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Reactions of complex ligands Part 94.[☆] Chromium-templated angular versus linear benzannulation of dibenzofuran and haptotropic metal migration in tetracyclic fused arenes

Holger Christian Jahr [a], Martin Nieger [b], Karl Heinz Dötz [a,*]

[a] *Kekulé-Institut für Organische Chemie und Biochemie der Rheinischen Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Straße 1, 53121 Bonn, Germany*

[b] *Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Straße 1, 53121 Bonn, Germany*

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Abstract

The chromium-templated [3 + 2 + 1]-benzannulation of dibenzofuryl(methoxy)carbene complex **1** with alkynes leads to hydroquinoid benzonaphthofurans. A competition of angular versus linear annulation affords angular-fused (η^6-1,2,3,4,4a,11c)-benzo[*b*]naphtho[1,2-*d*]furan tricarbonyl chromium complexes **2**–**6** along with considerable amounts of uncoordinated benzo[*b*]naphtho[2,3-*d*]furans as linear annulation products **7**–**9**. As demonstrated for **2** and **6** the $Cr(CO)_3$ complexes undergo a thermally induced haptotropic metal migration along the tetracyclic heteroaromatic π-system to give (η^6-7a,8,9,10,11,11a)-benzonaphthofuran complexes **10** and **11** in which the chromium fragment is coordinated to the terminal unsubstituted benzoid ring. The molecular structures of both the kinetic annulation products and the thermodynamic rearrangement products were established by NMR spectroscopy and single crystal X-ray analysis. © 2002 Published by Elsevier Science B.V.

Keywords: Chromium; Carbene complexes; Benzannulation; Benzonaphthofurans; Haptotropic metal migration

1. Introduction

Annulation provides an established access to bi- and oligocyclic ring systems. Whereas this approach generally keeps the balance of functionalization present in the starting material, a metal-templated assembly of building blocks may introduce additional functional groups along the cyclization sequence. In this respect, the benzannulation of arylcarbene ligands by an alkyne and carbon monoxide occurring at a $Cr(CO)_3$ template has received considerable attention as a straightforward route to densely substituted oxygenated arenes [2]. The reaction is compatible with a series of functional groups both in the alkyne and in the carbene ligand; when extended from phenyl to bi- and tricyclic arylcarbene ligands an angular annulation pattern has been generally observed [3], even in cases where an *ortho*-substitution has been applied to force the annulation to linear. So far, there is only a single early report of a linear benzannulation [4]; a more recent study confirmed the preference of angular over linear benzannulation [5] which, however, also may depend on the *ortho*-substitution pattern [6].

Organometallic fragments coordinated to fused arenes are capable of haptotropic migrations along the π-system. This process has been most extensively studied for (naphthalene)$Cr(CO)_3$ complexes; synthetic, kinetic and theoretical studies suggest an intramolecular metal shift along one face and close to the periphery of the aromatic π-system [7].

Following our interest to homologize fused arenes and label them by organometallic fragments, we applied the chromium-mediated benzannulation to dibenzofuran; we now report on its regioselectivity and on the haptotropic migration of the chromium template along the tetracyclic annulation product.

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* Corresponding author. Tel.: +49-228-735609; fax: +49-228-735813.

E-mail address: doetz@uni-bonn.de (K.H. Dötz).

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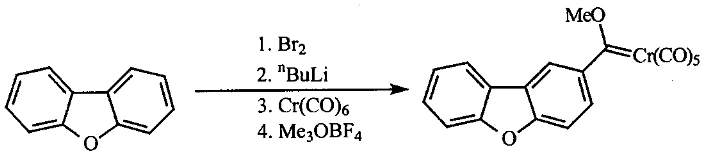

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Scheme 1. Synthesis of pentacarbonyl[2-dibenzofuryl(methoxy)carbene]chromium.

2. Benzonaphthofurans via [3 + 2 + 1]-benzannulation of a chromium dibenzofurylcarbene complex

Bromination of dibenzofuran according to a slightly modified literature procedure yielded 2-bromodibenzofuran [8] which after low-temperature lithiation with *n*-butyl lithium was applied to the *Fischer* carbene complex synthesis. Addition to hexacarbonyl chromium followed by alkylation with trimethyloxoniumtetrafluoroborate gave the pentacarbonyl[2-dibenzofuryl(methoxy)carbene] complex (**1**) (Scheme 1). Red crystals suitable for X-ray analysis (Fig. 1) were grown from a toluene solution of **1** by slow evaporation of the solvent.

[3 + 2 + 1]-Benzannulation of pentacarbonyl[2-dibenzofuryl(methoxy)carbene]chromium (**1**) with various alkynes in *tert*-butyl methyl ether at 50 °C and subsequent silylation with *tert*-butyldimethylsilyl chloride or trifluoromethanesulfonic acid *tert*-butyldimethylsilyl ester led to benzo[*b*]naphtho[1,2-*d*]furan complexes **2**–**6** (Scheme 2). In some cases, the silylation was not quantitative and less stable unprotected tricarbonyl complexes **4** and **6** were isolated; obviously an increasing steric demand of the substituent next to the phenolic group hampers the protection procedure with the bulky silylation reagent. Upon cooling of a toluene solution of **2** to − 30 °C, single crystals suitable for X-ray analysis were obtained (Fig. 2). The bond lengths between chromium and the carbon atoms of the coordinated hydroquinoid ring range from 2.23 to 2.30 Å. The conformation of the $Cr(CO)_3$-fragment is close to eclipsed with respect to the carbon atoms C1, C3 and C4a. Interestingly, the aromatic skeleton is screwed towards the chromium fragment, as indicated by torsion angles of up to 12° for the benzonaphthofuran system which also reveals alternating bond lengths within the coordinated hydroquinoid and its adjacent ring. As suggested by a donor–acceptor distance of 3.36 Å an intermolecular hydrogen bonding involving a carbonyl oxygen and an aromatic hydrogen atom is encountered in the solid state.

Whereas the chromium-templated benzannulation generally occurs in an angular fashion, the dibenzofurylcarbene complex **1** provides a rare example which also allows for a linear annulation. In addition to the angular benzonaphthofuran complexes **2**–**6** chromatographic workup of the reaction products afforded also uncoordinated benzo[*b*]naphtho[2,3-*d*]furans **7**–**9** (Scheme 2) as unprecedented linear benzannulation products. The relevant substitution pattern was first suggested by their ^{1}H-NMR data and finally confirmed by X-ray analysis of colourless prisms obtained upon slow evaporation of the solvent from a toluene solution of **7** (Fig. 3). Similar to the structure of **2** alternating bond lengths are observed within the naphthoid part of **7**.

The formation of benzo[*b*]naphtho[2,3-*d*]furans **7**–**9** provides the first example in which an arylcarbene ligand bearing two hydrogen atoms *ortho* to the ring carbon atom connected with the carbene carbon atom undergoes a linear benzannulation. The observation that — in contrast to the angular annulation product — the linear annulation is accompanied by decomplexation is remarkable and deserves further comment. The reason for this behaviour remains unclear at the moment. Loss of the chromium template

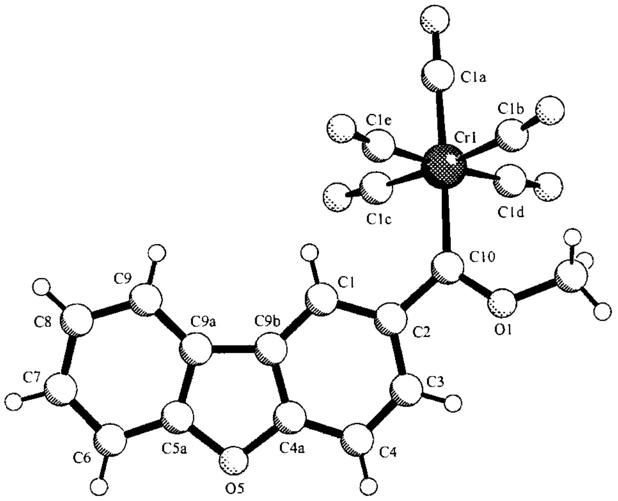
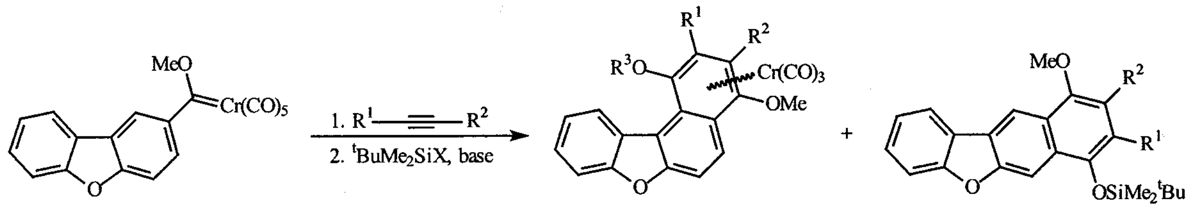


Fig. 1. Molecular structure of pentacarbonyl[2-dibenzofuryl(methoxy)carbene] complex (**1**). Selected bond lengths (Å): C2–C10, 1.496(4); C10–O1, 1.329(3); Cr1–C10, 2.072(3); Cr1–C1a, 1.879(4); Cr1–C1b, 1.902(3); Cr1–C1c, 1.911(3); Cr1–C1d, 1.895(3); Cr1–C1e, 1.898(3). Selected bond angles (°): O1–C10–C2, 104.8(2); C2–C10–Cr1, 127.8(2); O1–C10–Cr1, 127.20(19); C1a–Cr1–C10, 177.19(13); C1b–Cr1–C10, 96.20(12); C1c–Cr1–C10, 89.80(12); C1d–Cr1–C10, 91.71(11); C1e–Cr1–C10, 91.92(11). Selected torsion angles (°): C9–C9a–C9b–C1, − 2.5(6); C1–C2–C10–Cr1, − 23.2(4); C3–C2–C10–Cr1, 154.28(19); C1b–Cr1–C10–C2, 149.9(2); C1c–Cr1–C10–C2, − 30.7(2); C1d–Cr1–C10–C2, − 117.7(2); C1e–Cr1–C10–C2, 63.0(2).



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R1	R2	X
Et	Et	Cl
nPr	H	OTf
tBu	H	Cl
Ph	Ph	Cl
Ph	Ph	Cl

	R1	R2	R3
2	Et	Et	SiMe2tBu
3	nPr	H	SiMe2tBu
4	tBu	H	H
5	Ph	Ph	SiMe2tBu
6	Ph	Ph	H

	R1	R2
7	Et	Et
8	nPr	H
9	tBu	H

Scheme 2. Synthesis of benzonaphthofurans via [3 + 2 + 1]-benzannulation.

prior to the formation of the vinylketene intermediate seems unlikely, since this species is considered to result from a metal-mediated insertion of carbon monoxide into the η^3-vinylcarbene ligand to metal bond. The question whether the subsequent electrocyclization to the cyclohexadienone skeleton necessarily requires the assistance of the tricarbonyl chromium template is open to speculation. The cyclization of uncoordinated vinylketenes to naphthols has been reported to occur also in the absence of a transition metal [9] under mild conditions comparable to those applied in the chromium-assisted benzannulation of aryl(methoxy)carbene ligands such as in **1** [10]. This result may encourage to underestimate the influence of preorientation for the electrocyclization provided by the metal template. So far, there is neither evidence for the appealing idea that the annulation generally occurs in the coordination sphere of the metal and the reduced aromaticity of the terminal ring in the linear annulation product is responsable for the decomplexation, nor for the alternative that the competitive benzannulation simply reflects the kinetic stability of the vinylketene complex intermediate. A DFT study is underway to shed light on this issue.

3. Haptotropic rearrangement of chromium benzonaphthofuran complexes

The tricarbonyl complexes **2**–**6** represent the kinetic benzannulation products. Previous studies on naphthohydroquinoid complexes have demonstrated that under thermodynamic control the metal fragment migrates to the less oxygenated ring along the same arene face [3,7]. We were interested in whether the haptotropic metal migration is compatible with heterocyclic spacers and more extended fused arenes. In this context we studied the thermal behaviour of benzo[*b*]naphtho[1,2-*d*]furan complexes **2** and **6**. Upon warming in di-*n*-butyl ether to 90 °C they underwent a haptotropic rearrangement leading to isomeric complexes **10** and **11** (Scheme 3). The metal migration, which also occurs in non-coordinating solvents can easily be monitored by IR spectroscopy based on the hypsochromic shift of the A-band in the rearranged products. Their molecular structure bearing the chromium coordinated to the terminal benzoid ring was elucidated from their ^{1}H-NMR spectra and was finally established by X-ray analysis of complex **10** (Fig. 4). Suitable crystals for the structure determination were obtained by evaporation of the solvent from a toluene solution. The distances between chromium and the carbon atoms of the coordinated ring are between 2.20 and 2.29 Å. The carbonyl ligands are nearly eclipsed with the carbon atoms C7a, C9 and C11. Torsion angles along the aromatic skeleton are comparable to those found for isomeric com-

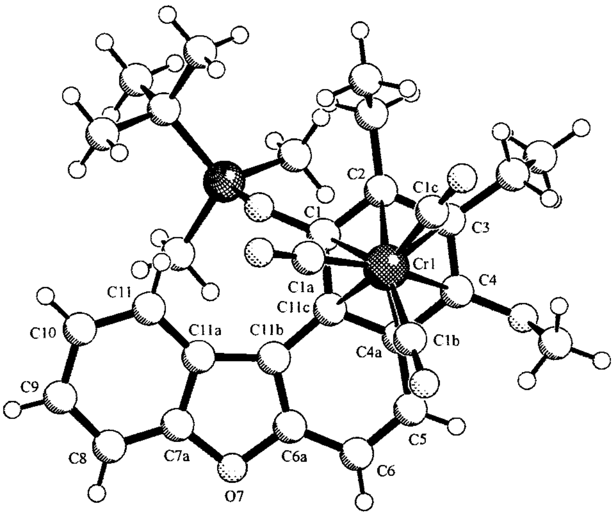


Fig. 2. Molecular structure of (η^6-1,2,3,4,4a,11c)-benzonaphthofuran complex (**2**). Selected bond lengths (Å): C1–C2, 1.408(4); C2–C3, 1.443(4); C3–C4, 1.391(4); C4–C4a, 1.430(4); C4a–C5, 1.438(4); C5–C6, 1.355(4); C6–C6a, 1.405(4); C6a–C11b, 1.384(4); C11b–C11c, 1.444(4); C11c–C1, 1.442(4); C4a–C11c, 1.441(4); Cr1–ZAr, 1.770(1); Cr1–C1, 2.304(3); Cr1–C2, 2.275(3); Cr1–C3, 2.230(3); Cr1–C4, 2.254(3); Cr1–C4a, 2.298(3); Cr1–C11c, 2.267(3); Cr1–C1a, 1.830(4); Cr1–C1b, 1.826(4); Cr1–C1c, 1.830(3). Selected torsion angles (°): C11–C11a–C11b–C11c, −5.8(6); C11a–C11b–C11c–C1, −12.2(6); C6a–C11b–C11c–C1, 169.6(3).

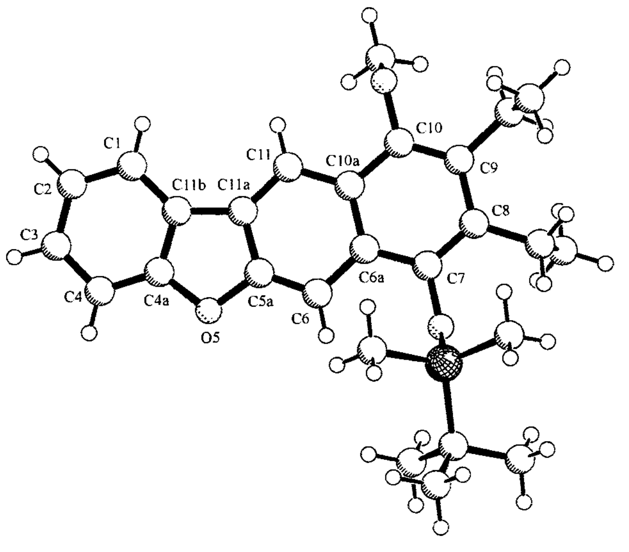


Fig. 3. Molecular structure of the linear benzannulation product **7**. Selected bond lengths (Å): C5a–C6, 1.358(3); C6–C6a, 1.420(3); C6a–C7, 1.424(3); C7–C8, 1.378(3); C8–C9, 1.440(3); C9–C10, 1.362(3); C10–C10a, 1.427(3); C10a–C11, 1.414(3); C11–C11a, 1.379(3); C11a–C5a, 1.409(3); C6a–C10a, 1.433(3). Selected torsion angles (°): C11–C11a–C11b–C1, −3.0(4); C10a–C11–C11a–C11b, −176.0(2); C10a–C11–C11a–C5a, 1.1(3).

plex **2**; however, in contrast to **2**, the benzonaphthofuran ligand is screwed away from the chromium fragment. The solid state structure reveals five different hydrogen bonds three of which involve carbonyl oxygen atoms; donor–acceptor distances range from 3.24 to 3.69 Å.

4. Conclusions

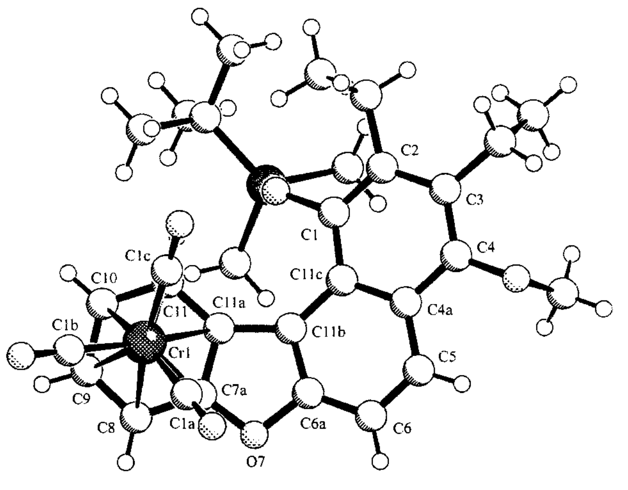


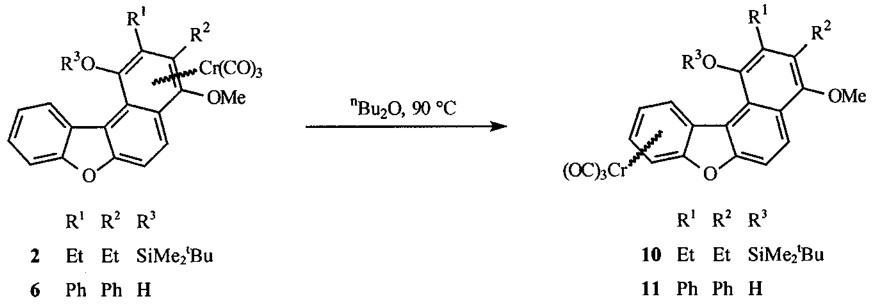
Fig. 4. Molecular structure of $(\eta^6$-7a,8,9,10,11,11a)-benzonaphthofuran complex **10**. Selected bond lengths (Å): C1–C2, 1.383(3); C2–C3, 1.427(3); C3–C4, 1.382(3); C4–C4a, 1.421(3); C4a–C5, 1.428(3); C5–C6, 1.358(3); C6–C6a, 1.390(3); C6a–C11b, 1.381(3); C11b–C11c, 1.441(2); C11c–C1, 1.415(3); C4a–C11c, 1.426(3); Cr1–ZAr, 1.728(1); Cr1–C7a, 2.2508(19); Cr1–C8, 2.237(2); Cr1–C9, 2.201(2); Cr1–C10, 2.200(2); Cr1–C11, 2.1960(18); Cr1–C11a, 2.2871(18); Cr1–C1a, 1.854(2); Cr1–C1b, 1.831(2); Cr1–C1c, 1.842(2). Selected torsion angles (°): C11–C11a–C11b–C11c, 0.5(4); C11a–C11b–C11c–C1, 11.3(3); C6a–C11b–C11c–C1, −174.72(17).

Benzannulation of chromium carbene complexes bearing polycyclic aromatic substituents by alkynes may lead to both angular and linear annulation products. Linear annulation is even compatible with an arylcarbene substitution pattern bearing two *ortho*-hydrogen atoms as shown for the reaction of dibenzofurylcarbene complex **1**. The kinetic benzo[*b*]naphtho[1,2-*d*]furan benzannulation products bearing the chromium fragment coordinated to the hydroquinoid ring undergo an extended haptotropic metal migration along which the metal is shifted to the opposite terminal benzene ring. These results demonstrate that this process, which has been extensively studied in the past for naphthalenes, can be also applied to larger fused π-systems and even tolerates heteroarene spacers.

5. Experimental

5.1. General reaction conditions

All reactions were carried out under Ar atmosphere. Solvents used for reactions and chromatography were dried by distillation from lithium aluminium hydride (Et_2O, petroleum ether, heptane), CaH_2 (*tert*-butyl methyl ether, di-*n*-butyl ether, CH_2Cl_2) or from sodium (toluene). Et_3N was dried by distillation from potas-



Scheme 3. Haptotropic rearrangement of the benzonaphthofuran complexes.

sium hydroxide, 2,6-lutidine by distillation from CaH_2. Chromatography was performed with silica gel (Merck, type 60, 0.063–0.2 mm and Machery Nagel, type 60, 0.015–0.025 mm), which was degassed at high vacuum prior to use.

5.2. Instrumentation

IR: Nicolet Magna 550 FT-IR. NMR: Bruker DRX 500, AM 400 and AM 250. MS (FAB, EI): Kratos Instruments Concept 1H (mNBA matrix) and MS 50 (70 eV). Elemental analysis: Elementar Analysensysteme Vario EL. HPLC: Knauer injection valve A0258, two pumps type 64, UV detector type K 2600, column Knauer Eurospher 100 RP C-18 (250 × 16 mm), Eurochrom 2000 for Windows.

5.3. X-ray crystallographic studies of **1**, **2**, **7** and **10**

Red crystals were obtained by cooling a toluene solution of complex **2** to − 30 °C; upon slow evaporation of the solvent from a toluene solution, **1** gave red crystals, **7** provided colourless prisms and **10** afforded light red crystals. Crystallographic data were collected with a Nonius KappaCCD at 123 K. The molecular structures have been solved by direct methods (**1** and **7**) or Patterson methods (**2** and **10**) (SHELXS-97) [11]. The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-97) [12]; hydrogen atoms were refined using a riding model. Details are presented in Table 1.

5.4. Reagents

2-Bromodibenzofuran was prepared according to a slightly modified literature procedure [8].

5.5. Synthesis of pentacarbonyl[2-dibenzofuryl-(methoxy)carbene]chromium (**1**)

To a solution of 5.9 g (23.9 mmol) of 2-bromodibenzofuran in 100 ml *tert*-butyl methyl ether 9.6 ml (24 mmol) of 2.5 M *n*-butyl lithium solution was added dropwise at − 70 °C. Stirring for 2 h and subsequent warming led to a yellow solution which was transferred into a suspension of 4.8 g (21.8 mmol) hexacarbonyl chromium in 100 ml *tert*-butyl methyl ether, cooled to − 60 °C. After stirring for 3 h the reaction mixture was allowed to warm to room temperature (r.t.). Trimethyl-

Table 1
Crystal data and structure refinement parameters for **1**, **2**, **7** and **10**

	1	**2**	**7**	**10**
Empirical formula	$C_{19}H_{10}CrO_7$	$C_{30}H_{34}CrO_6Si\cdot 1/2$ toluene	$C_{27}H_{34}O_3Si$	$C_{30}H_{34}CrO_6Si$
Formula weight	402.27	616.73	434.63	570.66
Temperature (K)	123(2)	123(2)	123(2)	123(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$C2/c$ (no. 15)
Unit cell dimensions				
a (Å)	7.5624(4)	8.3424(5)	9.9382(4)	18.0990(3)
b (Å)	8.9423(4)	10.5552(6)	10.8886(3)	11.3470(2)
c (Å)	13.2149(7)	17.9899(10)	12.0322(4)	28.4012(5)
α (°)	74.760(2)	79.520(3)	109.113(2)	90
β (°)	81.624(2)	82.589(3)	91.960(2)	98.948(1)
γ (°)	84.022(3)	88.207(2)	102.655(2)	90
V (Å^3)	851.00(7)	1544.63(15)	1192.43(7)	5761.75(17)
Z	2	2	2	8
D_{calc} (g cm^{-3})	1.570	1.326	1.211	1.316
μ (mm^{-1})	0.713	0.452	0.124	0.479
F(000)	408	650	468	2400
Crystal size (mm)	0.15 × 0.10 × 0.05	0.20 × 0.15 × 0.05	0.20 × 0.15 × 0.10	0.45 × 0.40 × 0.35
Diffractometer	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD	Nonius KappaCCD
Radiation	Mo–K_{α}	Mo–K_{α}	Mo–K_{α}	Mo–K_{α}
Max 2θ (°)	50.00	50.70	50.64	50.00
Index ranges	$-7 \leq h \leq 8$, $-10 \leq k \leq 10$, $-15 \leq l \leq 15$	$-9 \leq h \leq 10$, $-12 \leq k \leq 12$, $-21 \leq l \leq 20$	$-11 \leq h \leq 11$, $-13 \leq k \leq 12$, $-12 \leq l \leq 14$	$-21 \leq h \leq 16$, $-10 \leq k \leq 13$, $-33 \leq l \leq 28$
Total reflections	6793	11 966	9496	16 565
Unique reflections	2883	5250	4205	5034
Parameters/restraints	244/0	360/14	280/0	343/0
R for $I > 2\sigma(I)$	0.0387	0.0448	0.0440	0.0317
wR^2 for all data	0.0646	0.1127	0.1086	0.0914
Goodness-of-fit on F^2	0.892	0.963	0.926	1.052

oxoniumtetrafluoroborate (3.25 g, 22.0 mmol) was added to the brown solution at −60 °C, which was allowed to reach r.t. while stirring overnight. The solvent was removed and the residue was subjected to column chromatography at 0 °C using petroleum ether–CH_2Cl_2 2:1 as eluent.

Yield: 5.43 g (13.5 mmol, 62%) of a red solid. $R_f = 0.61$ (petroleum ether–CH_2Cl_2 2:1). IR (petroleum ether, cm^{-1}): $\nu_{CO} = 2062$ (m, A_1), 1961 (sh, A_1), 1952 (vs, E), 1942 (sh, E). ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): $\delta = 8.09$ (d, $^4J_{HH} = 2.0$ Hz, 1H, H1), 8.00 (d, $^3J_{HH} = 7.7$ Hz, 1H, H9/6), 7.71 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.0$ Hz, 1H, H3), 7.59 (d, $^3J_{HH} = 8.2$ Hz, 1H, H6/9), 7.57 (d, $^3J_{HH} = 8.8$ Hz, 1H, H4), 7.50 (td, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, H7/8), 7.39 (td, $^3J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, H8/7), 4.88 (s, 3H, OCH_3). ^{13}C-NMR (62.5 MHz, $CDCl_3$, ppm): $\delta = 346.5$ (C=Cr), 223.8 (*trans*-CO), 216.5 (*cis*-CO), 157.0, 149.1 (2ArCO), 128.0 (ArCH), 125.7 (ArCH), 124.0 (ArC), 123.9 (ArC), 123.3 (ArCH), 120.9 (ArCH), 117.5 (ArCH), 112.0 (ArCH), 111.2 (ArCH, 10ArC), 67.4 (OCH_3). FABMS; *m*/*z* (%): 402 (9) [M^+], 374 (20) [$M^+ - CO$], 346 (23) [$M^+ - 2CO$], 318 (13) [$M^+ - 3CO$], 307 (100) [$(2\ \text{matrix} + H)^+$], 290 (40) [$M^+ - 4CO$], 262 (25) [$M^+ - 5CO$] (Table 2).

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **1**

	x	*y*	*z*	U_{eq} [a]
Cr1	2140(1)	2342(1)	2547(1)	23(1)
C1a	2441(4)	443(4)	2163(2)	27(1)
O1a	2616(3)	−708(2)	1913(2)	37(1)
C1b	387(4)	2949(3)	1592(2)	28(1)
O1b	−665(3)	3161(3)	1021(2)	44(1)
C1c	3954(4)	1541(3)	3452(2)	24(1)
O1c	5087(3)	1000(2)	3945(2)	37(1)
C1d	4016(4)	3062(3)	1463(2)	25(1)
O1d	5196(3)	3407(2)	818(2)	35(1)
C1e	255(4)	1512(3)	3593(2)	23(1)
O1e	−916(3)	955(2)	4171(2)	34(1)
C1	2066(3)	3402(3)	4986(2)	21(1)
C2	2202(3)	4616(3)	4062(2)	18(1)
C3	2704(3)	6068(3)	4126(2)	22(1)
C4	3091(4)	6334(3)	5045(2)	25(1)
C4a	2941(4)	5095(4)	5932(2)	23(1)
O5	3328(2)	5146(2)	6918(1)	27(1)
C5a	3103(4)	3650(4)	7548(2)	24(1)
C6	3420(4)	3183(4)	8601(2)	30(1)
C7	3131(4)	1645(4)	9102(2)	33(1)
C8	2563(4)	644(4)	8587(2)	32(1)
C9	2263(4)	1167(4)	7525(2)	27(1)
C9a	2543(4)	2684(4)	7004(2)	23(1)
C9b	2435(3)	3642(3)	5925(2)	20(1)
C10	1907(3)	4398(3)	3016(2)	20(1)
O1	1600(2)	5828(2)	2423(1)	25(1)
C11	1416(4)	6201(3)	1309(2)	29(1)

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

*5.6. General procedure for the benzannulation of carbene complex **1** yielding tricarbonyl complexes **2**–**6** and linear benzannulation products **7**–**9***

To a solution of **1** in *tert*-butyl methyl ether an excess of alkyne was added and the solution was heated to 50 °C. Upon completion of the reaction the mixture was transferred into a suspension of *tert*-butyldimethylsilylchloride in Et_3N at r.t. or into a mixture of trifluoromethanesulfonic acid *tert*-butyldimethylsilyl ester and 2,6-lutidine at 0 °C, respectively, and stirred at r.t. overnight. After removal of volatile components, the products were separated by column chromatography at 0 °C.

*5.6.1. Tricarbonyl[(η^6-1,2,3,4,4a,11c)-1-tert-butyldimethylsilyloxy-2,3-diethyl-4-methoxybenzo[b]naphtho-[1,2-d]furan]chromium (**2**) and 7-tert-butyldimethylsilyloxy-8,9-diethyl-10-methoxybenzo[b]naphtho[1,2-d]-furan (**7**)*

Carbene complex **1**: 1.00 g (2.5 mmol); 3-hexyne: 0.85 ml (7.5 mmol); *tert*-butyl methyl ether: 60 ml; *tert*-butyldimethylsilylchloride: 3.77 g (25.0 mmol); Et_3N: 3.48 ml (25.0 mmol).

*5.6.1.1. Tricarbonyl[(η^6-1,2,3,4,4a,11c)-1-tert-butyldimethylsilyloxy-2,3-diethyl-4-methoxybenzo[b]-naphtho[1,2-d]furan]chromium (**2**).* Yield: 0.43 g (0.75 mmol, 30%) of red crystals. $R_f = 0.44$ (petroleum ether–Et_2O 10:1). IR (petroleum ether, cm^{-1}): $\nu_{CO} =$ 1959 (vs, A_1), 1894 (s, E), 1882 (s, E). ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): $\delta = 8.69$ (d, $^3J_{HH} = 7.3$ Hz, 1H, H11), 7.86 (d, $^3J_{HH} = 9.5$ Hz, 1H, H5/6), 7.78 (d, $^3J_{HH} = 9.5$ Hz, 1H, H5/6), 7.62 (d, $^3J_{HH} = 7.9$ Hz, 1H, H8), 7.49 (td, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, H9/10), 7.40 (td, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, H10/9), 4.03 (s, 3H, OCH_3), 2.99 (dq, $^2J_{HH} = 13.7$ Hz, $^3J_{HH} = 7.4$ Hz, 1H, CH_2), 2.75 (dq, $^2J_{HH} = 13.7$ Hz, $^3J_{HH} = 7.4$ Hz, 1H, CH_2), 2.70 (dq, $^2J_{HH} = 14.2$ Hz, $^3J_{HH} = 7.4$ Hz, 1H, CH_2), 2.34 (dq, $^2J_{HH} = 14.2$ Hz, $^3J_{HH} = 7.4$ Hz, 1H, CH_2), 1.50 (t, $^3J_{HH} = 7.4$ Hz, 3H, $CH_2C\underline{H}_3$), 1.29 (t, $^3J_{HH} = 7.4$ Hz, 3H, $CH_2C\underline{H}_3$), 1.12 (s, 9H, $C(CH_3)$), −0.21 (s, 3H, $SiCH_3$), −0.60 (s, 3H, $SiCH_3$). ^{13}C-NMR (62.5 MHz, $CDCl_3$, ppm): $\delta = 233.9$ ($Cr(CO)_3$), 155.6, 152.5 (C6a, C7a), 129.6 (ArC), 127.5, 126.9 (ArCH), 124.5, 122.7, 122.0, 119.4, 111.3 (ArCH), 111.2 (ArCH), 104.6 (ArCCr), 104.0 (ArCCr, 14ArC), 67.2 (OCH_3), 26.5 ($C(\underline{C}H_3)_3$), 21.6, 19.7 ($2CH_2$), 18.8, 18.7 ($\underline{C}(CH_3)_3$), $CH_2\underline{C}H_3$), 14.7 ($CH_2\underline{C}H_3$), −2.1, −4.9 ($Si(CH_3)_2$). EIMS; *m*/*z* (%): 570 (15) [M^+], 514 (5) [$M^+ - 2CO$], 486 (100) [$M^+ - 3CO$], 434 (39) [$M^+ - Cr(CO)_3$], 377 (12) [$M^+ - Cr(CO)_3 - C(CH_3)_3$], 348 (17) [$M^+ - Cr(CO)_3 - C(CH_3)_3 - C_2H_5$]. HRMS: Calc. for $C_{30}H_{34}O_6SiCr$: 570.1529. Found: 570.1527 (Table 3).

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

	x	y	z	U_{eq} [a]
Cr1	7654(1)	4645(1)	8039(1)	20(1)
C1a	9675(4)	5135(3)	7573(2)	24(1)
O1a	10951(3)	5469(2)	7277(1)	33(1)
C1b	6934(4)	6219(3)	7598(2)	24(1)
O1b	6510(3)	7233(2)	7317(1)	39(1)
C1c	8018(4)	5415(3)	8834(2)	25(1)
O1c	8216(3)	5922(2)	9331(1)	42(1)
C1	8262(4)	2562(3)	7873(2)	19(1)
C2	7783(4)	2567(3)	8652(2)	19(1)
C3	6256(4)	3132(3)	8879(2)	20(1)
C4	5257(4)	3628(3)	8331(2)	20(1)
C4a	5741(4)	3654(3)	7536(2)	20(1)
C5	4646(4)	4149(3)	6995(2)	25(1)
C6	5069(4)	4197(3)	6237(2)	26(1)
C6a	6644(4)	3794(3)	6002(2)	24(1)
O7	7227(3)	3889(2)	5245(1)	29(1)
C7a	8826(4)	3534(3)	5228(2)	25(1)
C8	9864(4)	3506(3)	4567(2)	33(1)
C9	11456(4)	3175(3)	4644(2)	34(1)
C10	11981(4)	2917(3)	5366(2)	30(1)
C11	10918(4)	2960(3)	6023(2)	25(1)
C11a	9290(4)	3225(3)	5960(2)	23(1)
C11b	7804(4)	3361(3)	6476(2)	20(1)
C11c	7327(3)	3189(3)	7288(2)	19(1)
O11	9670(2)	1950(2)	7658(1)	20(1)
Si1	9888(1)	356(1)	7631(1)	26(1)
C12	9508(4)	16(3)	6691(2)	38(1)
C13	8336(4)	−566(3)	8347(2)	38(1)
C14	12028(4)	−61(3)	7828(2)	34(1)
C15	13268(4)	596(4)	7186(2)	44(1)
C16	12233(5)	−1531(4)	7886(3)	79(2)
C17	12403(5)	308(5)	8576(2)	68(2)
C21	8825(4)	1920(3)	9245(2)	24(1)
C22	9981(4)	2795(3)	9499(2)	37(1)
C31	5653(4)	3115(3)	9715(2)	25(1)
C32	4669(4)	1882(3)	10054(2)	34(1)
O41	3696(2)	3993(2)	8568(1)	25(1)
C41	3398(4)	5338(3)	8576(2)	30(1)
C1t	3768(7)	−459(6)	4837(3)	40(2) [b]
C2t	4355(8)	645(6)	4344(3)	47(2) [b]
C3t	5755(8)	1218(6)	4463(3)	47(2) [b]
C4t	6569(7)	687(6)	5075(4)	53(3) [b]
C5t	5982(7)	−417(6)	5568(3)	38(2) [b]
C6t	4582(7)	−990(5)	5449(3)	36(2) [b]
C7t	3907(9)	−2191(7)	5979(4)	45(2) [b]

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

[b] s.o.f. = 0.50.

*5.6.1.2. 7-tert-Butyldimethylsilyloxy-8,9-diethyl-10-methoxybenzo[b]naphtho[1,2-d]furan (**7**).* Yield: 0.42 g (0.97 mmol, 39%) of colourless prisms. $R_f = 0.73$ (petroleum ether–Et_2O 10:1). ^1H-NMR (400 MHz, $CDCl_3$, ppm): $\delta = 8.59$ (s, 1H, H6), 8.15 (s, 1H, H11), 8.12 (d, $^3J_{HH} = 7.8$ Hz, 1H, H1), 7.59 (d, $^3J_{HH} = 8.2$ Hz, 1H, H4), 7.50 (t, $^3J_{HH} = 7.8$ Hz, 1H, H3), 7.38 (t, $^3J_{HH} = 7.2$ Hz, 1H, H2), 4.05 (s, 3H, OCH_3), 2.94 (q, $^3J_{HH} = 7.4$ Hz, 2H, $C\underline{H}_2CH_3$), 2.90 (q, $^3J_{HH} = 7.4$ Hz, 2H, $C\underline{H}_2CH_3$), 1.33 (t, $^3J_{HH} = 7.4$ Hz, 3H, $CH_2C\underline{H}_3$), 1.22 (t, $^3J_{HH} = 7.4$ Hz, 3H, $CH_2C\underline{H}_3$), 1.19 (s, 9H, $C(CH_3)_3$), 0.29 (s, 6H, $Si(CH_3)_2$). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): $\delta = 157.7$, 154.4, 148.5, 144.7 (C4a, C5a, C7, C10), 130.9, 129.6 (2ArC), 128.1 (ArCH), 127.6, 124.5, 124.3, 124.3 (4ArC), 122.7, 121.3, 113.5, 111.5, 103.2 (5ArCH), 62.5 (OCH_3), 26.2 ($C(\underline{C}H_3)_3$), 20.8, 20.2 ($2\underline{C}H_2CH_3$), 18.8 ($\underline{C}(CH_3)_3$), 16.1, 15.0 ($2CH_2\underline{C}H_3$), −2.9 ($Si(CH_3)_2$). EIMS; *m/z* (%): 434 (100) [M^+], 419 (42) [$M^+ - CH_3$], 377 (7) [$M^+ - C(CH_3)_3$], 348 (13) [$M^+ - C(CH_3)_3 - C_2H_5$], 333 (12) [$M^+ - C(CH_3)_3 - C_2H_5 - CH_3$], 73 (100) [$(Si(CH_3)_3)^+$]. HRMS: Calc. for $C_{27}H_{34}O_3Si$: 434.2277 Found: 434.2272 (Table 4).

*5.6.2. Tricarbonyl[(η^6-1,2,3,4,4a,11c)-1-tert-butyldimethylsilyloxy-4-methoxy-3-n-propylbenzo[b]naphtho[1,2-d]furan]chromium (**3**) and 7-tert-butyldimethylsilyloxy-10-methoxy-8-n-propylbenzo[b]naphtho[2,3-d]furan (**8**)*

Carbene complex **1**: 1.38 g (3.4 mmol); 1-pentyne: 2.71 ml (27.4 mmol); *tert*-butyl methyl ether: 10 ml; trifluoromethanesulfonic acid *tert*-butyldimethylsilyl ester: 3.90 ml (17.0 mmol); 2,6-lutidine: 1.98 ml (17.0 mmol).

*5.6.2.1. Tricarbonyl[(η^6-1,2,3,4,4a,11c)-1-tert-butyldimethylsilyloxy-4-methoxy-3-n-propylbenzo[b]naphtho-[1,2-d]furan]chromium (**3**).* Yield: 0.28 g (0.50 mmol, 15%) of a red solid. $R_f = 0.39$ (petroleum ether–CH_2Cl_2 2:1). IR (petroleum ether, cm^{-1}): $\nu_{CO} = 1961$ (vs, A_1), 1898 (s, E), 1888 (s, E). ^1H-NMR (500 MHz, CD_2Cl_2, ppm): $\delta = 8.59$ (ddd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.4$ Hz, $^5J_{HH} = 0.6$ Hz, 1H, H11), 8.11 (d, $^3J_{HH} = 9.4$ Hz, 1H, H5/6), 7.76 (d, $^3J_{HH} = 9.4$ Hz, 1H, H5/6), 7. 59 (ddd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 1.1$ Hz, $^5J_{HH} = 0.6$ Hz, 1H, H8), 7.52 (td, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.4$ Hz, 1H, H9), 7.43 (td, $^3J_{HH} = 7.6$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, H10), 5.50 (s, 1H, H3), 4.00 (s, 3H, OCH_3), 2.90 (ddd, $^2J_{HH} = 15.9$ Hz, $^3J_{HH} = 12.4$ Hz, $^3J_{HH} = 4.7$ Hz, 1H, $C\underline{H}_2CH_2CH_3$), 2.71 (ddd, $^2J_{HH} = 15.9$ Hz, $^3J_{HH} = 12.1$ Hz, $^3J_{HH} = 5.0$ Hz, 1H, $C\underline{H}_2CH_2CH_3$), 2.07 (m, 1H, $CH_2C\underline{H}_2CH_3$), 1.85 (m, 1H, $CH_2C\underline{H}_2CH_3$), 1.18 (t, $^3J_{HH} = 7.3$ Hz, 3H, $CH_2C\underline{H}_3$), 1.12 (s, 9H, $C(CH_3)_3$), −0.18 (s, 3H, $SiCH_3$), −0.57 (s, 3H, $SiCH_3$). ^{13}C-NMR (125 MHz, CD_2Cl_2, ppm): $\delta = 233.9$ ($Cr(CO)_3$), 155.7, 154.5 (2ArCO), 135.8 (ArC), 128.0, 126.7 (2ArCH), 125.0 (ArC), 123.8, 122.8 (2ArCH), 117.7 (ArC), 116.6, 111.2 (2ArCH), 103.0, 97.2 (ArCCr), 73.6 (ArCHCr), 56.7 (OCH_3), 32.7 ($\underline{C}H_2CH_2CH_3$), 26.5 ($C(\underline{C}H_3)_3$), 21.5 ($\underline{C}H_2CH_3$), 19.0 ($\underline{C}(CH_3)_3$), 14.1 ($CH_2\underline{C}H_3$), −2.3, −4.9 ($Si(CH_3)_2$). EIMS; *m/z* (%): 556 (5) [M^+], 500 (2) [$M^+ - 2CO$], 472 (27) [$M^+ - 3CO$], 420 (100) [$M^+ - Cr(CO)_3$], 363 (87) [$M^+ - Cr(CO)_3 - C(CH_3)_3$], 320 (59) [$M^+ - Cr(CO)_3 - C(CH_3)_3 - CH_2CH_2CH_3$], 305 (25) [$M^+ - Cr(CO)_3 - C(CH_3)_3 - CH_2CH_2CH_3 -$

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

	x	y	z	U_{eq} [a]
C1	2652(2)	2964(2)	5808(2)	27(1)
C2	1688(2)	3679(2)	6264(2)	30(1)
C3	1406(2)	4640(2)	5820(2)	29(1)
C4	2071(2)	4915(2)	4907(2)	26(1)
C4a	3024(2)	4188(2)	4461(2)	22(1)
O5	3789(1)	4324(1)	3546(1)	24(1)
C5a	4627(2)	3426(2)	3390(2)	20(1)
C6	5557(2)	3266(2)	2585(2)	22(1)
C6a	6384(2)	2353(2)	2579(2)	20(1)
C7	7428(2)	2157(2)	1802(2)	20(1)
C8	8362(2)	1420(2)	1900(2)	21(1)
C9	8206(2)	732(2)	2743(2)	21(1)
C10	7159(2)	847(2)	3443(2)	21(1)
C10a	6232(2)	1674(2)	3422(2)	19(1)
C11	5207(2)	1844(2)	4207(2)	21(1)
C11a	4411(2)	2731(2)	4198(2)	21(1)
C11b	3344(2)	3225(2)	4886(2)	22(1)
O71	7544(1)	2803(1)	979(1)	21(1)
Si71	6673(1)	2168(1)	−383(1)	20(1)
C71	4783(2)	1632(2)	−302(2)	29(1)
C72	7247(2)	681(2)	−1324(2)	27(1)
C73	7081(2)	3586(2)	−984(2)	26(1)
C74	8535(2)	3729(2)	−1403(2)	37(1)
C75	5989(3)	3279(3)	−2044(2)	38(1)
C76	7024(3)	4902(2)	−32(2)	38(1)
C81	9593(2)	1416(2)	1197(2)	24(1)
C82	10884(2)	2472(2)	1898(2)	35(1)
C91	9123(2)	−202(2)	2773(2)	26(1)
C92	8616(2)	−1571(2)	1800(2)	32(1)
O101	6962(2)	140(1)	4235(1)	25(1)
C101	7740(3)	883(2)	5376(2)	35(1)

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

CH_3]. HRMS: Calc. for $C_{29}H_{32}O_6SiCr$: 556.1373. Found: 556.1375. Elemental analysis: Calc. for $C_{29}H_{32}O_6SiCr$: C, 62.57; H, 5.79. Found: C, 62.72; H, 5.99%.

*5.6.2.2. 7-tert-Butyldimethylsilyloxy-10-methoxy-8-n-propylbenzo[b]naphtho[2,3-d]furan (**8**).* Yield: 0.21 g (0.50 mmol, 15%) of a white solid. $R_f = 0.68$ (petroleum ether–CH_2Cl_2 2:1). ^{1}H-NMR (500 MHz, $CDCl_3$, ppm): $\delta = 8.77$ (d, $^5J_{HH} = 0.8$ Hz, 1H, H6), 8.10 (d, $^5J_{HH} = 0.8$ Hz, 1H, H11), 8.06 (ddd, $^3J_{HH} = 7.7$ Hz, $^4J_{HH} = 1.3$ Hz, $^5J_{HH} = 0.6$ Hz, 1H, H1), 7.56 (ddd, $^3J_{HH} = 8.2$ Hz, $^4J_{HH} = 0.9$ Hz, $^5J_{HH} = 0.6$ Hz, 1H, H4), 7.47 (td, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.3$ Hz, 1H, H3), 7.35 (td, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 0.9$ Hz, 1H, H2), 6.61 (s, 1H, H9), 4.05 (s, 3H, OCH_3), 2.78 (t, $^3J_{HH} = 7.8$ Hz, 2H, $C\underline{H}_2CH_2CH_3$), 1.70 (tq, $^3J_{HH} = 7.8$ Hz, $^3J_{HH} = 7.4$ Hz, 2H, $C\underline{H}_2CH_3$), 1.17 (s, 9H, $C(CH_3)_3$), 1.00 (t, $^3J_{HH} = 7.4$ Hz, 3H, $CH_2C\underline{H}_3$), 0.22 (s, 6H, $Si(CH_3)_2$). ^{13}C-NMR (125 MHz, $CDCl_3$, ppm): $\delta = 157.6$, 155.1, 150.3, 141.3 (C4a, C5a, C7, C10), 128.9 (ArC), 127.8 (ArCH), 127.0, 124.4, 123.6 (3ArC), 122.7 (ArCH), 122.1 (ArC), 121.2, 113.7, 111.4, 104.2, 102.7 (5ArCH), 55.6 (OCH_3), 33.2 ($\underline{C}H_2CH_2CH_3$), 26.2 ($C(\underline{C}H_3)_3$), 23.7 ($\underline{C}H_2CH_3$), 18.7 ($\underline{C}(CH)_3)_3$), 14.1 ($CH_2\underline{C}H_3$), −3.1 ($Si(CH_3)_2$). EIMS; m/z (%): 420 (100) [M^+], 405 (7) [$M^+ - CH_3$], 363 (22) [$M^+ - C(CH_3)_3$], 320 (18) [$M^+ - C(CH_3)_3 - C_3H_7$], 305 (17) [$M^+ - C(CH_3)_3 - C_3H_7 - CH_3$]. HRMS: Calc. for $C_{26}H_{32}O_3Si$: 420.2121. Found: 420.2121.

*5.6.3. Tricarbonyl[(η^6-1,2,3,4,4a,11c)-2-tert-butyl-1-hydroxy-4-methoxybenzo[b]naphtho[1,2-d]furan]-chromium (**4**) and 8-tert-butyl-7-tert-butyldimethyl-silyloxy-10-methoxybenzo[b]naphtho[2,3-d]furan (**9**)*

Carbene complex **1**: 2.45 g (6.1 mmol); 3,3-dimethyl-1-butyne: 3.71 ml (30.5 mmol); *tert*-butyl methyl ether: 15 ml; *tert*-butyldimethylsilylchloride: 9.19 g (61.0 mmol); Et_3N: 8.48 ml (61.0 mmol).

*5.6.3.1. Tricarbonyl[(η^6-1,2,3,4,4a,11c)-2-tert-butyl-1-hydroxy-4-methoxybenzo[b]naphtho[1,2-d]furan]chromium (**4**).* Yield: 0.65 g (1.42 mmol, 23%) of a red solid. $R_f = 0.73$ (petroleum ether–Et_2O 3:1). IR (CH_2Cl_2, cm^{-1}): $\nu_{CO} = 1951$ (vs, A_1), 1871 (s, br, E). ^{1}H-NMR (500 MHz, CD_2Cl_2, ppm): $\delta = 8.74$ (d, $^3J_{HH} = 8.1$ Hz, 1H, H11), 8.22 (d, $^3J_{HH} = 9.4$ Hz, 1H, H5/6), 7.86 (d, $^3J_{HH} = 9.4$ Hz, 1H, H5/6), 7.72 (d, $^3J_{HH} = 8.2$ Hz, 1H, H8), 7.55 (t, $^3J_{HH} = 7.6$ Hz, 1H, H9/10), 7.47 (t, $^3J_{HH} = 7.7$ Hz, 1H, H10/9), 5.63 (s, 1H, H3), 5.49 (s, 1H, OH), 3.96 (s, 3H, OCH_3), 1.67 (s, 9H, $C(CH_3)_3$). ^{13}C-NMR (125 MHz, CD_2Cl_2, ppm): $\delta = 233.9$ ($Cr(CO)_3$), 127.1, 125.9, 124.5, 123.6, 117.1, 111.9 (6ArCH), 74.0 (ArCHCr), 57.1 OCH_3, 34.2 ($\underline{C}(CH_3)_3$), 30.5 ($C(\underline{C}H_3)_3$). EIMS; m/z (%): 456 (1) [M^+], 400 (1) [$M^+ - 2CO$], 372 (9) [$M^+ - 3CO$], 320 (100) [$M^+ - Cr(CO)_3$], 305 (63) [$M^+ - Cr(CO)_3 - CH_3$], 273 (16) [$M^+ - Cr(CO)_3 - 2CH_3 - OH$]. HRMS: Calc. for $C_{24}H_{20}O_6Cr$: 456.0666. Found: 456.0661.

*5.6.3.2. 8-tert-Butyl-7-tert-butyldimethylsilyloxy-10-methoxybenzo[b]naphtho[2,3-d]furan (**9**).* Yield: 0.51 g (1.16 mmol, 20%) of a white solid. $R_f = 0.80$ (petroleum ether–CH_2Cl_2 6:5). ^{1}H-NMR (250 MHz, $CDCl_3$, ppm): $\delta = 8.70$ (s, 1H, H6), 8.14 (s, 1H, H11), 8.05 (d, $^3J_{HH} = 7.9$ Hz, 1H, H1), 7.55 (d, $^3J_{HH} = 7.9$ Hz, 1H, H4), 7.47 (td, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 1.3$ Hz, 1H, H3), 7.34 (td, $^3J_{HH} = 7.4$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, H2), 6.81 (s, 1H, H9), 4.05 (s, 3H, OCH_3), 1.52 (s, 9H, $C(CH_3)_3$), 1.12 (s, 9H, $C(CH_3)_3$), 0.22 (s, 6H, $Si(CH_3)_2$). ^{13}C-NMR (62.5 MHz, $CDCl_3$, ppm): $\delta = 157.7$, 154.7, 149.4, 141.7 (C4a, C5a, C7, C10), 133.0, 129.4 (2ArC), 127.8 (ArCH), 124.4, 123.7 (2ArC), 122.6 (ArCH), 122.1 (ArC), 121.2, 113.1, 111.4, 103.8, 103.5 (5ArCH), 55.5 (OCH_3), 36.1 ($C\underline{C}(CH_3)_3$), 32.1 ($CC(\underline{C}H_3)_3$, 26.9 ($SiC(\underline{C}H_3)_3$), 19.2 ($Si\underline{C}(CH_3)_3$), −1.3 ($Si(CH_3)_2$). EIMS; m/z (%): 434 (100) [M^+], 419 (18) [$M^+ - CH_3$]. HRMS: Calc. for $C_{27}H_{34}O_3Si$: 434.2277. Found: 434.2271.

*5.6.4. Tricarbonyl[(η^6-1,2,3,4,4a,11c)-1-tert-butyldimethylsilyloxy-4-methoxy-2,3-diphenylbenzo[b]naphtho[1,2-d]furan]chromium (**5**) and tricarbonyl[(η^6-1,2,3,4,4a,11c)-1-hydroxy-4-methoxy-2,3-diphenylbenzo[b]naphtho[1,2-d]furan]chromium (**6**)*

Carbene complex **1**: 1.25 g (3.1 mmol); diphenylacetylene: 0.61 g (3.4 mmol); *tert*-butyl methyl ether: 15 ml; *tert*-butyldimethylsilylchloride: 4.67 g (31.0 mmol); Et_3N: 3.14 ml (31.0 mmol).

*5.6.4.1. Tricarbonyl[(η^6-1,2,3,4,4a,11c)-1-tert-butyldimethylsilyloxy-4-methoxy-2,3-diphenylbenzo[b]naphtho[1,2-d]furan]chromium (**5**).* Yield: 0.03 g (0.04 mmol, 1%) of a red solid and 0.38 g of a **5** containing fraction. $R_f = 0.43$ (petroleum ether–CH_2Cl_2 2:1). IR (petroleum ether, cm^{-1}): $\nu_{CO} = 1961$ (vs, A_1), 1902 (s, E), 1890 (s, E). ^{1}H-NMR (500 MHz, $CDCl_3$, 50 °C, ppm): $\delta = 8.11$ (d, $^3J_{HH} = 9.1$ Hz, 1H, H5/6), 8.07 (d, $^3J_{HH} = 9.1$ Hz, 1H, H5/6), 8.04 (d, $^3J_{HH} = 7.8$ Hz, 1H, H11/8), 7.81 (d, $^3J_{HH} = 8.2$ Hz, 1H, H8/11), 7.57 (t, $^3J_{HH} = 7.8$ Hz, 1H, H9/10), 7.54–7.51 (3H, C_5H_6), 7.49 (t, $^3J_{HH} = 8.2$ Hz, 1H, H10/9), 7.30–7.15 (7H, C_5H_6), 3.72 (s, 3H, OCH_3), 1.03 (s, 9H, $C(CH_3)_3$), -0.02 (s, 3H, $SiCH_3$), -0.37 (s, 3H, $SiCH_3$). ^{13}C-NMR (125 MHz, $CDCl_3$, ppm): $\delta =$ 233.1 ($Cr(CO)_3$), 156.6, 149.9 (C6a, C7a), 134.9, 133.0, 132.8, 132.3, 132.0, 130.4, 130.1, 128.0 (ArCH), 127.9 (ArCH), 127.2 (ArCH), 126.9, 123.6 (ArCH), 123.5, 121.7, 121.1 (ArCH), 120.7 (ArCH), 120.3 (ArCH), 112.3 (22ArC), 108.4, 104.3, 96.9, 93.8 (C2, C3, C4a, C11c), 65.8 (OCH_3), 26.0 ($C(\underline{C}H_3)_3$), 18.8 ($\underline{C}(CH_3)_3$), -3.5, -4.1 ($Si(CH_3)_2$). EIMS; m/z (%): 666 (2) [M^+], 582 (37) [$M^+ - 3CO$], 530 (100) [$M^+ - Cr(CO)_3$], 473 (86) [$M^+ - Cr(CO)_3 - C(CH_3)_3$], 458 (48) [$M^+ - Cr(CO)_3 - C(CH_3)_3 - CH_3$]. HRMS: Calc. for $C_{38}H_{34}O_6SiCr$: 666.1529. Found: 666.1534.

*5.6.4.2. Tricarbonyl[(η^6-1,2,3,4,4a,11c)-1-hydroxy-4-methoxy-2,3-diphenylbenzo[b]naphtho[1,2-d]furan]chromium (**6**).* Yield: 0.52 g (0.94 mmol, 30%) of a red solid. $R_f = 0.37$ (petroleum ether–Et_2O 2:1). IR (CH_2Cl_2, cm^{-1}): $\nu_{CO} = 1957$ (vs, A_1), 1886 (s, br, E). ^{1}H-NMR (500 MHz, acetone-d_6, ppm): $\delta = 8.97$ (d, $^3J_{HH} = 8.4$ Hz, 1H, H11), 8.35 (d, $^3J_{HH} = 9.3$ Hz, 1H, H5/6), 8.15 (d, $^3J_{HH} = 9.7$ Hz, 1H, H5/6), 7.78 (d, $^3J_{HH} = 8.4$ Hz, 1H, H8), 7.60–7.15 (m, 12H, H9, H10, $2C_6H_5$), 3.47 (s, 3H, OCH_3). ^{13}C-NMR (125 MHz, acetone-d_6, ppm): $\delta = 234.2$ ($Cr(CO)_3$), 157.3, 156.1 (C6a, C7a), 134.1, 133.0, 132.6, 132.0, 129.6, 129.5, 129.4, 128.9, 128.8, 128.6, 128.4, 128.3, 128.1, 127.3, 127.2, 126.8, 124.3, 123.6, 119.1, 114.3, 112.4, 112.1 (26ArC), 64.2 (OCH_3). EIMS; m/z (%): 552 (2) [M^+], 468 (54) [$M^+ - 3CO$], 416 (100) [$M^+ - Cr(CO)_3$], 401 (50) [$M^+ - Cr(CO)_3 - CH_3$]. HRMS: Calc. for $C_{32}H_{20}O_6Cr$: 552.0664. Found: 552.0673.

*5.7. General procedure for the haptotropic rearrangement of the tricarbonylchromium complexes **2** and **6** yielding the isomeric complexes **10** and **11***

A solution of the tricarbonylchromium complex in di-*n*-butyl ether was heated to 90 °C. Within 4 h the colour of the solution changed from intense red to bright yellow. The reaction was monitored by IR spectroscopy; upon completion of the rearrangement the solvent was removed and the product was purified by column chromatography at 0 °C.

*5.7.1. Tricarbonyl[(η^6-7a,8,9,10,11,11a)-1-tert-butyldimethylsilyloxy-2,3-diethyl-4-methoxybenzo[b]naphtho[1,2-d]furan]chromium (**10**)*

Tricarbonylchromium complex **2**: 57 mg (100 μmol); di-*n*-butyl ether: 10 ml.

Yield: 12 mg (21 μmol, 21%) of a light red solid. $R_f = 0.54$ (petroleum ether–CH_2Cl_2 5:6). IR (petroleum ether, cm^{-1}): $\nu_{CO} = 1975$ (vs, A_1), 1913 (s, E), 1905 (s, E). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): $\delta = 8.09$ (d, $^3J_{HH} = 9.4$ Hz, 1H, H5/6), 7.51 (d, $^3J_{HH} = 9.4$ Hz, 1H, H5/6), 7.47 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, H11), 6.18 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, H8), 5.56 (td, $^3J_{HH} = 5.9$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, H9/10), 4.99 (td, $^3J_{HH} = 6.3$ Hz, $^4J_{HH} = 1.0$ Hz, 1H, H10/9), 3.93 (s, 3H, OCH_3), 3.09 (dq, $^2J_{HH} = 13.3$ Hz, $^3J_{HH} =$ 7.4 Hz, 1H, CH_2), 2.96 (dq, $^2J_{HH} = 13.3$ Hz, $^3J_{HH} = 7.4$ Hz, 1H, CH_2), 2.75 (dq, $^2J_{HH} = 13.3$ Hz, $^3J_{HH} = 7.4$ Hz, 1H, CH_2), 2.67 (dq, $^2J_{HH} = 13.3$ Hz, $^3J_{HH} = 7.4$ Hz, 1H, CH_2), 1.26 (t, $^3J_{HH} = 7.4$ Hz, 3H, $CH_2C\underline{H}_3$), 1.25 (t, $^3J_{HH} = 7.4$ Hz, 3H, $CH_2C\underline{H}_3$), 1.15 (s, 9H, $C(CH_3)_3$), -0.35 (s, 3H, $SiCH_3$), -0.43 (s, 3H, $SiCH_3$). ^{13}C-NMR (125 MHz, $CDCl_3$, ppm): $\delta = 232.7$ ($Cr(CO)_3$), 157.2, 149.4, 144.2 (C1, C4, C6a), 136.7, 135.1, 132.7, 124.8, 124.6, 121.7, 116.2, 111.2 (8ArC), 97.8 (C11a), 92.8, 91.9, 85.5, 77.2 (C8, C9, C10, C11), 62.7 (OCH_3), 26.8 ($C(\underline{C}H_3)_3$), 21.2, 20.2 ($2CH_2$), 18.9 ($\underline{C}(CH_3)_3$), 15.6, 15.3 ($2CH_2\underline{C}H_3$), -2.2, -5.4 ($Si(CH_3)_2$). EIMS; m/z (%): 570 (9) [M^+], 514 (3) [$M^+ - 2CO$], 486 (49) [$M^+ - 3CO$], 434 (96) [$M^+ - Cr(CO)_3$], 419 (20) [$M^+ - Cr(CO)_3 - CH_3$], 377 (45) [$M^+ - Cr(CO)_3 - C(CH_3)_3$], 348 (63) [$M^+ - Cr(CO)_3 - C(CH_3)_3 - C_2H_5$], 333 (24) [$M^+ - Cr(CO)_3 - C(CH_3)_3 - C_2H_5 - CH_3$]. HRMS: Calc. for $C_{27}H_{34}O_3SiCr$ [$M^+ - 3CO$]: 486.1651. Found: 486.1667 (Table 5).

*5.7.2. Tricarbonyl[(η^6-7a,8,9,10,11,11a)-1-hydroxy-4-methoxy-2,3-diphenylbenzo[b]naphtho[1,2-d]furan]chromium (**11**)*

Tricarbonylchromium complex **6**: 100 mg (181 μmol); di-*n*-butyl ether: 20 ml.

Yield: 2.2 mg (4.0 μmol, 2%) of a yellow solid. $R_f = 0.37$ (petroleum ether–CH_2Cl_2 1:1). IR (petroleum ether, cm^{-1}): $\nu_{CO} = 1975$ (vs, A_1), 1911 (s, E), 1905 (s, E). ^{1}H-NMR (500 MHz, acetone-d_6, ppm): $\delta = 8.40$ (d,

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

	x	y	z	U_{eq} [a]
Cr1	5269(1)	9350(1)	3529(1)	20(1)
C1a	4905(1)	9964(2)	4052(1)	28(1)
O1a	4672(1)	10350(1)	4373(1)	45(1)
C1b	4643(1)	10349(2)	3149(1)	25(1)
O1b	4253(1)	10990(1)	2910(1)	37(1)
C1c	4514(1)	8247(2)	3468(1)	30(1)
O1c	4039(1)	7553(1)	3420(1)	48(1)
C1	6080(1)	5311(2)	4122(1)	19(1)
C2	5836(1)	4246(2)	4278(1)	20(1)
C3	5815(1)	4062(2)	4773(1)	21(1)
C4	6041(1)	4970(2)	5086(1)	21(1)
C4a	6243(1)	6097(2)	4929(1)	20(1)
C5	6448(1)	7023(2)	5265(1)	23(1)
C6	6607(1)	8127(2)	5125(1)	24(1)
C6a	6534(1)	8321(2)	4637(1)	21(1)
O7	6610(1)	9439(1)	4450(1)	23(1)
C7a	6417(1)	9319(2)	3968(1)	21(1)
C8	6380(1)	10259(2)	3646(1)	25(1)
C9	6180(1)	9985(2)	3163(1)	26(1)
C10	5998(1)	8822(2)	3013(1)	25(1)
C11	5986(1)	7911(2)	3346(1)	21(1)
C11a	6235(1)	8139(2)	3836(1)	19(1)
C11b	6335(1)	7486(2)	4286(1)	19(1)
C11c	6225(1)	6290(2)	4431(1)	18(1)
O11	6183(1)	5422(1)	3649(1)	19(1)
Si11	7003(1)	5111(1)	3467(1)	21(1)
C12	7610(1)	6448(2)	3511(1)	29(1)
C13	7508(1)	3959(2)	3859(1)	35(1)
C14	6765(1)	4627(2)	2825(1)	27(1)
C15	6279(2)	5542(2)	2527(1)	45(1)
C16	7500(1)	4490(2)	2620(1)	47(1)
C17	6353(2)	3443(2)	2776(1)	48(1)
C21	5565(1)	3307(2)	3914(1)	26(1)
C22	4812(1)	3620(2)	3621(1)	35(1)
C31	5585(1)	2895(2)	4958(1)	27(1)
C32	6208(1)	1968(2)	4989(1)	37(1)
O41	6015(1)	4833(1)	5568(1)	26(1)
C42	6697(1)	4439(2)	5846(1)	38(1)

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

$^3J_{HH} = 9.2$ Hz, 1H, H5/6), 7.98 (s, 1H, OH), 7.86 (d, $^3J_{HH} = 9.2$ Hz, 1H, H5/6), 7.84 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, H11), 7.32–7.13 (m, 10H, $2C_6H_5$), 6.56 (dd, $^3J_{HH} = 6.9$ Hz, $^4J_{HH} = 0.9$ Hz, 1H, H8), 5.98 (td, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 1.1$ Hz, 1H, H9), 5.29 (td, $^3J_{HH} = 6.4$ Hz, $^4J_{HH} = 0.9$ Hz, 1H, H10), 3.47 (s, 3H, OCH_3). ^{13}C-NMR (125 MHz, acetone-d_6, ppm): $\delta =$ 234.5 ($Cr(CO)_3$), 137.8–112.1 (ArC), 95.8, 95.3, 88.7, 79.3 (C8, C9, C10, C11), 61.9 (OCH_3). EIMS; m/z (%): 416 (6) [$M^+ - Cr(CO)_3$], 400 (100) [$C_{28}H_{16}O_3^+$].

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 168735, 168736, 168737 and 168738 for compounds **1**, **2**, **7** and **10**, respectively. 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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