO), 6.95 (dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, ArH), 7.12 (dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, ArH), 7.88 (d, $^3J_{HH}$ = 8.8 Hz, 2H, ArH), 8.03 (d, $^3J_{HH}$ = 8.8 Hz, 1H, ArH) ppm. ^{13}C-NMR (100 MHz, C_6D_6): δ = −3.5, −1.3 ($2CH_3$), 15.1, 17.5, 21.1 ($3CH_3$), 22.0 ($C(CH_3)_3$), 23.9 (CH_2), 26.0 (CH), 26.2 ($C(CH_3)_3$), 31.4 (CH), 34.4 (CH_2), 39.7 (CH_2), 50.0 (CH), 82.9 (HCO), 107.1, 107.5 (2ArC), 124.0, 125.1, 126.8, 127.8 (6ArC), 130.6, 132.4 (2ArC), 234.6 ($Cr(CO)_3$) ppm. EIMS (70 eV): m/z (%) = 604 (3) [M^+], 548 (2) [$M^+ - 2CO$], 520 (100) [$M^+ - 3CO$], 468 (8) [$M^+ - Cr(CO)_3$], 330 (44) [$M^+ - C_{10}H_{18}$]. IR (petroleum ether): $\nu_{C=O}$ = 1559 (vs, A_1), 1894, 1878 (s, E) cm^{-1}.

3.4.2.3. Benzannulation of carbene complexes **8** *and* **9** *with 3,3-dimethylbutyne and protection as tert-butyldimethylsilyl ether.*

3.4.2.3.1. General procedure. A solution of 2 mmol (0.87 g of **8**, 0.93 g of **9**) carbene complex and 1 ml (8 mmol) alkyne in 5 ml *tert*-BuOMe was degassed in three cycles and warmed at 55 °C for 1 h (respectively 8 h in case of complex **9**). After cooling to r.t. 1.6 g (8 mmol) TBDMSCl and 1.1 ml (8 mmol) Et_3N were added, and the solution was stirred at r.t. for 3 h. The solvent was removed under reduced pressure and chromatographic purification with petroleum ether–CH_2Cl_2 afforded the products as red oils (0.87 g, 1.2 mmol, 59% of **20** and 0.61 g, 1.0 mmol, 48% of **21**)

*3.4.2.3.2. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2-tert-butyl-4-(1R,2S,5R)-(−)-menthyloxynaphthalene]chromium (**20**).* ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 0.34$, 0.53 (s, 6H, CH_3), 0.80, 0.93, 1.01 (d, $^3J_{HH} = 7.0$ Hz, 9H, $3CH_3$), 1.09 (s, 9H, $SiC(CH_3)_3$), 1.52 (s, 9H, $C(CH_3)_3$), 1.15–1.70 (m, 5H, $2CH_2$, 1CH), 1.75 (m, 2H, CH_2), 2.11 (m, 1H, CH), 2.65 (m, 1H, CH), 4.00 (ddd, $^3J_{HH} = 10.6$ Hz, 9.8 Hz, 5.3 Hz, 1H, HCO), 5.60 (s, 1H, ArH), 7.33 (ddd, $^3J_{HH} = 9.1$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, ArH), 7.45 (ddd, $^3J_{HH} = 8.9$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, ArH), 8.05 (m, 2H, ArH) ppm. ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = -1.0$, 0.4 ($2CH_3Si$), 16.9, 20.8, 22.2 ($3CH_3$), 19.9 ($SiC(CH_3)$), 23.6 (CH_2), 26.0 (CH), 27.0 ($SiC(CH_3)_3$), 30.9 ($C(CH_3)_3$), 31.5 (CH), 34.2 (CH_2), 34.9 ($C(CH_3)_3$), 39.3 (CH_2), 48.1 (CH), 76.9 (HCO) 79.7 (ArC), 99.0, 101.0, 108.6 (3ArC), 123.4, 125.4, 126.6, 127.8 (4ArC), 128.9, 130.6 (2ArC), 234.4 ($Cr(CO)_3$) ppm. EIMS (70 eV): *m/z* (%) = 604 (5) [M^+], 548 (1) [M^+-2CO], 520 (100) [M^+-3CO], 468 (1) [$M^+-Cr(CO)_3$], 330 (18) [$M^+-C_{10}H_{18}$]. IR (petroleum ether): $\nu_{C=O} = 1958$ (s, A_1), 1890, 1877 (vs, E) cm^{-1}.

*3.4.2.3.3. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2-tert-butyl-4-(1R,2S,5R)-(−)-menthyloxy-5-methoxynaphthalene]chromium (**21**).* ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 0.28$, 0.49 (s, 6H, $2CH_3$), 0.81, 0.92 (d, $^3J_{HH} = 6.4$ Hz, 6H, $2CH_3$), 1.08 (s, 3H, CH_3), 1.08 (s, 9H, $SiC(CH_3)_3$), 1.20 (d, $^3J_{HH} = 6.6$ Hz, 1H, CH), 1.42 (m, 2H, CH_2), 1.50-1.61 (m, 2H, CH_2), 1.59 (s, 9H, $C(CH_3)_3$), 2.34 (m, 1H, CH), 2.98 (m, 1H, CH), 2.56 (s, 3H, OCH_3), 4.03 (m, 1H, HCO), 5.68 (s, 1H, ArH), 6.25 (d, $^3J_{HH} = 7.8$ Hz, 1H, ArH), 6.96 (t, $^3J_{HH} = 7.8$ Hz, 1H, ArH), 7.64 (d, $^3J_{HH} = 7.8$ Hz, 1H, ArH) ppm. ^{13}C-NMR (125 MHz, C_6D_6): $\delta = -0.6$, 0.9 ($2CH_3$), 17.2, 21.4, 22.6 ($3CH_3$), 20.3 ($SiC(CH_3)_3$), 24.1 (CH_2), 26.5 (CH), 27.5 ($SiC(CH_3)_3$), 31.9 ($C(CH_3)_3$), 32.0 (CH), 34.8 (CH_2), 35.3 ($C(CH_3)_3$), 40.0 (CH_2), 48.9 (CH), 56.0 (OCH_3), 78.3 (HCO) 81.2 (ArC), 102.4, 105.4, 107.9, 117.5, 126.5 (5ArC), 130.7, 142.1, 151.5, 158.7 (4ArC), 235.4 ($Cr(CO)_3$) ppm. EIMS (70 eV): *m/z* (%) = 634 (2) [M^+], 578 (4) [M^+-2CO], 550 (100) [M^+-3CO], 498 (1) [$M^+-Cr(CO)_3$], 360 (18) [$M^+-C_{10}H_{18}$]. IR (petroleum ether): $\nu_{C=O} = 1954$ (vs, A_1), 1886, 1875 (s, E) cm^{-1}.

*3.4.2.4. Benzannulation of carbene complex **1** with 3-hexyne.* A solution of 3.12 g (10 mmol) carbene complex **1** and 5 ml (40 mmol) alkyne in 25 ml *tert*-BuOMe was degassed in three cycles and warmed at 55 °C for 1 h. The solvent was removed under reduced pressure, and chromatographic purification with petroleum ether–CH_2Cl_2 (1:1) afforded 2.63 g of complex **22** as a red solid (7.2 mmol, 72%).

*3.4.2.5. Protection of complex **22** with MeOTf.* To a solution of 0.73 g (2 mmol) of complex **22** in 20 ml methylene chloride were added 0.93 ml (8 mmol) 2,6-lutidine and 0.91 ml (8 mmol) MeOTf at 0 °C and stirred at this temperature for 3 h. The solvent was removed under reduced pressure and chromatographic purification with petroleum ether–CH_2Cl_2 (1:2) afforded 0.37 g (1.0 mmol, 48%) of complex **23** as a red solid.

*3.4.2.5.1. Tricarbonyl[1,2,3,4,9,10-η^6-2,3-diethyl-1,4-dimethoxynaphthalene]chromium (**23**).* ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 1.21$ (t, $^3J_{HH} = 7.5$ Hz, 6H, $2CH_3$), 2.45–2.68 (m, $^3J_{HH} = 7.5$ Hz, 4H, $2CH_2$), 3.93 (s, 6H, $2OCH_3$), 7.28 (ddd, $^3J_{HH} = 6.7$ Hz, $^4J_{HH} = 2.9$ Hz, $^5J_{HH} = 0.9$ Hz, 2H, 2ArH), 7.57 (ddd, $^3J_{HH} = 6.7$ Hz, $^4J_{HH} = 2.9$ Hz, $^5J_{HH} = 0.9$ Hz, 2H, 2ArH) ppm. ^{13}C-NMR (125 MHz, C_6D_6): $\delta = 16.9$ (CH_3), 23.4 (CH_2), 66.9 (OCH_3), 103.3, 109.5, 123.9, 126.8, 129.9 (10ArCH), 234.9 ($Cr(CO)_3$) ppm. EIMS (70 eV): *m/z* (%) = 380 (12) [M^+], 324 (14) [M^+-2CO], 296 (100) [M^+-3CO], 52 (40) [$C_4H_4^+$]. IR (petroleum ether): $\nu_{C=O} = 1967$ (s, A_1), 1905, 1889 (s, E) cm^{-1}.

*3.4.2.6. Protection of complex **22** with AcBr.* To a solution of 0.73 g (2 mmol) of complex **22** in 20 ml methylene chloride were added 0.3 ml (2.2 mmol) Et_3N and 0.17 ml (2.2 mmol) AcBr at −30 °C and stirred at this temperature for 5 min. The solvent was removed under reduced pressure, and chromatographic purification with petroleum ether–CH_2Cl_2 (1:2) afforded 0.78 g (2.0 mmol, 96%) of complex **24** as a red solid.

*3.4.2.6.1. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-acetoxy-2,3-diethyl-4-methoxynaphthalene]chromium (**24**).* ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 1.11$ (t, $^3J_{HH} = 7.5$ Hz, 6H, $2CH_3$), 1.83 (s, 3H, $AcCH_3$), 2.40–2.72 (m, $^3J_{HH} = 7.5$ Hz, 4H, $2CH_2$), 3.44 (s, 3H, OCH_3), 6.96 (td, $^3J_{HH} = 5.1$ Hz, $^4J_{HH} = 2.4$ Hz, 2H, 2ArH), 7.41 (m, 1H, ArH), 7.59 (m, 1H, ArH) ppm. ^{13}C-NMR (62.5 MHz, C_6D_6): $\delta = 15.1$ (CH_3), 15.6 (CH_3), 18.7 ($AcCH_3$), 21.1 (CH_2), 21.4 (CH_2), 64.7 (OCH_3), 99.6, 101.5, 104.8, 107.6 (4ArC), 123.6, 124.2, 128.2, 133.6 (6ArC), 169.6 (AcC), 232.8 ($Cr(CO)_3$) ppm. EIMS (70 eV): *m/z* (%) = 408 (10) [M^+], 352 (16) [M^+-2CO], 324 (100) [M^+-3CO], 309 (24) [$M^+-3CO-CH_3$], 52 (21) [$C_4H_4^+$]. IR (petroleum ether): $\nu_{C=O} = 1963$ (s, A_1), 1895, 1876 (s, E) cm^{-1}.

*3.4.2.7. Protection of complex **22** with camphanic acid chloride.* To a solution of 0.73 g (2 mmol) of complex **22** in 20 ml methylene chloride 0.3 ml (2.2 mmol) Et_3N and 0.40 ml (2.2. mmol) CamphCl were added at −10 °C and stirred at this temperature for 1 h. The solvent was removed under reduced pressure, and chromatographic purification with petroleum ether–CH_2Cl_2 (1:4) afforded 0.85 g (1.6 mmol, 78%) of complex **25** as a red solid.

*3.4.2.7.1. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2,3-diethyl-4-[(1S)-3-oxo-4,7,7-trimethyl-2-oxabicyclo[2.2.1]heptane-1-carbonyloxy]naphthalene]chromium (**25**).* ^{1}H-NMR (500 MHz, CH_2Cl_2): both diastereomers (1:1) $\delta = 0.13$ (s, 1H, CH), 1.21 (s, 6H, 2CH_3), 1.24 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.39–1.42 (m, 12H, 4CH_3), 1.84 (m, 2H, CH_2), 2.08 (m, 2H, CH_2), 2.34 (m, 1H, CH), 2.39 (m, 1H, CH), 2.67–2.95 (m, 8H, 4CH_2), 4.04 (s, 3H, OCH_3), 7.44–7.55 (m, 6H, ArH), 7.94 (6, $^3J_{HH} = 9.1$ Hz, 2H, ArH) ppm. ^{13}C-NMR (125 MHz, CH_2Cl_2): $\delta = 0.89$ (*C*(CH_3), 9.54 (C(*C*H_3), 15.4, 15.5, 15.6, 16.9 (4CH_2*C*H_3), 17.0, 20.9, 21.3, 21.4 (4*C*H_2CH_3), 28.9 (CH_3), 31.5 (CH_3), 31.6 (CH_3), 54.6, 55.1 (2HCO), 65.3, 65.4 (2OCH_3), 90.8, 90.9, 98.8, 98.9, 101.2, 101.3, 104.7, 104.9, 107.8, 107.9 (10ArC), 120.9, 123.5, 124.5, 124.5, 127.6, 128.0, 128.7, 128.9, 129.9, 133.8 (10ArC), 167.2 (CO), 177.3 (CO), 232.2 ($Cr(CO)_3$) ppm. EIMS (70 eV): *m/z* (%) = 546 (1) [M^+], 462 (28) [$M^+ - 2CO$], 410 (62) [$M^+ - 3CO$], 229 (100) [$M^+ - Cr(CO)_3 - C_{10}H_{13}O_3$]. IR ($CH_2Cl_2$): $\nu_{C=O} = 1963$ (s, A_1), 1899, 1872 (s, E) cm^{-1}.

*3.4.2.8. Benzannulation of carbene complex **1** with ethynyltrimethylsilane and protectection as tert-butyldimethylsilyl ether.* A solution of 0.64 g (2 mmol) of carbene complex **1** and 1 ml (8 mmol) ethynyltrimethylsilane in 5 ml *tert*-BuOMe was degassed in three cycles and warmed at 55 °C for 1 h. After cooling to r.t. 1.6 g (8mmol) TBDMSCl and 1.1 ml mmol (8 mmol) Et_3N were added, and the solution was stirred at r.t. for 3 h. The solvent was removed under reduced pressure and chromatographic purification with petroleum ether–CH_2Cl_2 (5:1) afforded 0.91 g (1.8 mmol, 92%) of complex **26** as a red solid.

*3.4.2.8.1. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsilyloxy-2-trimethylsilyl-4-methoxynaphthalene]chromium (**26**).* ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 0.06$ (s, 3H, CH_3), 0.31 (s, 3H, CH_3), 0.57 (s, 9H, C(*C*$H_3)_3$), 1.06 (s, 9H, $Si(CH_3)_3$), 3.31 (s, 3H, OCH_3), 5.15 (s, 1H, ArH), 7.07 (td, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 1.2$ Hz, 2H, ArH), 8.07 (dt, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 1.2$ Hz, 2H, ArH) ppm. ^{13}C-NMR (62.5 MHz, C_6D_6): $\delta = -1.7$ (CH_3), -0.4 (CH_3), 0.7 ($Si(CH_3)_3$), 19.6 (*C*$(CH_3)_3$), 26.9 (C(*C*$H_3)_3$), 56.3 (OCH_3), 79.3, 86.8, 98.9, 103.0 (4ArC), 123.8, 125.5, 126.8, 128.6 (4ArCH), 130.2, 136.4 (2ArC), 234.0 ($Cr(CO)_3$) ppm. EIMS (70 eV): *m/z* (%) = 496 (16) [M^+], 440 (8) [$M^+ - 2CO$], 412 (100) [$M^+ - 3CO$], 356 (28) [$M^+ - 3CO - C_4H_8$], 126 (23) [$C_3H_9Si^+$]. IR (petroleum ether): $\nu_{C=O} = 1961$ (s, A_1), 1898, 1886 (s, E) cm^{-1}.

*3.4.2.9. Benzannulation of carbene complex **1** with ethynyltributylstannane and protection as tert-butyldimethylsilyl ether.* A solution of 0.64 g (2 mmol) of carbene complex **1** and 1 ml (8 mmol) ethynyltributylstannane in 5 ml *tert*-BuOMe was degassed in three cycles and warmed at 55 °C for 1 h. After cooling to r.t. 1.6 g (8 mmol) TBDMSCl and 1.1 ml mmol (8 mmol) Et_3N were added, and the solution was stirred at r.t. for 3 h. The solvent was removed under reduced pressure and chromatographic purification with mixtures of petroleum ether–CH_2Cl_2 afforded 0.73 g (1.1 mmol, 51%) of the isomeric complexes **27** and **28** (7:1) as a red oil and 0.17 g (0.3 mmol, 15%) of complex **29** as a red solid.

*3.4.2.9.1. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-3-tributylstannyl-4-methoxynaphthalene]chromium (**27**).* ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 0.09$ (s, 3H, CH_3), 0.28 (s, 3H, CH_3), 1.04 (t, $^3J_{HH} = 7.5$ Hz, 9H, 3CH_3), 1.14 (s, 9H, $C(CH_3)_3$), 1.46 (m, 12H, 6CH_2), 1.78–1.84 (m, 6H, 3CH_2), 3.37 (s, 3H, OCH_3), 5.25 (t, $^3J_{HSn} = 11.9$ Hz, 1H, ArH), 6.92 (t, $^3J_{HH} = 6.7$ Hz, 1H, ArH), 7.05 (t, $^3J_{HH} = 7.0$ Hz, 1H, ArH), 8.11 (dd, $^3J_{HH} = 9.1$ Hz, $^4J_{HH} = 2.7$ Hz, 1H, ArH) ppm. ^{13}C-NMR (125 MHz, C_6D_6): $\delta = -2.5$ (CH_3), -1.3 (CH_3), 12.7 (C(*C*$H_3)_3$), 19.5 (*C*$(CH_3)_3$), 25.9 (3CH_2), 26.9 (3CH_3), 28.1 (t, $^2J_{CSn} = 33.1$ Hz, 3CH_2), 29.7 (t, $^3J_{CSn} = 9.1$ Hz, 3CH_2), 56.5 (OCH_3), 81.1 (t, $^2J_{CSn} = 12.4$ Hz, ArH), 87.0, 100.5, 103.0 (3ArC), 124.2, 125.8, 127.0, 128.6 (4ArCH), 133.9, 136.0 (2ArC), 234.2 ($Cr(CO)_3$) ppm. EIMS (70 eV): *m/z* (%) = 714 (11) [M^+], 657 (4) [$M^+ - C_4H_9$], 630 (13) [$M^+ - 3CO$], 574 (14) [$M^+ - 3CO - C_4H_9$], 521 (78) [$M^+ - Cr(CO)_3 - C_4H_9$], 460 (100) [$M^+ - Cr(CO)_3 - C_7H_{18}O$], 329 (26) [$M^+ - Cr(CO)_3 - CH_3$], 73 (100) [$C_3H_9Si^+$]. IR (petroleum ether): $\nu_{C=O} = 1957$ (s, A_1), 1889, 1880 (s, E) cm^{-1}.

*3.4.2.9.2. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-tert-butyldimethylsiloxy-2-tributylstannyl-4-methoxynaphthalene]chromium (**28**).* ^{1}H-NMR (500 MHz, C_6D_6): $\delta = 0.31$ (s, 3H, CH_3), 0.52 (s, 3H, CH_3), 1.02 (t, $^3J_{HH} = 7.5$ Hz, 9H, 3CH_3), 1.06 (s, 9H, 3CH_3), 1.44 (m, 12H, 6CH_2), 1.78–1.84 (m, 6H, 3CH_2), 3.55 (s, 3H, OCH_3), 5.34 (t, $^3J_{HSn} = 11.9$ Hz, 1H, ArH), 6.97 (td, $^3J_{HH} = 6.7$ Hz, $^4J_{HH} = 0.9$ Hz, 1H, ArH), 7.05 (td, $^3J_{HH} = 6.7$ Hz, $^4J_{HH} = 0.9$ Hz, 1H, ArH), 7.66 (d, $^3J_{HH} = 8.8$ Hz, 1H, ArH), 8.18 (d, $^3J_{HH} = 8.8$ Hz, 1H, ArH) ppm. ^{13}C-NMR (125 MHz, C_6D_6): $\delta = -4.3$ (CH_3), -4.2 (CH_3), 11.9 (C(*C*$H_3)_3$), 18.6 (*C*$(CH_3)_3$), 25.9 (3CH_2), 26.9 (3CH_3), 28.0 (t, $^2J_{CSn} = 33.1$ Hz, 3CH_2), 29.7 (t, $^3J_{CSn} = 9.1$ Hz, 3CH_2), 64.3 (OCH_3), 85.1 (t, $^2J_{CSn} = 11.6$ Hz, ArH), 93.3, 102.9, 103.4 (3ArCH), 124.8, 125.5, 128.2, 128.3 (4ArCH), 131.6, 137.0 (2ArC), 233.9 ($Cr(CO)_3$) ppm. EIMS (70 eV): *m/z*

(%) = 714 (11) [M^+], 657 (4) [$M^+ - C_4H_9$], 630 (13) [$M^+ - 3CO$], 574 (14) [$M^+ - 3CO - C_4H_9$], 521 (78) [$M^+ - Cr(CO)_3 - C_4H_9$], 460 (100) [$M^+ - Cr(CO)_3 - C_7H_{18}O$], 329 (26) [$M^+ - Cr(CO)_3 - CH_3$], 73 (100) [$C_3H_9Si^+$]. IR (petroleum ether): $\nu_{C=O} = 1957$ (s, A_1), 1889, 1880 (s, E) cm^{-1}.

*3.4.2.9.3. R,S-Tricarbonyl[1,2,3,4,9,10-η^6-1-hydroxy-3-tributylstannyl-4-methoxynaphthalene]chromium (**29**).* ^{1}H-NMR (250 MHz, C_6D_6): $\delta = 1.04$ (t, $^3J_{HH} = 7.2$ Hz, 9H, $3CH_3$), 1.42–1.56 (m, 12H, $6CH_2$), 1.78–1.88 (m, 6H, $3CH_2$), 3.33 (s, 3H, OCH_3), 4.22 (s, 1H, OH), 5.14 (t, $^3J_{HSn} = 11.6$ Hz, ArH), 6.90 (s, 2H, ArH), 7.01 (m, 1H, ArH), 8.01 (d, $^3J_{HH} = 8.6$ Hz, 1H, ArH) ppm. ^{13}C-NMR (62.5 MHz, C_6D_6): $\delta = 11.4$ ($3CH_3$), 13.9 ($3CH_2$), 27.8 ($3CH_2$), 29.4 ($3CH_2$), 56.3 (OCH_3), 79.8, 85.9, 98.7, 101.8 (4ArCH), 122.3, 125.1, 128.1, 129.5, 131.7, 133.3 (6ArC), 234.2 ($Cr(CO)_3$) ppm. EIMS (70 eV): m/z (%) = 600 (6) [M^+], 464 (38) [$M^+ - Cr(CO)_3$], 346 (24) [$M^+ - Cr(CO)_3 - C_7H_{18}O$], 291 (30) [$C_{12}H_{27}Sn^+$], 235 (81) [$C_8H_{19}Sn^+$], 179 (100) [$C_4H_{11}Sn^+$], 158 (98) [$C_{11}H_{10}O^+$]. IR (petroleum ether): $\nu_{C=O} = 1959$ (s, A_1), 1894, 1880 (s, E) cm^{-1}.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 173982 (**5**), 173983 (**16**), 173984 (**18**), 173985 (**23**), 173986 (**24**), and 173987 (**26**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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