Tetracyclic Arenes by Benzannulation of Tricyclic Carbene Complexes of Chromium with Alkynes: Chemo-, Regio-, and Stereoselectivity**

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Dedicated to Professsor Wolfgang Steglich on the occasion of his 65th birthday

Abstract: The tricarbonyl chromium complexes **7**–**9** and the tetracyclic arenes **11**–**13** were synthesized from 1-hexyne and the tricyclic chromium carbene complexes **3**–**5**, which are derived from diazo precursors. The nonplanar dibenzocycloheptenylidene complex **4** afforded the benzannulation product S_pM_h/R_pP_h-**8** stereoselectively, as established by NMR spectra and an X-ray crystal structure analysis. The benzannulation failed with the carbene complexes **1** and **2,** presumably due to their reduced propensity for decarbonylation. Upon reaction with 1-hexyne, carbene complex **21**, bearing two electronically different arene substituents, revealed only a low regioselectivity (1.6:1) in favour of chromium complex **22**, which results from the annulation of the less electron-rich arene ring.

Keywords: arenes · benzannulation · carbenes · chromium · helical structures

Introduction

Fischer-type carbene complexes[1] have become valuable tools for stereoselective carbon–carbon bond formation within the last three decades.[2] One of the most important synthetic applications is the reaction of alkenyl- or aryl-substituted alkoxycarbene complexes of chromium with alkynes, which results in the formation of densely functionalized phenols or naphthohydroquinones, respectively, by sequential coupling of the alkyne, the carbene and one carbonyl ligand at a $Cr(CO)_3$ template (Figure 1).[3] This formal [3+2+1] cycloaddition proceeds with considerable regioselectivity in case of alkyne substituents of distinctly different size.[4, 5] Generally, the arene formation is the major reaction path; however, depending both on the substrates and the reaction conditions, other cycloaddition products have been observed as well.[6] The synthetic potential of the benzannulation reaction has been demonstrated in the synthesis of various naturally occuring compounds like vitamins of the E and K series,[7] antibiotics like deoxyfrenolicin,[8] various daunomycinones[9] and fredericamycin.[10] Kinetic studies[11] indicate that the benzannulation reaction starts with a reversible decarbonylation that is followed by coordination of the alkyne to form a tetracarbonyl alkynecarbene complex **A** as the first intermediate.[12, 13] Further support for the mechanism has been provided by isolation and structural characterization of

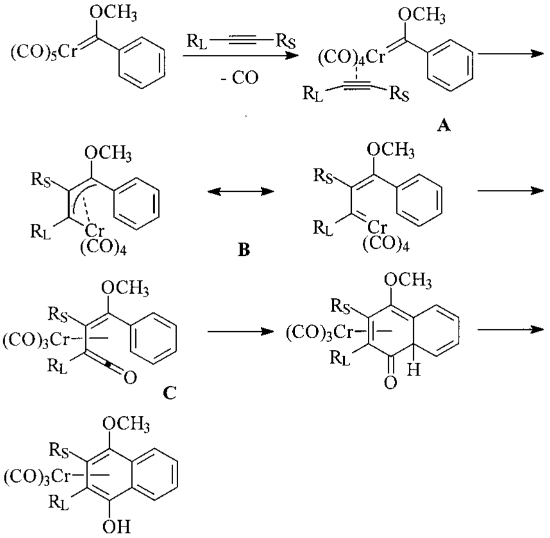

Figure 1. Mechanism of the benzannulation reaction.

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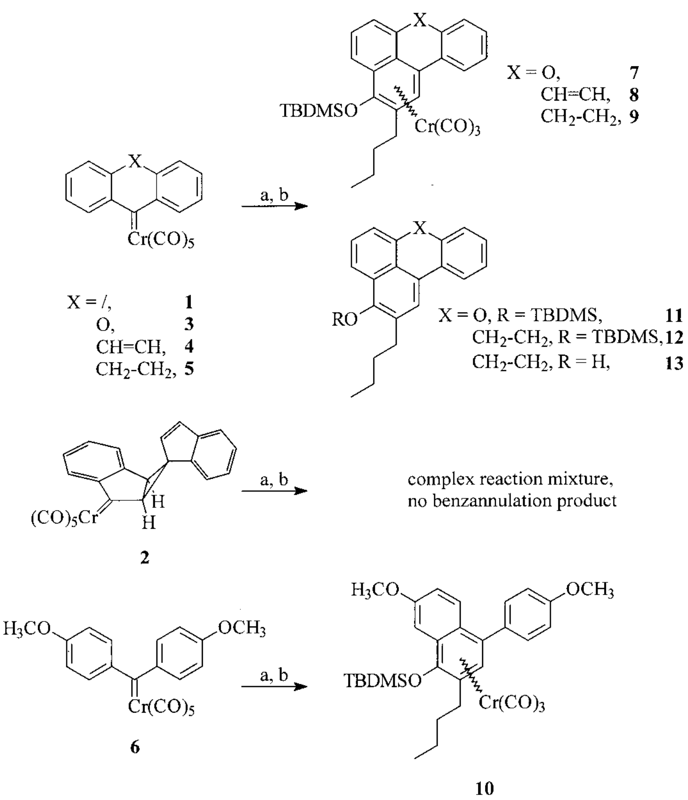
presumed intermediates relevant to **B**[14] and **C**,[15] as well as by extended Hückel molecular orbital (EHMO)[16] and quantum chemical calculations.[17, 18] We recently reported the synthesis and first benzannulation reactions of tricyclic carbene complexes of chromium derived from diazo precursors.[19] We now present a full account of the regio- and stereochemical implications, as well as of the chemoselectivity of this type of reaction.

Results and Discussion

Reactions with 1-hexyne: The chromium carbene complexes **1**–**6**[19] derived from diazo precursors were treated with 1-hexyne (4 equiv) in *tert*-butyl methyl ether at room temperature (reaction of **3** required warming to 40 °C). After consumption of the starting compounds, silylation with NEt_3/*tert*-butyldimethylsilyl chloride (TBDMSCl) and column chromatographic workup, the tricarbonyl chromium complexes **7**–**10** and the tetracyclic arenes **11**–**13** were obtained in good overall yields with complete regioselectivity (Scheme 1, Table 1). Surprisingly, no benzannulation reaction products could be obtained from the reactions of the carbene complexes **1** and **2** under various reaction conditions. Instead, a 78% yield of the formal carbene dimer 9,9′-[bis-(9*H*)-fluorenylidene] (**14**) (see Scheme 2), which results from thermal decomposition of carbene complex **1**,[19] was isolated, while reaction of **2** only gave a complex reaction mixture.[20]

Molecular structure of the tricarbonyl chromium complexes 8 and 9 in solution: Compounds **8** and **9**, obtained from the benzannulation reactions of the carbene complexes **4** and **5**, respectively, with 1-hexyne, contain a plane of chirality and are known to adopt a helical conformation.[21] As a result, two diastereomers may be formed in each case. For the tricarbonyl complex **9**, containing a CH_2–CH_2 bridge, a temperature dependence of the NMR spectra was observed that can be rationalized in terms of a conformational flexibility of the tetracyclic carbon skeleton (Figure 2). The ^{13}C NMR spectrum of **9** measured at 253 K showed all expected resonances as sharp signals. Warming to 298 K led to broadening of some signals, for example, the resonance of the carbonyl groups; moreover, several signals of the arene carbon atoms coordinated to the $Cr(CO)_3$ fragment could not be detected. Further increase in temperature to 323 K resulted in sharp signals once again. This behaviour can be explained by the presence of the thermodynamically more stable S_pM_h/R_pP_h[22] diastereomer at 253 K as a single stereoisomer. At 323 K the interconversion of the helical conformers is fast with respect to the NMR time scale. In the temperature range between 253 and 323 K the interconversion is slow, but the observation of both diastereomers together could not be achieved. The NMR spectra of the annulation product **8** revealed a single set of signals and no temperature dependence of the NMR spectra was observed; this is in accordance with a less pronounced flexibility of the unsaturated seven-membered ring of **8**.



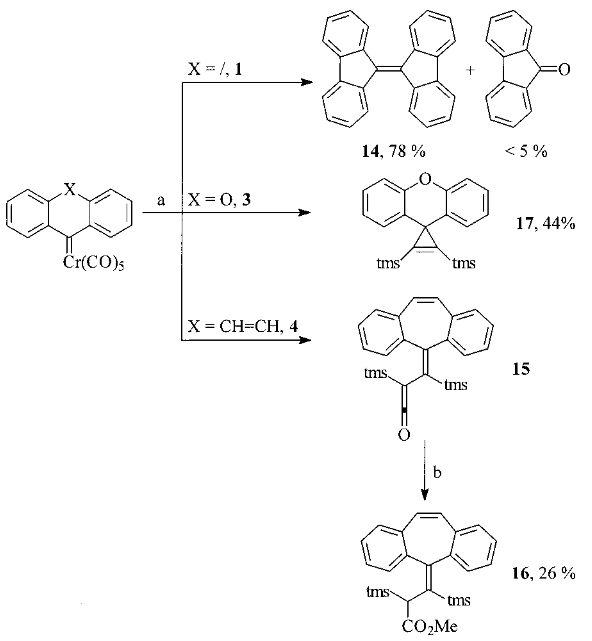
Scheme 1. Reactions of the carbene complexes **1**–**6** with 1-hexyne. Reagents and conditions: a) 1-hexyne (4 equiv), *t*BuOMe, 20 °C (40 °C in case of **3**), 2 h; b) TBDMSCl (4 equiv), NEt_3 (4 equiv), 20 °C, 2 h.

Table 1. Products from the reactions of carbene complexes **1**–**6** with 1-hexyne.

	Products	Yield [%]	Σ [%][a]
1	**14**	78	
2	[b]		
3	**7**	26	68
	11	42	
4	**8**	55	55
5	**9**	27	53[c]
	12	< 5	
	13	26	
6	**10**	62	62

[a] Sum of all benzannulation products. [b] Only an unseparable reaction mixture was obtained. [c] Without **12**.

Abstract in German: *Die aus Diazovorstufen erhaltenen Carbenkomplexe des Chroms* ***3**–**5*** *reagieren mit 1-Hexin unter Benzanellierung zu den tetracyclischen Tricarbonylchromkomplexen* ***7**–**9*** *und den tetracyclischen Arenen* ***11**–**13**. *Anhand der Temperaturabhängigkeit der NMR-Spektren sowie durch eine Röntgenstrukturanalyse konnte die stereoselektive Bildung von* S_pM_h/R_pP_h-***8*** *aus* ***4*** *nachgewiesen werden. Keine Benzanellierung gehen dagegen die Carbenkomplexe* ***1*** *und* ***2*** *mit 1-Hexin ein, was sich durch deren geringere Neigung zur Abspaltung eines Kohlenmonoxidliganden erklären läßt. Bei der Reaktion von 1-Hexin mit dem Carbenkomplex* ***21**, *der zwei elektronisch verschiedene Arylsubstituenten aufweist, trat eine mäßig bevorzugte Anellierung des elektronenärmeren Arylrings ein (****22**:**23*** *= 1.6:1).*



Scheme 2. Reactions of the carbene complexes **1**, **3** and **4** with bis(trimethylsilyl)ethyne. Reagents and conditions: a) tms−C≡C−tms (4 equiv), *t*BuOMe, 20 °C (40 °C in case of **3**), 2 h; b) MeOH, 20 °C, 1 h.

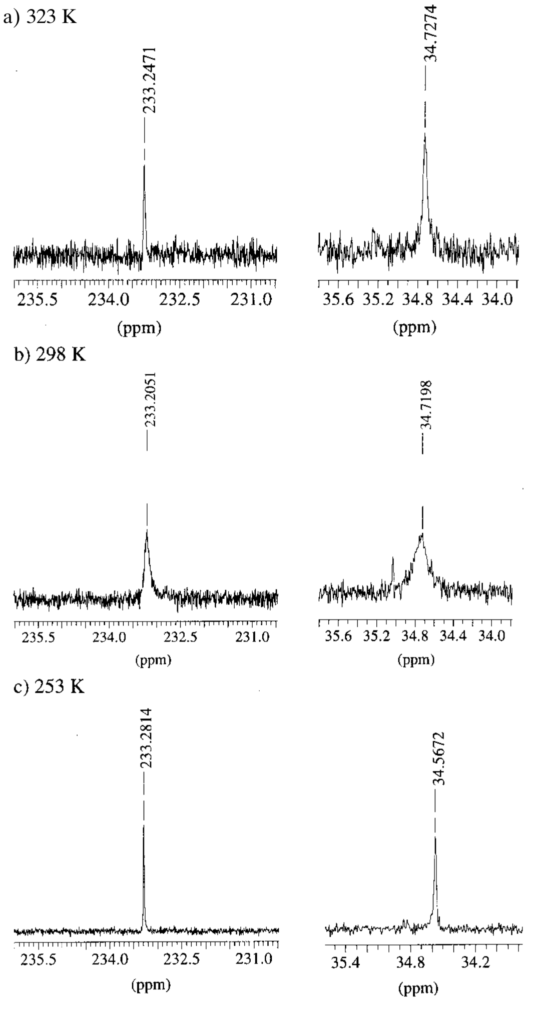
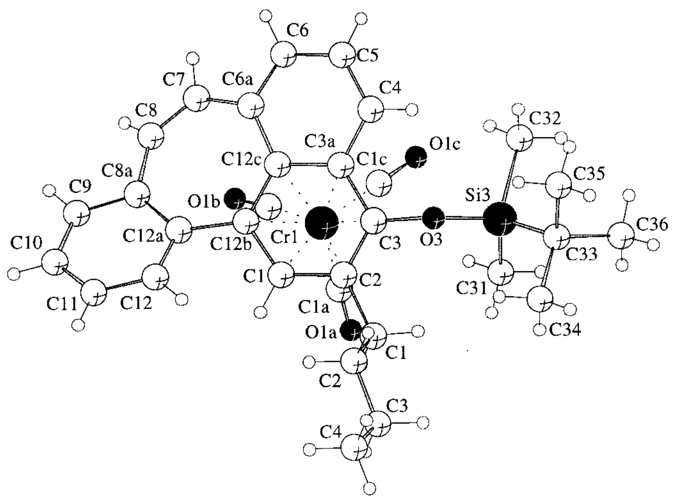


Figure 2. Temperature dependence of the CO (left) and one of the CH_2–CH_2 bridge carbon atoms (right) of chromium complex **9** (125.6 MHz, $CDCl_3$).

X-ray crystal structure of tricarbonyl chromium complex 8: The relative configuration of the benzannulation reaction product **8** in the solid state was unequivocally established by X-ray crystal structure analysis after suitable crystals had been obtained from a saturated solution in *n*-hexane at −28 °C (Figure 3, Table 2). As expected, the tricarbonyl chromium moiety in **8** is coordinated to the sterically less

a) Top view:



b) Side view:

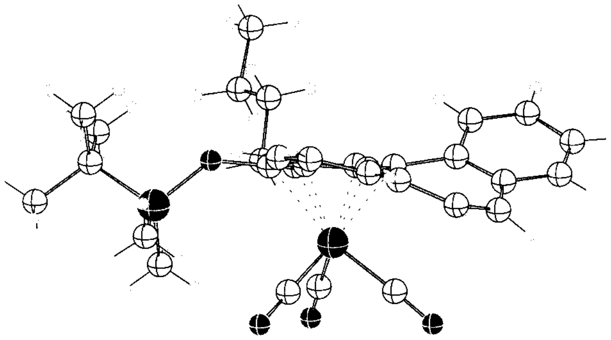


Figure 3. Molecular structure of chromium complex **8**.[23]

Table 2. Selected bond lengths and dihedral angles of **8** (for atom numbering see Figure 3, standard deviations are given in parentheses).

bond lengths [pm]	
Cr1−C1	219.7(6)
Cr1−C2	226.1(7)
Cr1−C3	230.9(8)
Cr1−C3a	233.9(7)
Cr1−C12c	225.8(7)
Cr1−C12b	224.7(7)
dihedral angles [°]	
C1-C12b-C12c-C3a	− 6.5 (0.9)
C3-C3a-C12c-C12b	9.2 (1.0)
C2-C3-C3a-C12c	− 6.5 (1.0)
C3a-C3-C2-C1	1.1 (1.0)
C3-C2-C1-C12b	1.4 (1.0)
C2-C1-C12b-C12c	1.5 (1.0)
C12-C12a-C12b-C1	32.2 (0.9)
C7-C6a-C12c-C12b	− 17.9 (1.1)

crowded face of the carbon skeleton to form the S_pM_h/R_pP_h diastereomer as a single stereoisomer (Figure 3). As already known from related compounds, the tricarbonyl chromium moiety is bound to the arene ring in a staggered conformation in the solid state.[24] In addition, the tricarbonyl chromium fragment is coordinated in a noncentrosymmetric manner and shifted away from the seven-membered ring as indicated by the unequal $\eta\text{-C}_{arene}\text{–Cr}$ bond lengths (Table 2).[25] The diastereoselectivity of the benzannulation reaction of **4**, which does not contain any stereochemical information, can be explained by the reaction mechanism and the structure of the central seven-membered ring of carbene complex **4**. According to theoretical studies,[16–18] the formation of the vinyl carbene complexes $\mathbf{A}_{anti}$ or $\mathbf{A}_{syn}$ represents the side-differentiating step of the reaction mechanism (Figure 4). The rigid nonplanar structure of the 5-(5*H*)-dibenzo[a.d]cycloheptenylidene moiety[26] offers an explanation for the preferred formation of the vinyl carbene complexes $\mathbf{A}_{anti}$ that leads to the benzannulation product **8** with the S_pM_h/R_pP_h stereochemistry.

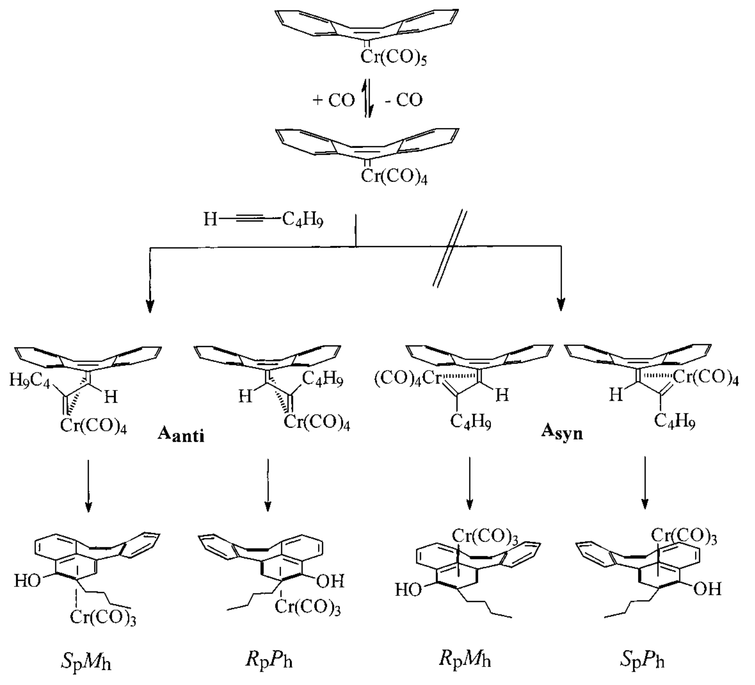
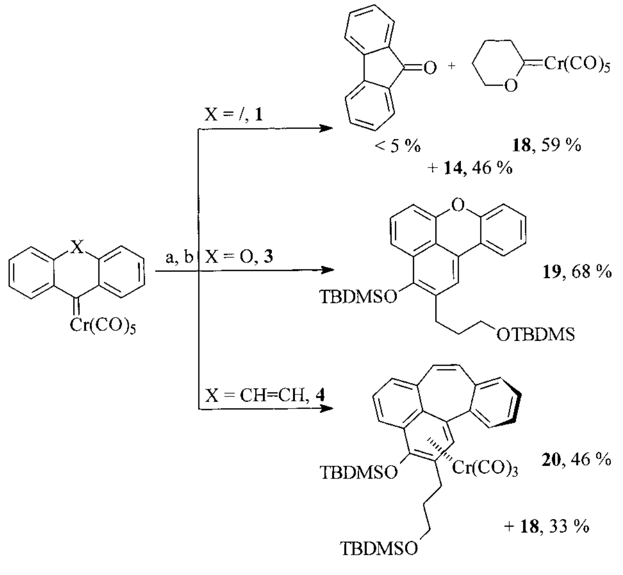


Figure 4. Diastereoselective formation of S_pM_h/R_pP_h-**8**.

Reactions with bis(trimethylsilyl)ethyne and 4-pentyn-1-ol: Two strategies have been applied in order to explain the lack of reactivity of the carbene complexes **1** and **2** towards 1-hexyne. Reaction of the carbene complexes **1**, **3** and **4** with bis(trimethylsilyl)ethyne led only in case of **4** to the expected[15] vinyl ketene **15**, which could not be isolated in pure form (Scheme 2); addition of methanol gave a 26 % yield of methyl ester **16** after purification by preparative HPLC. As with 1-hexyne, only the carbene dimer **14** (82 % yield) could be isolated from the reaction of carbene complex **1** with bis(trimethylsilyl)ethyne along with a small amount of (9*H*)-fluorene-9-one. Surprisingly, reaction of carbene complex **3** gave no vinyl ketene; instead, cyclopropene **17** was obtained in a 44 % yield after sublimation, representing the first example of a cyclopropenation of an alkyne by a chromium carbene complex.[27] The different reactivity of carbene complexes **3** and **4** may be rationalized in terms of the conformative flexibility of the xanthene moiety.[28] As a result, in the presumed vinyl carbene intermediate the α-trimethylsilyl substituent and the xanthene carbon skeleton are occasionally in the same plane. This coplanar conformation imposes a steric strain that may be reduced by an intramolecular rearrangement accompanied by loss of the tetracarbonyl chromium fragment. As a result, the formation of cyclopropene **17** is assumed to be faster than the $\text{C}_{carbene}\text{–C=O}$ coupling leading to a vinyl ketene.

Reaction of 4-pentyn-1-ol with the carbene complexes **1**, **3** and **4** was expected to yield either the benzannulation reaction products or δ-lactones by intramolecular addition of the hydroxy group to the vinyl ketene intermediate. In case of **1**, carbene dimer **14** and (9*H*)-fluorene-9-one were isolated once again along with a 59 % yield of pentacarbonyl(2-oxacyclohexylidene)chromium(0) (**18**), resulting from alkynol cyclization[29] of 4-pentyn-1-ol with the pentacarbonyl chromium fragment, which evolves during the thermal decomposition of carbene complex **1** (Scheme 3). Reaction of the xanthenylidene complex **3** afforded the tetracyclic arene **19** after silylation of the benzannulation product, whereas reaction of **4** gave the chromium tricarbonyl complex **20** along with a 33 % yield of 2-oxacyclohexylidene complex **18**. As in the reaction of carbene complex **4** with 1-hexyne, the benzannulation product **20** is presumed to adopt the S_pM_h/R_pP_h configuration.

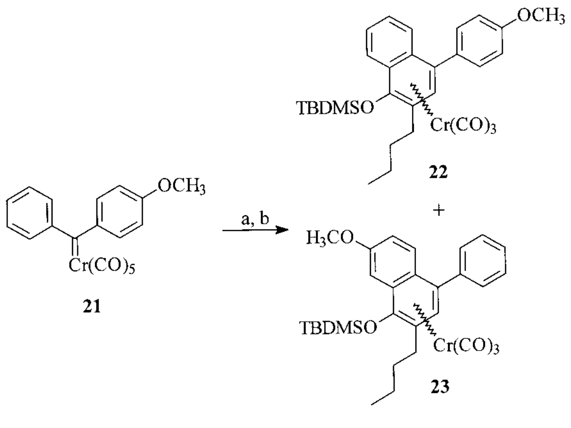
Because no reaction giving evidence for decarbonylation occurred between the carbene complexes **1** and **2** and the



Scheme 3. Reactions of the carbene complexes **1**, **3** and **4** with 4-pentyn-1-ol. Reagents and conditions: a) 4-pentyn-1-ol (4 equiv), *t*BuOMe, 20 °C (40 °C in case of **3**), 2 h; b) TBDMSCl (4 equiv), NEt_3 (4 equiv), 20 °C, 2 h.

alkynes employed, we presume that the diverse reaction behaviour of the carbene complexes **1**–**5** reflects their different propensity for decarbonylation.[30] Assuming a slow rate of carbon monoxide dissociation from the carbene complex **1**, which benefits from a more efficient stabilization (compared with **4**) of the metal carbene moiety as a result of the almost planar carbene ligand,[19] thermal decomposition to yield the carbene dimer **14** is much faster than decarbonylation. In contrast, the nonplanarity of the dibenzo[a.d]cycloheptenylidene ligand of **4** results in an enhanced propensity for decarbonylation, which enables the alkyne coordination that is crucial for the benzannulation reaction. In all reactions of xanthenylidene complex **3**, representing the most stable of the carbene complexes employed, warming to 40 °C was required to achieve decarbonylation; this is in accordance with the electron-donating character of the xanthenylidene ligand.

Reaction of pentacarbonyl[(4-methoxyphenyl)(phenyl)carbene]chromium(0) (21) with 1-hexyne: Studies directed towards the regioselectivity of the formal [3+2+1] cycloaddition reaction of diarylcarbene complexes containing two electronically different arene substituents remain controversial so far.[4a, 31–32] In order to address this aspect of the benzannulation reaction, carbene complex **21** was treated with 1-hexyne. After silylation, the two regioisomeric tricarbonyl complexes (**22** and **23**) were obtained (Scheme 4). The regioselectivity (isomer ratio **22**:**23** = 1.6:1), which was found to be in accordance with a preference for the less electron-rich arene already reported earlier by this group,[31] was very low. The regioisomers **22** and **23** have been assigned on the basis of their ^1H NMR spectra. The spectrum of the major isomer **22** is characterized by an ABCD spin system of the resonances assigned to the protons H5 to H8. In contrast, substitution of proton H6 by a methoxy group results in an ABC spin system in **23** that is characterized by the coupling constant between H5 and H7 ($^4J_{HH}$ = 1.96 Hz).



Scheme 4. Reaction of carbene complex **21** with 1-hexyne. Reagents and conditions: a) 1-hexyne (4 equiv), *t*BuOMe, 20 °C, 2 h; b) TBDMSCl (4 equiv), NEt_3 (4 equiv), 20 °C, 2 h.

In summary, the benzannulation reaction of the tricyclic carbene complexes **3**–**5** provides an efficient synthetic strategy to obtain tetracyclic arenes with a defined substitution pattern on the newly formed arene ring.

Experimental Section

General: All operations were carried out in flame-dried glassware under an atmosphere of argon with standard Schlenk techniques. ^1H and ^{13}C NMR spectra were recorded on Bruker AM250, AM400 and DRX500 spectrometers. All chemical shifts are given relative to TMS as external standard. FT-IR spectra were recorded on a Nicolet Magna 550 spectrometer. MS(EI) and HR-MS(EI) were determined on a Kratos MS-50 spectrometer. Elemental analyses were carried out with an Elementar-analysator CHN-O-Rapid (Heraeus). Melting points were recorded with a Büchi SMP20 and are uncorrected. Thin-layer chromatography (TLC): Merck precoated sheets, $60F_{254}$; column chromatography was performed with Merck silica gel, grade 60 (0.062–0.200 mm).

Starting compounds: Dichloromethane, *tert*-butyl methyl ether, *n*-hexane and petroleum ether (40/60) were dried by distillation from calcium hydride under argon. Liquid starting compounds were degassed by the freeze, pump and thaw technique and stored over molecular sieves (4 Å). The carbene complexes **1**–**6** and **21** were prepared according to published procedures.[19] All other chemicals were used as received from commercial sources.

Crystal structure determination of tricarbonyl chromium complex 8: $C_{31}H_{34}CrO_4Si \cdot 0.25$ hexane, $M = 572.2$, triclinic, space group $P\bar{1}$ (no. 2), red crystals, dimensions $0.05 \times 0.13 \times 0.40$ mm³, $a = 11.787(1)$, $b = 12.912(1)$, $c = 21.191(1)$ Å, $\alpha = 85.06(1)°$, $\beta = 79.17(1)°$, $\gamma = 75.73(1)°$, $V = 3067.3(4)$ mm³, $D_c = 1.24$ Mg m^{-3}, $Z = 4$, μ $(Cu_{K\alpha}) = 3.708$ mm^{-1}, $T = 200(2)$ K, $F(000) = 1210$; 8286 reflections were collected on an Enraf-Nonius CAD4 diffractometer ($2\theta_{max} = 110°$, $-12 \leq h \leq 0$, $-13 \leq k \leq 13$, $-22 \leq l \leq 22$), 7708 symmetry independent reflections ($R_{int} = 0.043$) were used for the structure solution (direct methods)[33] and refinement (full-matrix least squares on F^2,[34] 691 parameters, 58 restraints), non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined with a riding model; $wR_2 = 0.214$ [$R_1 = 0.076$ for $I > 2\sigma(I)$]. An empirical absorption correction was applied.[35] The solvent *n*-hexane was disordered. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101048. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

General procedure for the reactions of carbene complexes 1–6 and 21 with alkynes*:* The carbene complex (1 mmol) was dissolved in *tert*-butyl methyl ether (10 mL) at −20 °C. After addition of the corresponding alkyne (4 mmol) and three cycles of the freeze, pump and thaw technique, the reaction mixture was stirred at room temperature until consumption of the carbene complex was complete (1–2 h, TLC control; the reactions of carbene complex **3** required gentle warming to 40 °C). This was accompanied by a colour change from violet (**1**), red (**2**, **4**–**6**, **21**) or blue (**3**) to orange or colourless. After transferring the reaction mixture by syringe into a Schlenk tube containing TBDMSCl (4 mmol, 0.6 g) and NEt_3 (4 mmol, 0.4 g), the mixture was stirred for another two hours. After removal of the solvent under reduced pressure the residue was separated by column chromatography under argon at −20 °C.

Reaction of pentacarbonyl[9-(9*H*)-fluorenylidene]chromium(0) (1) with 1-hexyne: The reaction of **1** (1 mmol, 0.35 g) with 1-hexyne (4 mmol, 0.33 g) afforded 9,9′-[bis-(9*H*)-fluorenylidene] (**14**) (0.13 g, 0.39 mmol, 78 % with regard to **1**) after column chromatographic workup (eluent: petroleum ether/dichloromethane = 3:1).

*9,9′-[Bis-(9H)-fluorenylidene] (**14**)*: Red crystals, m.p. 186 °C (lit.: 185–187 °C[36]); $R_f = 0.8$ (petroleum ether/dichloromethane = 3:1); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.32$ (t, $^3J_{HH} = 7.82$ Hz, 4H; ArH), 7.40 (t, $^3J_{HH} = 7.43$ Hz, 4H; ArH), 7.70 (d, $^3J_{HH} = 7.43$, 4H; H4, H4′, H5, H5′), 8.32 (d, $^3J_{HH} = 7.82$ Hz, 4H; H1, H1′, H8, H8′); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 119.63$ (4C; ArC_t), 119.82 (2C; C9, C9′), 125.79 (4C; ArC_t), 127.55 (4C;

ArC_t), 129.16 (4 C; ArC_t), 136.51 (4 C; ArC_q), 140.18 (4 C; ArC_q); IR (KBr): $\tilde{\nu}$ = 3055 (m), 1477 (m), 1444 (s, C=C), 1348 (m), 763 (s), 721 cm^{-1} (vs); MS (70 eV, EI): *m/z* (%): 328 (100) [M^+], 300 (10), 163 (15); HR-MS (EI): calcd for $C_{26}H_{16}$: 328.1252; found 328.1247 (100%, [M^+]).

Reaction of *exo*-pentacarbonyl{spiro-(1′′*H*)-indeno-(1′′,1′)-cycloprop[2′,3′-b]-1-(1*H*)-indanylidene}chromium(0) (2) with 1-hexyne: The reaction of **2** (1 mmol, 0.42 g) with 1-hexyne (4 mmol, 0.33 g) followed by column chromatographic workup (eluent: petroleum ether/dichloromethane = 1:1) afforded 0.36 g of an orange mixture of compounds that could not be separated.

Reaction of pentacarbonyl[9-(9*H*)-xanthenylidene]chromium(0) (3) with 1-hexyne: The reaction of **3** (1 mmol, 0.37 g) with 1-hexyne (4 mmol, 0.33 g) at 40 °C afforded an orange solution. Column chromatographic workup (eluent: petroleum ether/dichloromethane = 2:1) gave the benzannulation product **11** (0.17 g, 0.42 mmol, 42%) and the corresponding tricarbonyl chromium complex **7** (0.14 g, 0.26 mmol, 26%).

*2-Butyl-3-tert-butyldimethylsilyloxy-benzo[k.l]xanthene (**11**)*: Colourless crystals; $R_f = 0.9$ (petroleum ether/dichloromethane = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.20$ (s, 6 H; $Si(CH_3)_2$), 0.95 (t, $^3J_{HH} = 7.34$ Hz, 3 H; H4′), 1.11 (s, 9 H; $C(CH_3)_3$), 1.42 (psex, $^3J_{HH} = 7.34$ Hz, 2 H; H3′), 1.64 (pquin, $^3J_{HH} = 7.34$ Hz, 2 H; H2′), 2.76 (t, $^3J_{HH} = 7.34$ Hz, 2 H; H1′), 6.85 (d, $^3J_{HH} = 7.45$ Hz, 1 H; ArH), 7.05 (d, $^3J_{HH} = 8.34$ Hz, 1 H; ArH), 7.07 (t, $^3J_{HH} = 7.95$ Hz, 1 H; ArH), 7.21 (t, $^3J_{HH} = 7.25$ Hz, 1 H; ArH), 7.32 (t, $^3J_{HH} = 7.95$ Hz, 1 H; ArH), 7.45 (s, 1 H; H1), 7.47 (d, $^3J_{HH} = 8.75$ Hz, 1 H; ArH), 7.77 (d, $^3J_{HH} = 7.55$ Hz, 1 H; ArH); ^{13}C NMR (125.6 MHz, $CDCl_3$): $\delta = -3.12$ (2 C; $Si(CH_3)_2$), 14.08 (C4′), 16.69 ($\mathit{C}(CH_3)_3$), 22.69 (C3′), 26.08 (3 C; $C(\mathit{CH}_3)_3$), 30.55 (C2′), 32.60 (C1′), 107.32 (ArC_t), 115.37 (ArC_t), 116.89 (ArC_t), 116.93 (ArC_t), 120.32 (ArC_q), 121.00 (ArC_q), 121.55 (ArC_q), 122.13 (ArC_t), 123.24 (ArC_t), 126.23 (ArC_t), 128.77 (ArC_t), 129.47 (ArC_q), 129.49 (ArC_q), 146.86 (C3), 151.06, 151.54 (2 C; C6a, C6b); MS (70 eV, EI): *m/z* (%): 404 (100) [M^+], 347 (15) [$M^+ - C_4H_9$], 290 (60) [$M^+ - 2\,C_4H_9$], 73 (30) [$Si(CH_3)_3^+$]; HR-MS (EI): calcd for $C_{26}H_{32}O_2Si$: 404.2171; found 404.2167 (100%, [M^+]); $C_{26}H_{32}O_2Si$ (404.62): calcd C 77.18, H 7.91; found C 77.08, H 8.04.

*Tricarbonyl[1-3a:11c-11b-η-(2-butyl-3-tert-butyldimethylsilyloxy-benzo[k.l]xanthene)]chromium(0) (**7**)*: Orange crystals; m.p. 85 °C (decomp); $R_f = 0.45$ (petroleum ether/dichloromethane = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$, 253 K): $\delta = 0.49$ (s, 3 H; $SiCH_3$), 0.52 (s, 3 H; $SiCH_3$), 1.02 (t, $^3J_{HH} = 7.66$ Hz, 3 H; H4′), 1.15 (s, 9 H; $C(CH_3)_3$), 1.5 (psex, $^3J_{HH} = 7.66$ Hz, 2 H; H3′), 1.69 (pquin, $^3J_{HH} = 7.66$ Hz, 2 H; H2′), 2.48 (dt, $^2J_{HH} = 13.55$ Hz, $^3J_{HH} = 7.66$ Hz, 1 H; H1′), 2.85 (dt, $^2J_{HH} = 13.55$ Hz, $^3J_{HH} = 7.66$ Hz, 1 H; H1′), 5.81 (s, 1 H; H1), 6.81 (d, $^3J_{HH} = 6.08$ Hz, 1 H; H6), 7.09 (t, $^3J_{HH} = 7.65$ Hz, 1 H; H10), 7.07 (d, $^3J_{HH} = 7.65$ Hz, 1 H; H8), 7.36 (t, $^3J_{HH} = 7.65$ Hz, 1 H; H9), 7.45 (m, 2 H; H4, H5), 7.69 (d, $^3J_{HH} = 7.64$ Hz, 1 H; H11);[37] ^{13}C NMR (125.6 MHz, $CDCl_3$, 253 K): $\delta = -3.73$ (q; $SiCH_3$), -1.89 (q; $SiCH_3$), 14.14 (q; C4′), 18.76 (s; $\mathit{C}(CH_3)_3$), 22.89 (t; C3′), 25.92 (q, 3 C; $C(\mathit{CH}_3)_3$), 30.28 (t; C2′), 33.06 (t; C1′), 82.30 (d; C1), 92.06 (s; Ar-η-C_q), 92.56 (s; Ar-η-C_q), 104.11 (s; Ar-η-C_q), 104.55 (s; Ar-η-C_q), 108.22 (d; ArC_t), 116.08 (d; ArC_t), 117.15 (d; ArC_t), 117.68 (s; C10a), 122.46 (d; ArC_t), 124.04 (d; ArC_t), 127.53 (s; C3), 130.04 (d; ArC_t), 130.78 (d; ArC_t), 150.64, 151.52 (s, 2 C; C6a, C6b), 233.39 (s; 3C, CO); FT-IR (hexane): $\tilde{\nu}$ = 1963 (vs, C=O, A_1), 1901 (s, C=O, E), 1889 cm^{-1} (sh, C=O, E); MS (70 eV, EI): *m/z* (%): 540 (18) [M^+], 484 (5) [$M^+ - 2\,CO$], 456 (100) [$M^+ - 3\,CO$], 404 (95) [$M^+ - Cr(CO)_3$], 290 (40) [$M^+ - Cr(CO)_3 - 2\,C_4H_9$], 126 (40), 73 (30) [$Si(CH_3)_3^+$], 52 (14) [$Cr^+$]; HR-MS (EI): calcd for $C_{29}H_{32}CrO_5Si$: 540.1424; found 540.1404 (18%, [M^+]).

Reaction of pentacarbonyl{5-(5*H*)-dibenzo[a.d]cycloheptenylidene}chromium(0) (4) with 1-hexyne: The reaction of **4** (1 mmol, 0.38 g) with 1-hexyne (4 mmol, 0.33 g) afforded an orange solution. After silylation and column chromatographic workup (eluent: petroleum ether/dichloromethane = 2:1) 0.30 g S_pM_h/R_pP_h-**8** were obtained.

*S_pM_h/R_pP_h-Tricarbonyl{1-3a:12c-12b-η-(2-butyl-3-tert-butyldimethylsilyloxy-benzo[4,5]cyclohepta[1,2,3-de]naphthalene)}chromium(0) (**8**)*: Orange crystals; m.p. 105–108 °C (decomp), $R_f = 0.55$ (petroleum ether/dichloromethane = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$, 253 K): $\delta = 0.45$ (s, 6 H; $Si(CH_3)_2$), 1.01 (t, $^3J_{HH} = 7.55$ Hz, 3 H; H4′), 1.12 (s, 9 H; $C(CH_3)_3$), 1.51 (m, 2 H; H3′), 1.72 (pquin, $^3J_{HH} = 7.55$ Hz, 2 H; H2′), 2.52 (dt, $^2J_{HH} = 15.51$ Hz, $^3J_{HH} = 7.55$ Hz, 1 H; H1′), 2.82 (dt, $^2J_{HH} = 15.51$ Hz, $^3J_{HH} = 7.55$ Hz, 1 H; H1′), 5.67 (s, 1 H; H1), 6.46 (d, $^3J_{HH} = 12.32$ Hz, 1 H; H7), 6.58 (d, $^3J_{HH} = 12.32$ Hz, 1 H; H8), 7.05 (d, $^3J_{HH} = 6.76$ Hz, 1 H; H6), 7.15 (d, $^3J_{HH} = 6.95$ Hz, 1 H; H9), 7.31 (dd, $^3J_{HH} = 6.76$, 8.74 Hz, 1 H; H5), 7.33–7.37 (m, 2 H; H10, H11), 7.39 (d, $^3J_{HH} = 7.15$ Hz, 1 H; H12), 7.65 (d, $^3J_{HH} = 8.74$ Hz, 1 H; H4);[37] ^{13}C NMR (125.6 MHz, $CDCl_3$, 253 K): $\delta = -3.53$ ($SiCH_3$), -2.04 ($SiCH_3$), 14.23 (C4′), 18.73 ($\mathit{C}(CH_3)_3$), 22.99 (C3′), 25.59 (3 C; $C(\mathit{CH}_3)_3$), 29.97 (C2′), 33.18 (C1′), 93.93 (C1), 103.08 (Ar-η-C_q), 105.06 (Ar-η-C_q), 106.11 (Ar-η-C_q), 106.61 (Ar-η-C_q), 122.63 (C4), 127.74 (C5), 129.42 (C11), 129.76 (C10), 130.24 (C6), 130.69 (C3), 131.16 (C9), 131.89 (C12), 132.66 (C8), 133.75 (C7), 135.83 (ArC_q), 137.13 (ArC_q), 137.29 (ArC_q), 233.68 (3 C; CO);[38] FT-IR (hexane): $\tilde{\nu}$ = 1957 (vs, C=O, A_1), 1894 (s, C=O, E), 1880 cm^{-1} (s, C=O, E); MS (70 eV, EI): *m/z* (%): 550 (8) [M^+], 494 (4) [$M^+ - 2\,CO$], 466 (100) [$M^+ - 3\,CO$], 414 (40) [$M^+ - Cr(CO)_3$], 357 (14) [$M^+ - Cr(CO)_3 - C_4H_9$], 300 (16) [$M^+ - Cr(CO)_3 - 2\,C_4H_9$], 126 (31), 73 (9) [$Si(CH_3)_3^+$], 52 (3) [$Cr^+$]; HR-MS (EI): calcd for $C_{31}H_{34}CrO_4Si$: 550.1631; found 550.1629 (8%, [M^+]); $C_{31}H_{34}CrO_4Si$ (550.69): calcd C 67.61, H 6.22; found C 67.93, H 6.34.

Reaction of pentacarbonyl{5-(5*H*)-dibenzo[a.d]cycloheptylidene}chromium(0) (5) with 1-hexyne: The reaction of **5** (1 mmol, 0.38 g) with 1-hexyne (4 mmol, 0.33 g) afforded an orange reaction mixture. Silylation and column chromatographic workup (eluent: petroleum ether/dichloromethane = 2:1) gave impure 2-butyl-3-*tert*-butyldimethylsilyloxy-7,8-dihydro-benzo[4,5]cyclohepta[1,2,3-de]naphthalene (**12**) (< 5%, identified by mass spectrometry), tricarbonyl chromium complex **9** (0.15 g, 0.27 mmol, 27%) and the thermolabile unprotected tetracyclic benzannulation product **13**[39] (0.08 g, 0.26 mmol, 26%).

*2-Butyl-3-tert-butyldimethylsilyloxy-7,8-dihydro-benzo[4,5]cyclohepta[1,2,3-de]-naphthalene (**12**)*: Colourless oil; $R_f = 0.7$; MS (70 eV, EI): *m/z* (%): 416 (3) [M^+], 359 (3) [$M^+ - C_4H_9$], 302 (100) [$M^+ - 2\,C_4H_9$], 274 (15), 259 (30) [$M^+ - 2\,C_4H_9 - CH_3 - Si$], 245 (19) [$M^+ - C_4H_9 - TBDMS$], 231 (45); HR-MS (EI): calcd for $C_{28}H_{36}OSi$: 416.2535; found 416.2544 (3%, [M^+]).

*Tricarbonyl{1-3a:12c-12b-η-[2-butyl-3-tert-butyldimethylsilyloxy-7,8-dihydrobenzo[4,5]cyclohepta[1,2,3-de]naphthalene]}chromium(0) (**9**)*: Red crystals; m.p. 76 °C (decomp); $R_f = 0.4$ (petroleum ether/dichloromethane = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 0.49$ (s, 3 H; $SiCH_3$), 0.53 (s, 3 H; $SiCH_3$), 0.95 (t, $^3J_{HH} = 7.25$ Hz, 3 H; H4′), 1.13 (s, 9 H; $C(CH_3)_3$), 1.28 (psex, $^3J_{HH} = 7.35$ Hz, 2 H; H3′), 1.62 (m, 2 H; H2′), 2.68 (ddd, $^{2,3}J_{HH} = 5.12$, 11.72, 14.00 Hz, 1 H; H1′), 2.84 (ddd, $^{2,3}J_{HH} = 5.12$, 11.52, 14.11 Hz, 1 H; H1′), 3.01 (br, 2 H; H7 or H8), 3.27 (br, 2 H; H7 or H8), 5.88 (s, 1 H; H1), 6.86 (d, $^3J_{HH} = 6.26$ Hz, 1 H; ArH), 6.99 (d, $^3J_{HH} = 7.35$ Hz, 1 H; ArH), 7.03 (dd, $^3J_{HH} = 6.75$, 8.84 Hz, 1 H; ArH), 7.17 (t, $^3J_{HH} = 6.85$ Hz, 1 H; ArH), 7.23 (t, $^3J_{HH} = 7.63$ Hz, 1 H; ArH), 7.81 (d, $^3J_{HH} = 7.83$ Hz, 1 H; ArH), 8.18 (d, $^3J_{HH} = 8.74$ Hz, 1 H; ArH); ^{13}C NMR (125.6 MHz, $CDCl_3$, 298 K): $\delta = -3.06$ ($SiCH_3$), -2.23 ($SiCH_3$), 13.99 (C4′), 18.94 ($\mathit{C}(CH_3)_3$), 23.00 (C3′), 25.94 (3 C; $C(\mathit{CH}_3)_3$), 29.77 (C2′), 32.72 (C1′), 34.66 (br; C8), 40.03 (C7), 100.97 (Ar-η-C_q), 103.05 (Ar-η-C_q), 125.3 (ArC_t), 125.45 (ArC_t), 126.86 (ArC_t), 127.18 (ArC_t), 127.93 (ArC_t), 128.68 (ArC_t), 132.24 (ArC_t), 137.44 (ArC_q), 141.19 (ArC_q), 143.49 (ArC_q), 233.23 (3 C; CO); ^{13}C NMR (125.6 MHz, $CDCl_3$, 253 K): $\delta = -3.45$ ($SiCH_3$), -2.24 ($SiCH_3$), 14.15 (C4′), 18.82 ($\mathit{C}(CH_3)_3$), 22.97 (C3′), 25.71 (3 C; $C(\mathit{CH}_3)_3$), 29.54 (C2′), 32.98 (C1′), 34.56 (C8), 39.83 (C7), 100.97 (Ar-η-C_q), 101.32 (Ar-η-C_q), 102.51 (C1), 103.28 (Ar-η-C_q), 106.48 (Ar-η-C_q), 124.97 (ArC_t), 125.76 (ArC_t), 126.79 (ArC_t), 127.01 (ArC_t), 127.84 (ArC_t), 128.72 (ArC_t), 130.62 (C3), 132.29 (ArC_t), 137.21 (ArC_q), 141.16 (ArC_q), 143.28 (ArC_q), 233.28 (3 C; CO);[40] FT-IR (KBr): $\tilde{\nu}$ = 2958 (m), 2927 (m), 2858 (m), 1952 (vs, C=O, A_1), 1880 (vs, C=O, E), 1849 (vs, C=O, E), 1460 (m, C=C), 1363 (m), 1261 (m), 1103 (m, Si-O-C), 864 (m), 804 cm^{-1} (m); MS (70 eV, EI): *m/z* (%): 552 (0.3) [M^+], 496 (0.2) [$M^+ - 2\,CO$], 468 (33) [$M^+ - 3\,CO$], 416 (100) [$M^+ - Cr(CO)_3$], 359 (32) [$M^+ - Cr(CO)_3 - C_4H_9$], 302 (40) [$M^+ - Cr(CO)_3 - 2\,C_4H_9$], 287 (20) [$M^+ - Cr(CO)_3 - C_4H_9 - CH_3$], 84 (20) [$C_4H_8Si^+$], 73 (22) [$Si(CH_3)_3^+$]; HR-MS (EI): calcd for $C_{31}H_{36}CrO_4Si$: 552.1788; found 552.1787 (0.3%, [M^+]); $C_{31}H_{36}CrO_4Si$ (552.71): calcd C 67.37; H 6.57; found C 66.59, H 6.56.

*2-Butyl-7,8-dihydro-3-hydroxybenzo[4,5]cyclohepta[1,2,3-de]naphthalene (**13**)*: Colourless unstable solid; $R_f = 0.25$ (petroleum ether/dichloromethane = 2:1); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 0.92$ (t, $^3J_{HH} = 7.50$ Hz, 3 H; H4′), 1.31 (psex, $^3J_{HH} = 7.50$ Hz, 2 H; H3′), 1.55 (pquin, $^3J_{HH} = 7.50$ Hz, 2 H; H2′), 2.52 (t, $^3J_{HH} = 7.50$ Hz, 2 H; H1′), 3.06 (br, 2 H; H7 or H8), 3.28 (br, 2 H; H7 or H8), 4.86 (s, 1 H; OH), 7.14 (d, $^3J_{HH} = 7.25$ Hz, 1 H; ArH), 7.18 (d, $^3J_{HH} = 6.85$ Hz, 1 H; ArH), 7.27–7.29 (m, 1 H; ArH), 7.34 (t, $^3J_{HH} = 8.09$ Hz, 1 H; ArH), 7.35 (t, $^3J_{HH} = 7.91$ Hz, 1 H; ArH), 7.54 (s, 1 H; H1), 7.69 (d, $^3J_{HH} = 7.65$ Hz, 1 H; ArH), 8.39 (d, $^3J_{HH} = 8.35$ Hz, 1 H; ArH);

^{13}C NMR (125.6 MHz, C_6D_6): $\delta = 14.12$ (C4′), 22.79 (C3′), 29.69 (C2′), 32.36 (C1′), 35.33 (C8), 40.33 (C7), 120.64 (ArC_t), 121.39 (ArC_q), 124.49 (ArC_t), 126.54 (ArC_q), 126.72 (ArC_t), 127.04 (ArC_t), 127.11 (ArC_t), 127.75 (ArC_t), 131.12 (ArC_q), 131.42 (ArC_q), 132.19 (ArC_t), 133.31 (ArC_t), 140.43 (ArC_q), 141.86 (ArC_q), 143.77 (ArC_q), 149.31 (C3); FT-IR (KBr): $\tilde{\nu} = 3566$ (m, O–H), 3022 (m), 2953 (m), 2926 (m), 2853 (m), 1598 (w), 1504 (w), 1377 (w), 1171 (m), 770 (s), 752 cm^{-1} (m); MS (70 eV, EI): *m/z* (%): 302 (100) [M^+], 287 (5) [$M^+ - CH_3$], 259 (38) [$M^+ - C_3H_7$], 245 (18) [$M^+ - C_4H_9$], 231 (14) [$M^+ - C_4H_9 - CH_2$], 215 (20), 202 (8); HR-MS (EI): calcd for $C_{22}H_{22}O$: 302.1671, found 302.1672 (100%, [M^+]).

Reaction of pentacarbonyl[bis(4-methoxyphenyl)carbene]chromium(0) (6) with 1-hexyne: The reaction of **6** (1 mmol, 0.42 g) with 1-hexyne (4 mmol, 0.33 g) gave tricarbonyl chromium complex **10** (0.36 g, 0.62 mmol, 62%) after silylation and column chromatographic workup (eluent: petroleum ether/dichloromethane = 1:1).

*Tricarbonyl{1-4a:8a-η-[3-butyl-4-tert-butyldimethylsilyloxy-6-methoxy-1-(4′-methoxy)phenyl-naphthalene]}chromium(0) (**10**)*: Red crystals; $R_f = 0.6$ (petroleum ether/dichloromethane = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.52$ (s, 3H; $SiCH_3$), 0.58 (s, 3H; $SiCH_3$), 0.97 (t, $^3J_{HH} = 7.52$ Hz, 3H; H4″), 1.18 (s, 9H; $C(CH_3)_3$), 1.49 (psex, $^3J_{HH} = 7.52$ Hz, 2H; H3″), 1.68 (pquin, $^3J_{HH} = 7.52$ Hz, 2H; H2″), 2.58 (dt, $^2J_{HH} = 15.51$ Hz, $^3J_{HH} = 7.52$ Hz, 1H; H1″), 2.87 (dt, $^2J_{HH} = 15.51$ Hz, $^3J_{HH} = 7.52$ Hz, 1H; H1″), 3.89 (s, 3H; OCH_3), 3.95 (s, 3H; OCH_3), 5.48 (s, 1H; H2), 7.04 (d, $^3J_{HH} = 8.54$ Hz, 2H; H3′, H5′), 7.06 (dd, $^3J_{HH} = 9.49$ Hz, $^4J_{HH} = 2.53$ Hz, 1H; H7), 7.15 (d, $^4J_{HH} = 2.53$ Hz, 1H; H5), 7.57 (br, 2H; H2′, H6′), 7.73 (d, $^3J_{HH} = 9.49$ Hz, 1H; H8); ^{13}C NMR (125.6 MHz, $CDCl_3$): $\delta = -3.07$ ($SiCH_3$), -1.69 ($SiCH_3$), 13.97 (C4″), 18.88 ($\mathit{C}(CH_3)_3$), 22.88 (C3″), 25.84 (3C; $C(\mathit{CH}_3)_3$), 29.99 (C2″), 32.71 (C1″), 55.37 (OCH_3), 55.52 (OCH_3), 95.61 (C2), 99.85 (Ar-η-C_q), 100.35 (C5), 102.05 (Ar-η-C_q), 105.25 (Ar-η-C_q), 107.80 (Ar-η-C_q), 113.89 (2C; C3′, C5′), 122.42 (C7), 128.02 (C4), 129.72 (C8), 129.89 (C1′), 132.16 (2C; C2′, C6′), 158.77, 159.76 (2C; C6, C4′), 233.94 (3C; CO);[38] FT-IR (hexane): $\tilde{\nu} = 1956$ (vs, C=O, A_1), 1889 (s, C=O, E), 1876 cm^{-1} (s, C=O, E); MS (70 eV, EI): *m/z* (%): 586 (9) [M^+], 530 (2) [$M^+ - 2CO$], 502 (100) [$M^+ - 3CO$], 450 (78) [$M^+ - Cr(CO)_3$], 393 (109 [$M^+ - Cr(CO)_3 - C_4H_9$], 336 (26) [$M^+ - Cr(CO)_3 - 2C_4H_9$], 126 (29), 73 (53) [$Si(CH_3)_3^+$], 52 (25) [Cr^+]; HR-MS (EI): calcd for $C_{31}H_{38}CrO_6Si$: 586.1843; found 586.1843 (9%, [M^+]); $C_{31}H_{38}CrO_6Si$ (586.72): calcd C 63.46, H 6.53; found C 63.53, H 6.57.

Reaction of pentacarbonyl[9-(9*H*)-fluorenylidene]chromium(0) (1) with bis(trimethylsilyl)ethyne: The reaction of **1** (1 mmol, 0.35 g) with bis(trimethylsilyl)ethyne (4 mmol, 0.68 g) afforded 9,9′-[bis-(9*H*)-fluorenylidene] (**14**) (0.14 g, 0.41 mmol, 82% with regard to **1**) and a small amount of (9*H*)-fluorene-9-one (<5%) after column chromatographic workup (eluent: petroleum ether/dichloromethane = 3:1).

Reaction of pentacarbonyl[9-(9*H*)-xanthenylidene]chromium(0) (3) with bis(trimethylsilyl)ethyne: The reaction of **3** (1 mmol, 0.37 g) with bis(trimethylsilyl)ethyne (4 mmol, 0.68 g) afforded a pale yellow reaction mixture. Column chromatographic workup (eluent: petroleum ether/dichloromethane = 2:1) followed by sublimation gave cyclopropene **17** (0.15 g, 0.44 mmol, 44%).

*2,3-Bis(trimethylsilyl)-spiro{cyclopropene[1.9′]-(9′H)-xanthene} (**17**)*: Pale yellow crystals; m.p. 85 °C; $R_f = 0.6$; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.17$ (s, 18H; $2 \times Si(CH_3)_3$), 6.57 (d, $^3J_{HH} = 6.86$ Hz, 2H; ArH), 6.85–6.93 (m, 4H; ArH), 7.00–7.05 (m, 2H; ArH); ^{13}C NMR (125.6 MHz, $CDCl_3$): $\delta = -0.68$ (6C; $2 \times Si(CH_3)_3$), 29.79 (C1), 115.12 (2C; ArC_t), 122.10 (2C; C2, C3), 122.29 (2C; ArC_t), 124.38 (2C; ArC_t), 125.73 (2C; ArC_t), 131.87 (2C; C8a′, C9a′), 153.25 (2C; C4a′, C4b′); FT-IR (KBr): $\tilde{\nu} = 3037$ (w), 2960 (w), 1728 (m), 1483 (s), 1446, (s), 1261 (vs), 847 (vs), 760 cm^{-1} (vs); MS (70 eV, EI): *m/z* (%): 350 (45) [M^+], 335 (3) [$M^+ - CH_3$], 277 (80) [$M^+ - Si(CH_3)_3$], 262 (85) [$M^+ - Si(CH_3)_3 - CH_3$], 247 (5) [$M^+ - Si(CH_3)_3 - 2CH_3$], 73 (100) [$Si(CH_3)_3^+$]; HR-MS (EI): calcd for $C_{21}H_{26}OSi_2$: 350.1522; found 350.1519 (45%, [M^+]); $C_{21}H_{26}OSi_2$ (350.61): calcd C 71.94, H 7.47; found C 71.89, H 7.79.

Reaction of pentacarbonyl{5-(5*H*)-dibenzo[a.d]cycloheptenylidene}chromium(0) (4) with bis(trimethylsilyl)ethyne: The reaction of **4** (1 mmol, 0.38 g) with bis(trimethylsilyl)ethyne (4 mmol, 0.68 g) afforded a colourless reaction mixture. Column chromatographic workup (eluent: petroleum ether/dichloromethane = 5:1) gave impure vinyl ketene **15** as colourless solid. After dissolving in CH_2Cl_2 (20 mL) and addition of methanol (1 mL) the reaction mixture was strirred at room temperature for one hour. Separation by preparative HPLC (*n*-hexane/diethyl ether = 95:5) gave methyl ester **16** (0.11 g, 0.26 mmol, 22%).

*{[5′-(5′H)-Dibenzo[a.d]cycloheptenylidene]trimethylsilyl}methyltrimethylsilylketene (**15**)*: $R_f = 0.4$ (dichloromethane); FT-IR (KBr): $\tilde{\nu} = 2954$ (m), 2923 (m), 2853 (m), 2077 (vs, C=C=O), 1257 (s), 842.9 (vs), 802 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 388 (18) [M^+], 360 (40) [$M^+ - CO$], 287 (35) [$M^+ - CO - Si(CH_3)_3$], 272 (100) [$M^+ - CO - Si(CH_3)_3 - CH_3$], 218 (27), 73 (88) [$Si(CH_3)_3^+$]; HR-MS (EI): calcd for $C_{24}H_{28}OSi_2$: 388.1679; found 388.1680 (18%, [M^+]).

*Methyl-2,3-bis(trimethylsilyl)-3-{5′-(5′H)-dibenzo[a.d]cycloheptenylidene}-propionate (**16**)*: Colourless solid; m.p. 101 °C; $R_f = 0.55$ (petroleum ether/diethyl ether = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -0.22$ (s, 9H; $Si(CH_3)_3$), -0.17 (s, 9H; $Si(CH_3)_3$), 3.67 (s, 3H; OCH_3), 4.04 (s, 1H; H2), 6.93 (d, $^3J_{HH} = 11.68$ Hz, 1H; H_{alkene}), 6.98 (d, $^3J_{HH} = 11.68$ Hz, 1H; H_{alkene}), 7.19 (d, $^3J_{HH} = 7.63$ Hz, 1H; ArH), 7.23 (t, $^3J_{HH} = 7.55$ Hz, 1H; ArH), 7.26–7.28 (m, 2H; ArH), 7.32–7.39 (m, 4H; ArH); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = -0.15$ (3C; $Si(CH_3)_3$), 2.19 (3C; $Si(CH_3)_3$), 42.77 (C2), 50.92 (OCH_3), 126.33 (ArC_t), 126.89 (ArC_t), 127.16 (ArC_t), 127.60 (ArC_t), 128.03 (ArC_t), 128.32 (ArC_t), 128.50 (2C; ArC_t), 131.14 (ArC_t), 131.35 (ArC_t), 133.79 (ArC_q), 135.01 (ArC_q), 137.95 (ArC_q), 139.49 (ArC_q), 141.13 (ArC_q), 149.41 (ArC_q), 175.19 (C=O); FT-IR (KBr): $\tilde{\nu} = 3063$ (m), 3013 (m), 2949 (m), 2897 (m), 1724 (s), 1703 (vs, C=O), 1433 (m), 1246 (vs), 843 (vs), 791 cm^{-1} (m); MS (70 eV, EI): *m/z* (%): 420 (35) [M^+], 405 (25) [$M^+ - CH_3$], 316 (28) [$M^+ - OCH_3 - Si(CH_3)_3$], 301 (20) [$M^+ - OCH_3 - Si(CH_3)_3 - CH_3$], 287 (10) [$M^+ - OCH_3 - Si(CH_3)_3 - CHO$], 272 (26) [$M^+ - OCH_3 - Si(CH_3)_3 - CHO - CH_3$], 215 (80) [$M^+ - OCH_3 - CO - 2Si(CH_3)_3$], 147 (30), 89 (20), 73 (100) [$Si(CH_3)_3^+$]; HR-MS (EI): calcd for $C_{25}H_{32}O_2Si_2$: 420.1941; found 420.1949 (35%, [M^+]); $C_{25}H_{32}O_2Si_2$ (420.7): calcd C 71.38, H 7.67; found C 71.26, H 7.71.

Reaction of pentacarbonyl[9-(9*H*)-fluorenylidene]chromium(0) (1) with 4-pentyn-1-ol: The reaction of **1** (1 mmol, 0.35 g) with 4-pentyn-1-ol (4 mmol, 0.33g) afforded **14** (0.075 g, 0.23 mmol, 46% with regard to **1**) and 2-oxacyclohexylidene complex **18** (0.16 g, 0.59 mmol, 59%) after column chromatographic workup (eluent: petroleum ether/dichloromethane = 3:1).

*Pentacarbonyl(2-oxacyclohexylidene)chromium(0) (**18**)*: Orange crystals; m.p. 48 °C (decomp); $R_f = 0.5$ (petroleum ether/dichloromethane = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.65$ (pquin, $^3J_{HH} = 7.13$ Hz, 2H; CH_2), 1.87 (pquin, $^3J_{HH} = 6.68$ Hz, 2H; CH_2), 3.49 (t, $^3J_{HH} = 6.85$ Hz, 2H; H6), 4.62 (t, $^3J_{HH} = 5.96$ Hz, 2H; H3); ^{13}C NMR (125.6 MHz, $CDCl_3$): $\delta = 15.7$ (CH_2), 21.3 (CH_2), 52.8 (C6), 74.9 (C3), 216.6 (4C; CO_{cis}), 224.1 (1C; CO_{trans}), 355.7 (1C; $C_{carbene}$); FT-IR (hexane): $\tilde{\nu} = 2063$ (m, C=O, A_1), 1986 (w, C=O, B), 1944 cm^{-1} (vs, C=O, E, A_1); MS (70 eV, EI): *m/z* (%): 276 (25) [M^+], 248 (12) [$M^+ - CO$], 220 (8) [$M^+ - 2CO$], 192 (12) [$M^+ - 3CO$], 164 (24) [$M^+ - 4CO$], 136 (90) [$M^+ - 5CO$], 108 (12), 80 (22), 52 (100) [Cr^+]; $C_{10}H_8CrO_6$ (276.17): calcd C 43.49, H 2.92; found C 43.44, H 3.09.

Reaction of pentacarbonyl[9-(9*H*)-xanthenylidene]chromium(0) (3) with 4-pentyn-1-ol: The reaction of **3** (1 mmol, 0.37 g) with 4-pentyn-1-ol afforded a pale yellow reaction mixture. In situ silylation and column chromatographic workup (eluent: petroleum ether/dichloromethane = 2:1) gave the benzannulation product **19** (0.12 g, 0.24 mmol, 68%) as a yellow oil, which slowly decomposed even at −38 °C.[39]

*2-(3-tert-Butyldimethylsilyloxy)propyl-3-tert-butyldimethylsilyloxybenzo[k.l]xanthene (**19**)*: Yellow unstable oil; $R_f = 0.5$ (petroleum ether/dichloromethane = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.06$ (s, 6H; $Si(CH_3)_2$), 0.19 (s, 6H; $Si(CH_3)_2$), 0.92 (s, 9H; $C(CH_3)_3$), 1.11 (s, 9H; $C(CH_3)_3$), 1.87 (m, 2H; H2′), 2.82 (m, 2H; H1′), 3.66 (t, $^3J_{HH} = 6.31$ Hz, 2H; H3′), 6.84 (d, $^3J_{HH} = 7.65$ Hz, 1H; ArH), 7.04 (d, $^3J_{HH} = 8.12$ Hz, 1H; ArH), 7.07 (t, $^3J_{HH} = 7.75$ Hz, 1H; ArH), 7.20 (t, $^3J_{HH} = 7.75$ Hz, 1H; ArH), 7.29 (t, $^3J_{HH} = 8.05$ Hz, 1H; ArH), 7.46 (s, 1H; H1), 7.47 (d, $^3J_{HH} = 8.49$ Hz, 1H; ArH), 7.78 (d, $^3J_{HH} = 7.35$ Hz, 1H; ArH); ^{13}C NMR (125.6 MHz, $CDCl_3$): $\delta = -5.26$ (2C; $Si(CH_3)_2$), -3.07 (2C; $Si(CH_3)_2$), 18.40 ($\mathit{C}(CH_3)_3$), 18.71 ($\mathit{C}(CH_3)_3$), 26.02 (3C; $C(\mathit{CH}_3)_3$), 26.12 (3C; $C(\mathit{CH}_3)_3$), 27.28 (C2′), 33.30 (C1′), 62.80 (C3′), 107.39 (ArC_t), 115.34 (ArC_t), 116.94 (2C; ArC_t), 120.37 (ArC_q), 120.96 (ArC_q), 121.62 (ArC_q), 122.15 (ArC_t), 123.27 (ArC_t), 126.26 (ArC_t), 128.07 (ArC_q), 128.80 (ArC_t), 129.52 (ArC_q), 146.99 (C3), 151.06, 151.52 (C6a, C6b); FT-IR (film): $\tilde{\nu} = 2954$ (s), 2929 (s), 2858 (s), 1600 (m), 1485 (s), 1402 (s), 1263 (vs, CO-Si), 1108 (s), 966 (s), 843 (vs), 768 cm^{-1} (s); MS (70 eV, EI): *m/z* (%): 520 (100) [M^+], 505 (2) [$M^+ - CH_3$], 463 (5) [$M^+ - C_4H_9$], 348 (12) [$M^+ - C_4H_9 - TBDMS$], 147 (20), 73 (50)

$[Si(CH_3)_3^+]$; HR-MS (EI): calcd for $C_{31}H_{44}O_3Si_2$: 520.2829; found 520.2821 (100 %, $[M^+]$).

Reaction of pentacarbonyl{5-(5*H*)-dibenzo[a.d]cycloheptenylidene}chromium(0) (4) with 4-pentyn-1-ol: The reaction of **4** (1 mmol, 0.38 g) with 4-pentyn-1-ol (4 mmol, 0.33 g) afforded an orange reaction mixture. Silylation followed by column chromatographic workup (eluent: petroleum ether/dichloromethaner = 2:1) gave carbene complex **18** (0.09 g, 0.33 mmol, 33 %) and tricarbonyl chromium complex **20** (0.30 g, 0.46 mmol, 46 %).

*Tricarbonyl{1-3a:12c-12b-η-[2-(3-tert-butyldimethylsilyloxy)propyl-3-tert-butyldimethylsilyloxybenzo[4,5]cyclohepta[1,2,3-de]naphthalene]}chromium(0) (**20**)*: Red crystals; m.p. 84 °C (decomp); $R_f = 0.5$ (petroleum ether/dichloromethane = 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.09$ (s, 6H; $Si(CH_3)_2$), 0.43 (s, 3H; $SiCH_3$), 0.44 (s, 3H; $SiCH_3$), 0.93 (s, 9H; $C(CH_3)_3$), 1.12 (s, 9H; $C(CH_3)_3$), 1.98 (m, 2H; H2′), 2.69 (ddd, $^{2,3}J_{HH} = 6.66$, 9.79, 14.62 Hz, 1H; H1′), 2.89 (ddd, $^{2,3}J_{HH} = 5.49$, 9.51, 14.62 Hz, 1H; H1′), 3.79 (m, 2H; H3′), 5.72 (s, 1H; H1), 6.42 (d, $^3J_{HH} = 12.27$ Hz, 1H; H7 or H8), 6.52 (d, $^3J_{HH} = 12.27$ Hz, 1H; H7 or H8), 7.01 (d, $^3J_{HH} = 6.76$ Hz, 1H; ArH), 7.10 (d, $^3J_{HH} = 6.56$ Hz, 1H; ArH), 7.20–7.30 (m, 3H; ArH), 7.41 (d, $^3J_{HH} = 7.26$ Hz, 1H; ArH), 7.66 (d, $^3J_{HH} = 8.64$ Hz, 1H; ArH); ^{13}C NMR (125.6 MHz, $CDCl_3$): $\delta = -5.26$ ($SiCH_3$), -5.25 ($SiCH_3$), -3.04 ($SiCH_3$), -1.99 ($SiCH_3$), 18.39 ($\mathit{C}(CH_3)_3$), 18.87 ($\mathit{C}(CH_3)_3$), 25.94 (3C; $C(\mathit{CH}_3)_3$), 25.98 (3C; $C(\mathit{CH}_3)_3$), 26.77 (C2′), 33.29 (C1′), 62.37 (C3′), 94.53 (C1), 102.41 (Ar-η-C_q), 104.14 (Ar-η-C_q), 105.53 (Ar-η-C_q), 107.05 (Ar-η-C_q), 123.37 (ArC_t), 127.22 (ArC_t), 129.26 (ArC_t), 129.74 (ArC_t), 130.37 (ArC_t), 131.26 (ArC_t), 131.60 (C3), 131.97 (ArC_t), 132.78 (ArC_t), 133.75 (ArC_t), 135.99 (ArC_q), 137.31 (ArC_q), 137.55 (ArC_q), 233.54 (3C; CO); FT-IR (hexane): $\tilde{\nu} = 1959$ (vs, C=O, A_1), 1897 (s, C=O, E), 1884 cm^{-1} (s, C=O, E); FT-IR (KBr): $\tilde{\nu} = 2963$ (m), 2931 (m), 2857 (m), 1950 (vs, C=O, A_1), 1871 (s, C=O, E), 1471 (m), 1370 (m), 1258 (m), 1100 (m), 833 (m), 781 cm^{-1} (m); MS (70 eV, EI): m/z (%): 666 (10) $[M^+]$, 582 (37) $[M^+ - 3CO]$, 530 (100) $[M^+ - Cr(CO)_3]$, 473 (8) $[M^+ - Cr(CO)_3 - C_4H_9]$, 268 (30) $[M^+ - Cr(CO)_3 - 2\,tBuMe_2SiO]$, 73 (78) $[Si(CH_3)_3^+]$; HR-MS (EI): calcd for $C_{33}H_{46}CrO_2Si_2$: 582.2441; found 582.2449 (37 %, $[M^+ - 3CO]$); $C_{36}H_{46}CrO_5Si_2$ (666.93): calcd C 64.83, H 7.14; found C 64.63, H 6.95.

Reaction of pentacarbonyl[4-methoxyphenyl(phenyl)carbene]chromium(0) (21) with 1-hexyne: The reaction of **21** (1 mmol, 0.39 g) with 1-hexyne (4 mmol, 0.33 g) afforded an orange solution. Silylation followed by column chromatographic workup (eluent: petroleum ether/diethyl ether = 3:1) gave the tricarbonyl chromium complexes **23** (0.14 g, 0.25 mmol, 25 %) and **22** (0.22 g, 0.4 mmol, 40 %).

*Tricarbonyl{1-4a:8a-η-[3-butyl-4-tert-butyldimethylsilyloxy-1-(4′-methoxy)-phenylnaphthalene]}chromium(0) (**22**)*: Red crystals; $R_f = 0.4$ (petroleum ether/diethyl ether = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.41$ (s, 3H; $SiCH_3$), 0.45 (s, 3H; $SiCH_3$), 0.95 (t, $^3J_{HH} = 7.25$ Hz, 3H; H4″), 1.13 (s, 9H; $SiC(CH_3)_3$), 1.45 (psex, $^3J_{HH} = 7.25$ Hz, 2H; H3″), 1.64 (pquin, $^3J_{HH} = 7.25$ Hz, 2H; H2″), 2.57 (m, 1H; H1″), 2.85 (m, 1H; H1″), 3.91 (s, 3H; OCH_3), 5.75 (s, 1H; H2), 6.95–7.15 (m, 4H; H2′, H3′, H5′, H6′), 7.39 (t, $^3J = 7.65$ Hz, 1H; ArH), 7.45 (t, $^3J_{HH} = 7.65$ Hz, 1H; ArH), 7.75 (d, $^3J_{HH} = 8.64$ Hz, 1H; ArH), 8.02 (d, $^3J_{HH} = 8.64$ Hz, 1H; ArH); ^{13}C NMR (125.6 MHz, $CDCl_3$): $\delta = -3.44$ ($SiCH_3$), -2.27 ($SiCH_3$), 14.11 (C4″), 18.78 ($\mathit{C}(CH_3)_3$), 22.95 (C3″), 25.62 (3C; $C(\mathit{CH}_3)_3$), 29.54 (C2″), 32.86 (C1″), 55.38 (OCH_3), 97.64 (C2), 100.47 (Ar-η-C_q), 101.04 (Ar-η-C_q), 105.57 (Ar-η-C_q), 106.38 (Ar-η-C_q), 113.34 (C1′), 125.46 (ArC_t), 126.54 (ArC_t), 126.88 (2C; ArC_t), 126.65 (ArC_t), 128.03 (2C; ArC_t), 131.13 (C4), 131.74 (ArC_t), 159.29 (C4′), 233.44 (3C; CO); FT-IR (hexane): $\tilde{\nu} = 1961$ (vs, C=O, A_1), 1894 (s, C=O, E), 1884 cm^{-1} (s, C=O, E); MS (70 eV, EI): m/z (%): 556 (20) $[M^+]$, 500 (46) $[M^+ - 2CO]$, 472 (100) $[M^+ - 3CO]$, 420 (28) $[M^+ - Cr(CO)_3]$, 363 (18) $[M^+ - Cr(CO)_3 - C_4H_9]$, 306 (31) $[M^+ - Cr(CO)_3 - 2C_4H_9]$, 126 (27), 73 (23) $[Si(CH_3)_3^+]$, 52 (25) $[Cr^+]$; HR-MS (EI): calcd for $C_{30}H_{36}CrO_5Si$: 556.1737; found 556.1757 (20 %, $[M^+]$); $C_{30}H_{36}CrO_5Si$ (556.59): calcd C 64.73, H 6.52; found C 64.63, H 6.45.[41]

*Tricarbonyl{1-4a:8a-η-(3-butyl-4-tert-butyldimethylsilyloxy-6-methoxy-1-phenylnaphthalene)}chromium(0) (**23**)*: Red crystals; $R_f = 0.5$ (petroleum ether/diethyl ether = 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.51$ (s, 3H; $SiCH_3$), 0.55 (s, 3H; $SiCH_3$), 0.93 (t, $^3J_{HH} = 7.35$ Hz, 3H; H4″), 1.18 (s, 9H; $C(CH_3)_3$), 1.43 (psex, $^3J_{HH} = 7.35$ Hz, 2H; H3″), 1.61 (pquin, $^3J_{HH} = 7.87$ Hz, 2H; H2″), 2.47 (dt, $^2J_{HH} = 14.15$ Hz, $^3J_{HH} = 8.40$ Hz, 1H; H1″), 2.78 (dt, $^2J_{HH} = 14.15$ Hz, $^3J_{HH} = 8.07$ Hz, 1H; H1″), 3.96 (s, 3H; OCH_3), 5.45 (s, 1H; H2), 7.04 (dd, $^3J_{HH} = 9.38$ Hz, $^4J_{HH} = 1.96$ Hz, 1H; H7), 7.09 (d, $^4J_{HH} = 1.96$ Hz, 1H; H5), 7.38–7.60 (m, 5H; H2′, H3′, H4′, H5′, H6′), 7.72 (d, $^3J_{HH} = 9.44$ Hz, 1H; H8); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -3.46$ ($SiCH_3$), -1.71 ($SiCH_3$), 14.07 (C4″), 18.76 ($\mathit{C}(CH_3)_3$), 22.85 (C3″), 25.81 (3C; $C(\mathit{CH}_3)_3$), 29.80 (C2″), 32.93 (C1″), 55.50 (OCH_3), 95.86 (C2), 98.79 (Ar-η-C_q), 99.28 (Ar-η-C_q), 101.93 (Ar-η-C_q), 105.34 (Ar-η-C_q), 122.43 (2C; C2′, C6′), 127.59 (C4), 128.49 (ArC_t), 129.45 (2C; C3′, C5′), 129.64 (ArC_t), 130.00 (ArC_t), 131.61 (ArC_t), 135.52 (C1′), 158.55 (C6), 233.83 (3C; CO); FT-IR (hexane): $\tilde{\nu} = 1959$ (vs, C=O, A_1), 1892 (s, C=O, E), 1881 cm^{-1} (s, C=O, E); MS (70 eV, EI): m/z (%): 556 (10) $[M^+]$, 500 (6) $[M^+ - 2CO]$, 472 (100) $[M^+ - 3CO]$, 420 (55) $[M^+ - Cr(CO)_3]$, 363 (22) $[M^+ - Cr(CO)_3 - C_4H_9]$, 306 (27) $[M^+ - Cr(CO)_3 - 2C_4H_9]$, 126 (30), 73 (23) $[Si(CH_3)_3^+]$, 52 (25) $[Cr^+]$; HR-MS (EI): calcd for $C_{30}H_{36}CrO_5Si$: 556.1737; found 556.1714 (10 %, $[M^+]$); $C_{30}H_{36}CrO_5Si$ (556.59): calcd C 64.73, H 6.52; found C 64.63, H 6.45.[41]

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[1] a) E. O. Fischer, A. Maasböl, *Angew. Chem.* **1964**, *76*, 645; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 580; b) K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, VCH, Weinheim, **1983**.

[2] a) K. H. Dötz, *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587; b) W. D. Wulff, in *Comprehensive Organometallic Chemistry II, Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, **1995**, pp. 469–547; c) L. S. Hegedus, *ibid. Vol. 12*, pp. 549–576; d) D. F. Harvey, M. Sigano, *Chem. Rev.* **1996**, *96*, 271; e) A. de Meijere, *Pure Appl. Chem.* **1996**, *68*, 61; f) J. Barluenga, *ibid.* **1996**, *68*, 543.

[3] K. H. Dötz, *Angew. Chem.* **1975**, *87*, 672; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 644.

[4] a) K. H. Dötz, R. Dietz, *Chem. Ber.* **1978**, *111*, 2517; b) K. H. Dötz, I. Pruskil, *ibid.* **1980**, *113*, 2876; c) W. D. Wulff, P. C. Tang, J. S. McCallum, *J. Am. Chem. Soc.* **1981**, *103*, 7677; d) K. H. Dötz, J. Mühlemeier, U. Schubert, O. Orama, *J. Organomet. Chem.* **1983**, *247*, 187; e) W. D. Wulff, K. S. Chan, P. C. Tang, *J. Org. Chem.* **1984**, *49*, 2293; f) A. Yamashita, A. Toy, *Tetrahedron Lett.* **1986**, *27*, 3471.

[5] Benzannulation with stannylalkynes shows the reversed regioselectivity: S. Chamberlain, M. L. Waters, W. D. Wulff, *J. Am. Chem. Soc.* **1994**, *116*, 3113.

[6] a) K. H. Dötz, *J. Organomet. Chem.* **1977**, *140*, 177; b) K. H. Dötz, I. Pruskil, *Chem. Ber.* **1978**, *111*, 2059; c) W. D. Wulff, S. R. Gilbertson, J. P. Springer, *J. Am. Chem. Soc.* **1986**, *107*, 5823; d) M. F. Semmelhack, J. Park, *Organometallics* **1986**, *5*, 2550; e) K. E. Garret, J. B. Sheridan, D. B. Pourreau, W. C. Weng, G. L. Geoffroy, D. L. Staley, A. L. Rheingold, *J. Am. Chem. Soc.* **1989**, *111*, 8383; f) A. Yamashita, *Tetrahedron Lett.* **1986**, *27*, 5915; g) K. H. Dötz, H. Larbig, *J. Organomet. Chem.* **1991**, *405*, C38; h) W. D. Wulff, B. A. Bax, B. A. Brandvold, K. S. Chan, A. M. Gilbert, R. P. Hsung, J. Mitchell, J. Clardy, *Organometallics* **1994**, *13*, 102.

[7] a) K. H. Dötz, I. Pruskil, *J. Organomet. Chem.* **1981**, *209*, C4; b) K. H. Dötz, I. Pruskil, J. Mühlemeier, *Chem. Ber.* **1982**, *115*, 1278; c) K. H. Dötz, W. Kuhn, *Angew. Chem.* **1983**, *95*, 750; *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 732.

[8] M. F. Semmelhack, J. J. Bozell, T. Sato, W. D. Wulff, E. Spiess, A. Zask, *J. Am. Chem. Soc.* **1982**, *104*, 5850.

[9] a) K. H. Dötz, M. Popall, *Angew. Chem.* **1987**, *99*, 1220; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1158; b) W. D. Wulff, Y.-C. Xu, *J. Am. Chem. Soc.* **1988**, *110*, 2312.

[10] a) D. L. Boger, I. C. Jacobsen, *J. Org. Chem.* **1991**, *56*, 2115; b) D. L. Boger, O. Hüter, K. Mbiya, M. Zhang, *J. Am. Chem. Soc.* **1995**, *117*, 11839.

[11] H. Fischer, J. Mühlemeier, R. Märkl, K. H. Dötz, *Chem. Ber.* **1982**, *115*, 1355.

[12] a) H. C. Foley, L. M. Strubinger, T. S. Targos, G. L. Geoffroy, *J. Am. Chem. Soc.* **1983**, *105*, 3064; b) J. R. Knorr, T. L. Brown, *Organometallics* **1994**, *13*, 2178.

0947-6539/98/0409-1850 $ 17.50+.50/0

[13] K. H. Dötz, T. Schäfer, F. Kroll, K. Harms, *Angew. Chem.* **1992**, *104*, 1257; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1236.

[14] J. Barluenga, F. Aznar, A. Martín, S. García-Granda, E. Pérez-Carreño, *J. Am. Chem. Soc.* **1994**, *116*, 11191.

[15] a) K. H. Dötz, *Angew. Chem.* **1979**, *91*, 1021; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 954; b) A. Yamashita, T. A. Scahill, *Tetrahedron Lett.* **1982**, *23*, 3765; c) B. A. Anderson, J. Bao, T. A. Brandvold, C. A. Challener, W. D. Wulff, Y.-C. Xu, *J. Am. Chem. Soc.* **1993**, *115*, 10671; d) K. H. Dötz, W. Sturm, *J. Organomet. Chem.* **1985**, *285*, 205; e) A. Mayr, M. F. Asaro, T. J. Glines, *J. Am. Chem. Soc.* **1987**, *109*, 2215; f) E. Chelain, R. Goumont, L. Hamon, A. Parlier, M. Rudler, H. Rudler, J. C. Daran, J. Vaissermann, *J. Am. Chem. Soc.* **1992**, *114*, 8088.

[16] a) P. Hofmann, M. Hämmerle, *Angew. Chem.* **1989**, *101*, 940; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 908; b) P. Hofmann, M. Hämmerle, G. Unfried, *New. J. Chem.* **1991**, *15*, 769.

[17] M. M. Gleichmann, K. H. Dötz, B. A. Hess, *J. Am. Chem. Soc.* **1996**, *118*, 10551.

[18] J. Möllmann, Ph.D. Thesis, University of Bonn, Bonn, **1997**.

[19] a) K. H. Dötz, J. Pfeiffer, *Chem. Commun.* **1996**, 895; b) J. Pfeiffer, K. H. Dötz, *Organometallics*, in press.

[20] An orange solid was isolated, the GC-MS of which reveals two substances with $m/z = 228$, and two compounds with $m/z = 230$. The first are presumed to result from *E/Z*-1,1′-[bis-(1*H*)-indenylidene], whereas the structures of the last two compounds remain unclear.

[21] A. C. Hazell, *Acta Crystallogr. B* **1978**, *34*, 3037.

[22] For the assignment of helical chiral enantiomers see: a) R. S. Cahn, C. K. Ingold, V. Prelog, *Angew. Chem.* **1966**, *78*, 413; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 385; b) R. H. Martin, G. Morren, J. J. Schurter, *Tetrahedron Lett.* **1969**, *10*, 3683. For the assignment of planar chiral enantiomers see: K. Schlögl, *Top. Curr. Chem.* **1984**, *125*, 27.

[23] K. Brandenburg, M. Berndt, DIAMOND, University of Bonn, Bonn, **1995**.

[24] A. Solladié-Cavallo, *Polyhedron* **1985**, *4*, 901.

[25] K. H. Dötz, G. Huttner, R. Dietz, A. von Imhof, H. Lorenz, *Chem. Ber.* **1976**, *109*, 2033.

[26] a) J. J. Looker, D. P. Maier, T. H. Regan, *J. Org. Chem.* **1972**, *37*, 3401; b) A. Ebnother, E. Jucker, A. Stoll, *Helv. Chim. Acta* **1965**, *48*, 1237; c) M. Sadek, D. J. Craik, J. G. Hall, P. R. Andrews, *J. Med. Chem.* **1990**, *33*, 1098.

[27] For a cyclopropenylium cation derived from a carbene complex, see: M. Brookhart, M. B. Humphrey, H. J. Kratzer, G. O. Nelson, *J. Am. Chem. Soc.* **1980**, *102*, 7803.

[28] a) M. J. Aroney, G. M. Hoskins, R. LeFevre, *J. Chem. Soc. B* **1969**, 980; b) S. V. McKinley, P. A. Grieco, A. E. Young, H. H. Freedman, *J. Am. Chem. Soc.* **1970**, *92*, 5900.

[29] a) K. H. Dötz, W. Sturm, H. G. Alt, *Organometallics* **1987**, *6*, 1424; b) F. E. McDonald, C. C. Schultz, *J. Am. Chem. Soc.* **1994**, *116*, 9363; c) A. Segundo, J. M. Moretó, J. M. Viñas, S. Ricart, *Organometallics* **1994**, *13*, 2467.

[30] This explanation is in accordance with a diverse product distribution observed in the chromium complex catalyzed reactions of various diazo compounds with electron-rich alkenes: J. Pfeiffer, M. Nieger, K. H. Dötz, *Eur. J. Org. Chem.* **1998**, *1*, 1011.

[31] K. H. Dötz, R. Dietz, *Chem. Ber.* **1977**, *110*, 1555.

[32] W. D. Wulff, P.-C. Tang, J. S. McCallum, *J. Am. Chem. Soc.* **1981**, *103*, 7677.

[33] G. M. Sheldrick, SHELXTL-Plus, Siemens Analytical X-Ray Instruments, Madison, Wi. (USA), **1989**.

[34] G. M. Sheldrick, SHELXTL-93, University of Göttingen, **1993**.

[35] N. Walker, D. Stuart, *Acta Crystallogr. A* **1983**, *39*, 158.

[36] C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, A. E. Brodhag, *J. Am. Chem. Soc.* **1956**, *78*, 1653.

[37] Assigned on the basis of a HH COSY experiment.

[38] Assigned on the basis of a CH COSY experiment.

[39] No analytically pure samples of compounds **13** and **19** could be obtained. Partial decomposition occurred within several hours at −38 °C.

[40] C7 and C8 have been assigned on the more pronounced temperature dependence of the signal broadening in case of C8.

[41] Mixture of **22** and **23**.