Alkyne–Carbene Chelate Complexes of Chromium: Arrested Intermediates in the Benzannulation Reaction and Precursors of Densely Functionalized Centrosymmetric Chrysenes**

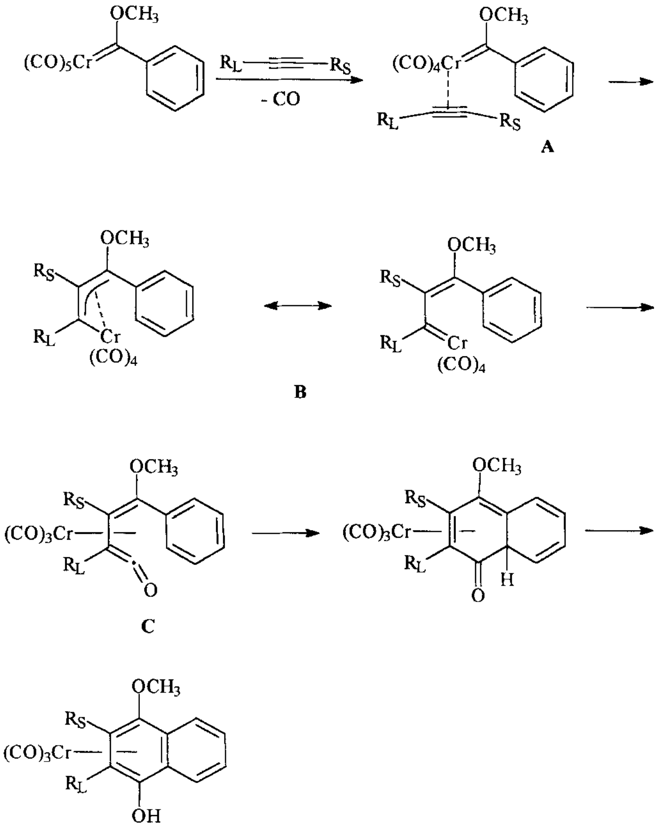
Frank Hohmann, Sabine Siemoneit, Martin Nieger, Sirpa Kotila and Karl Heinz Dötz*

Abstract: Tetracarbonyl-η^2-alkyne–carbene chromium(0) complexes **3a–c** stabilized by a rigid C_2-arene unit bridging the alkyne and the carbene ligands were synthesized from their pentacarbonyl precursors **2a–c** by low-temperature photodecarbonylation. The chelates **3a–c** are the first stable alkyne–carbene complexes containing a Group VIB metal carbonyl unit, and can be regarded as arrested intermediates in the chromium-mediated benzannulation reaction. Comparative X-ray and ^{13}C NMR studies indicate only weak coordination of the alkyne, both in the solid state and in solution. Decomposition of chelates **3a–c** as well as the thermal decarbonylation of their pentacarbonyl precursors **2a–c** results in dimerization of the alkynylcarbene ligands to give densely substituted oxygenated chrysene derivatives. A modification of the substitution pattern in the central chrysene rings results in a gradual distortion of the arene system across the central C–C arene bond.

Keywords
alkyne complexes · carbene complexes · chelates · chromium · chrysenes

Introduction

Fischer-type carbene complexes[1] have become valuable reagents for stereoselective carbon–carbon bond formation during the past 20 years.[2] One of the most important synthetic transformations involves the reaction of unsaturated chromium carbenes with alkynes, which generates densely substituted phenols by sequential coupling of the alkyne, the carbene and one carbonyl ligand at a $[Cr(CO)_3]$ template (Scheme 1).[3] This formal [3+2+1] cycloaddition proceeds with considerable regiocontrol provided that the alkyne substituents are distinctly different in size.[4] Generally, the phenol formation is the major reaction path; however, depending both on the substrates and the reaction conditions, additional varieties of cycloaddition reactions have been observed as well.[5] The synthetic potential of the benzannulation reaction has been demonstrated in natural product synthesis.[6] Support for the mechanism of this reac-



Scheme 1. Mechanism of the benzannulation reaction.

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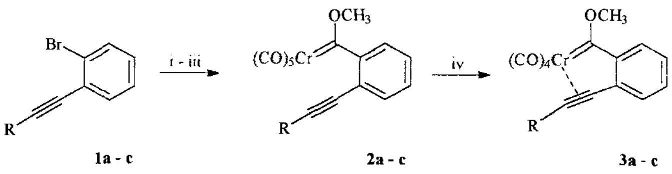
tion has been provided by isolation and structural characterization of presumed intermediates relevant to **B**[7] and **C**[8] as well as by extended Hückel molecular orbital (EHMO)[9] and quantum chemical calculations.[10, 11] From kinetic studies[12] it appears that the benzannulation starts with a reversible decarbonylation followed by alkyne coordination. The tetracarbonyl alkyne carbene complex **A** is generally accepted as the first intermediate;[13] however, experimental efforts aimed at its isolation or spectroscopic characterization have been unsuccessful so far. This is due to a low barrier of activation of ca. 12 kJ mol^{-1} for the subsequent C–C coupling process (indicated by a density functional theory (DFT) study[10]), which arises from an alkyne insertion into the metal–carbene bond to generate intermediate **B** and controls the regioselectivity of the annulation reaction. We anticipated that kinetic stabilization of the alkyne–carbene complex intermediate should result from connecting the alkyne and carbene ligands by a rigid C_2-arene bridge. This strategy resulted in the isolation of alkyne–carbene chelate complexes containing the metals of the chromium triad.[14] Subsequently, we focussed our interest on chromium carbenes, which are known for their unique role in metal-mediated cycloaddition reactions. Here we report on their synthesis and molecular structures as well as on a novel type of carbene dimerization that allows a direct entry into a densely functionalized chrysene skeleton.[14]

Results and Discussion

2-Alkynyl(phenyl)carbene complexes: The pentacarbonyl[2-alkynyl(phenyl)carbene] precursors **2a–c** were synthesized following a slightly modified Fischer procedure[15] starting from 2-alkynyl-1-bromobenzenes **1a–c**, which are accessible from 2-bromo-1-iodobenzene by a palladium-catalyzed coupling with terminal alkynes[16] (Scheme 2). Low-temperature photodecarbonylation resulted in an intramolecular substitution of the alkyne for a *cis*-carbonyl ligand to give alkyne–carbene chelates **3a–c**. In contrast to their pentacarbonyl precursors **2a–c**, which, according to low-temperature NMR studies, exist as pairs of (*E*)/(*Z*) isomers with respect to the carbene oxygen bond, their tetracarbonyl chelate analogues **3a–c** adopt the (*Z*) configuration exclusively. This phenomenon may be a consequence of increased stereoelectronic repulsion between the oxygen lone pairs and the $[Cr(CO)_4]$ moiety;[17] in the tetracarbonyl chelate complexes **3a–c** the chromium is expected to possess a higher electron density than in the pentacarbonyl species **2a–c**.



Scheme 2. Synthesis of **2a–c** and **3a–c**. R = Ph (**1a**, **2a**, **3a**), *n*Pr (**1b**, **2b**, **3b**), $Si(CH_3)_3$ (**1c**, **2c**, **3c**). Reagents and conditions: i) *n*-BuLi, Et_2O, 0 °C; ii) $[Cr(CO)_6]$, 0 °C → room temperature; iii) $(CH_3)_3OBF_4$, CH_2Cl_2; iv) hν, Et_2O, −40 °C.

Abstract in German: *Durch Tieftemperatur-Photodecarbonylierung der Pentacarbonyl-Vorstufen* **2a–c** *sind Tetracarbonyl-*η^2*-Alkin–Carben-Komplexe des Chroms* **3a–c** *zugänglich, in denen der Alkin- und der Carbenligand durch eine starre* C_2*-Brücke verbunden sind. Sie sind die ersten stabilen Verbindungen dieses Komplextyps und stellen chelatstabilisierte Zwischenstufen der Chrom-vermittelten Benzanellierung dar. Nach Röntgenstruktur- und* ^{13}*C-NMR-Untersuchungen ist das Alkin nur schwach an das Metall koordiniert. Der Zerfall von* **3a–c** *führt ebenso wie die thermische Decarbonylierung von* **2a–c** *über eine Dimerisierung der Carbenliganden zu hochsubstituierten oxygenierten Chrysenen. Eine stufenweise helicale Verdrillung des Chrysengerüsts läßt sich durch Modifizierung des Substitutionsmusters in den beiden zentralen Ringen erreichen.*

The formation of the tetracarbonyl chelates is obvious from the $\tilde{\nu}_{C=O}$ absorption pattern in the IR spectra. The ^{13}C NMR spectra indicate only a moderate upfield shift ($\delta(C{\equiv}C) = 103.1$, 99.8 for **2c**; $\delta = 96.5$, 76.5 for **3c**) for the alkyne carbon atoms upon coordination to the metal centre; this reveals that in **3a–c** the alkyne acts as an only weakly bound two-electron donor ligand.[18, 19]

For further insight into the nature of the alkyne coordination, the molecular structures of the trimethylsilyl analogues **2c** and **3c** were established by X-ray analysis (Figures 1 and 2, Table 1). The characteristic feature of the alkyne–carbene chelates, a weak coordination of the alkyne as indicated by NMR studies

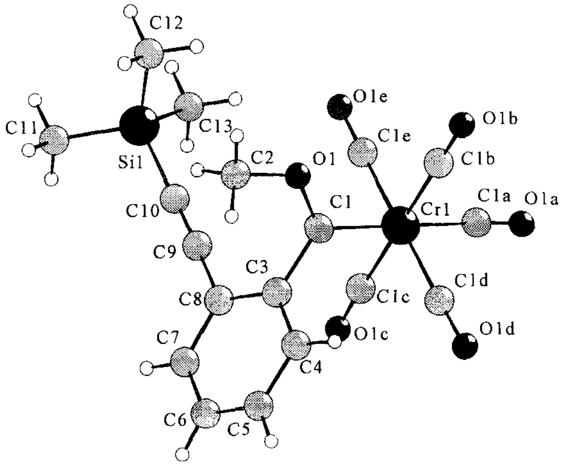


Figure 1. Structure of **2c**.

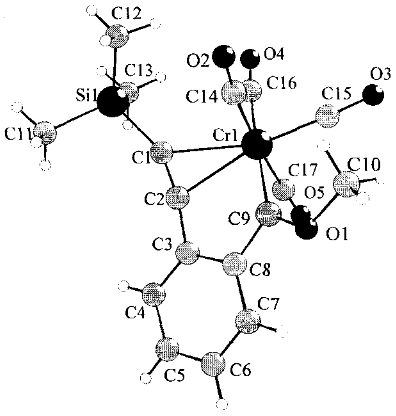


Figure 2. Structure of **3c**.

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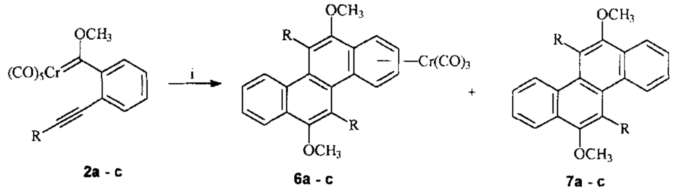
Table 1. Selected bond lengths, bond angles and dihedral angles of **2c** and **3c** (for atom numbering see Figures 1 and 2).

Compound **2c**		Compound **3c**	
bond lengths (pm)			
C9–C10	121.7(9)	C1–C2	122.7(5)
Cr1–C1	198.8(6)	Cr1–C9	205.0(4)
Cr1–C1a	189.1(7)	Cr1–C16	188.4(4)
Cr1–C1b	190.9(6)	Cr1–C14	191.0(4)
Cr1–C1c	189.2(6)	Cr1–C17	188.8(4)
Cr1–C1d	188.8(8)	Cr1–C15	182.9(4)
Cr1–C1e	188.7(8)		
		Cr1–C1	241.8(3)
		Cr1–C2	234.8(3)
bond angles (°)			
C9-C10-Si1	174.3(7)	C2-C1-Si1	157.2(3)
C10-C9-C8	177.2(7)	C1-C2-C3	171.0(3)
C1-C3-C8	119.3(6)	C9-C8-C3	114.7(3)
C3-C8-C9	120.7(6)	C8-C3-C2	115.6(3)
dihedral angles (°)			
Cr1-C1-C3-C8	−96.9	Cr1-C9-C8-C3	−20.3
		C9-Cr1-C1-C2	−23.1

in solution, also holds for the solid state: no significant elongation of the C≡C bond (121.7(9) pm for **2c** vs. 122.7(5) pm for **3c**) is observed as a consequence of the alkyne coordination; in addition, the Cr–C_{alkyne} distances (241.8(3) and 234.8(3) pm) are as long as the W–C_{alkyne} distances both in the analogous alkyne–carbene tungsten chelate complex[14] and in the alkyne-(pentacarbonyl)tungsten complex [(CO)$_5$W(PhC≡CH)].[20] In these compounds, the W–C_{alkyne} bond lengths are about 10% longer than those encountered in comparable tungsten(0)–alkyne complexes.[21] One might argue that the rigid arene-C$_2$ bridge prevents a more effective complexation of the alkyne; however, ab initio calculations on model systems such as [(CO)$_4$(HC≡CH)Cr=CH$_2$][11] and [(CO)$_4$(HC≡CH)Cr=C(C$_6$H$_5$)OH][10] using pseudopotentials for chromium or DFT methods gave similar metal–alkyne bond lengths. The weak interaction between the alkyne and the chromium centre is further reflected both by a *trans* effect observed for the *trans*-CO ligand and the minor deviation from linearity in the alkyne ligand. The Cr–CO_{trans} distance (182.9(4) pm) is significantly shorter than those for the remaining Cr–CO_{cis} ligands (mean value: 189.3 pm). This is a result of the fact that the alkyne cannot compete successfully with the *trans* carbonyl ligand for backbonding from the metal. The alkyne substituents are only slightly bent away from the metal (C2-C1-Si1: 157.2(3)° and C1-C2-C3: 171.0(3)°). Obviously, the carbonyl ligand is a much stronger π acceptor than the alkyne. The chelate formation is accompanied by a lengthening of the chromium–carbene bond (205.0(4) pm for **3c** vs. 198.8(6) pm for **2c**). This may be a consequence of the strain in the chelate ring imposed by the rigid C$_2$-bridge.

Carbene dimerization to chrysenes: The alkyne–carbene chelates **3** are thermolabile and undergo a novel type of controlled decomposition in solution at ambient temperature. For instance, the densely substituted oxygenated chrysene **7b** is obtained in a formal carbene dimerization from the *n*-propyl complex **3b**. The thermal decarbonylation of pentacarbonyl complex **2b** in refluxing *tert*-butyl methyl ether affords the same product. Monitoring of the reaction by IR reveals that a Cr(CO)$_3$ complex **6b** is formed as primary dimerization product, which undergoes subsequent metal–arene cleavage (Scheme 3). A careful workup procedure, however, allows the isolation of chromium-coordinated chrysene which, after recrystallization from diethyl ether, forms red crystals suitable for X-ray analysis.



Scheme 3. Synthesis of chrysenes **6a–c** and **7a–c**. R = Ph (**2a**, **6a**, **7a**), *n*Pr (**2b**, **6b**, **7b**), Si(CH$_3$)$_3$ (**2c**, **6c**, **7c**). Conditions: i) *t*BuOCH$_3$, 55 °C.

The tricarbonylchromium-complexed chrysene **6b** as well as the uncomplexed **7b** were crystallized from diethyl ether. The structures obtained by X-ray diffraction studies (Figures 3 and 4, Table 2) have a twisted aromatic skeleton owing to steric

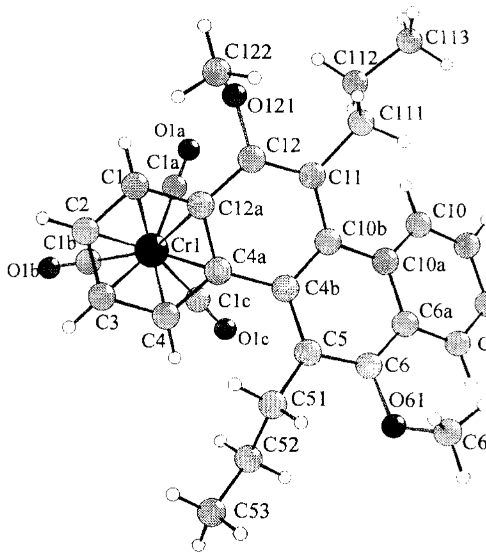


Figure 3. Structure of **6b**.

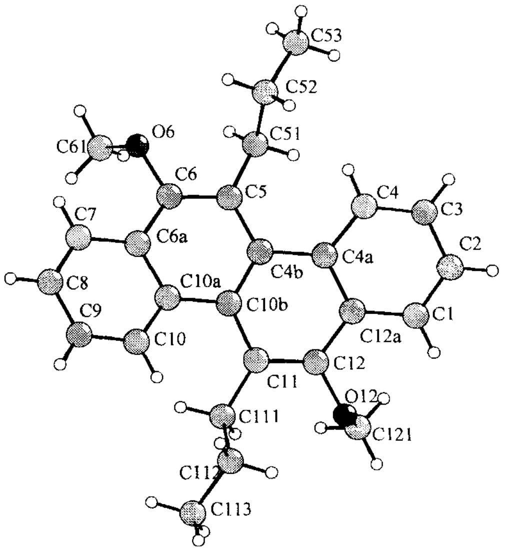
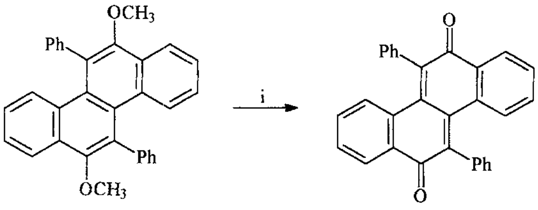


Figure 4. Structure of **7b**.

Table 2. Selected bond lengths, bond angles and dihedral angles of **6b** and **7b** (for atom numbering see Figure 3).

	Compound **6b**	Compound **7b**
bond lengths (pm)		
Cr1-C4a	230.0(4)	
Cr1-C1	219.2(4)	
Cr1-C2	220.9(4)	
Cr1-C12a	226.1(4)	
Cr1-C4	218.9(4)	
Cr1-C3	220.0(5)	
bond angles (°)		
C5-C6-C6a	123.8(4)	123.1(2)
C4b-C5-C6	117.2(4)	118.6(2)
C6-C6a-C10a	118.0(4)	118.4(2)
C10a-C10b-C4b	118.2(4)	118.0(2)
C4b-C5-C51	124.6(4)	124.6(2)
C6-C5-C51	117.8(4)	116.4(2)
C6a-C10a-C10b	118.9(4)	119.5(2)
C10b-C4b-C5	119.9(4)	119.3(2)
dihedral angles (°)		
C4a-C4b-C10b-C10a	−158.9	162.5
C4a-C4b-C10b-C11	22.8	−19.0
C5-C4b-C10b-C10a	22.2	−19.9
C5-C4b-C10b-C11	−156.1	157.8

repulsion between the substituents in positions 4, 5 and 10, 11. The dihedral angle across the central carbon–carbon bond (C5-C4b-C10b-C11) amounts to 24° for the $Cr(CO)_3$ complex **6b** compared with 22° in the uncoordinated analogue **7b**. A larger distortion (33°) is observed in chrysenedione **8a**, which was obtained by ether cleavage of **7a** with trimethylsilyliodide followed by oxidation in air (Scheme 4). The X-ray structure of **8a** (Figure 5, Table 3) shows a torsion angle of 33° across C9-C8-C17-C18. The reduced conjugation in the central rings in **8a** vs. **7b** might explain this phenomenon.



7a **8a**

Scheme 4. Oxidation of **7a** to **8a**. Reagents and conditions: i) $(CH_3)_3SiI$, CH_2Cl_2, room temperature, air, 79 h.

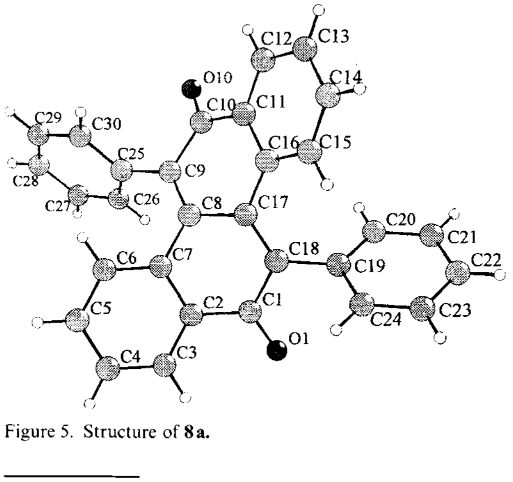


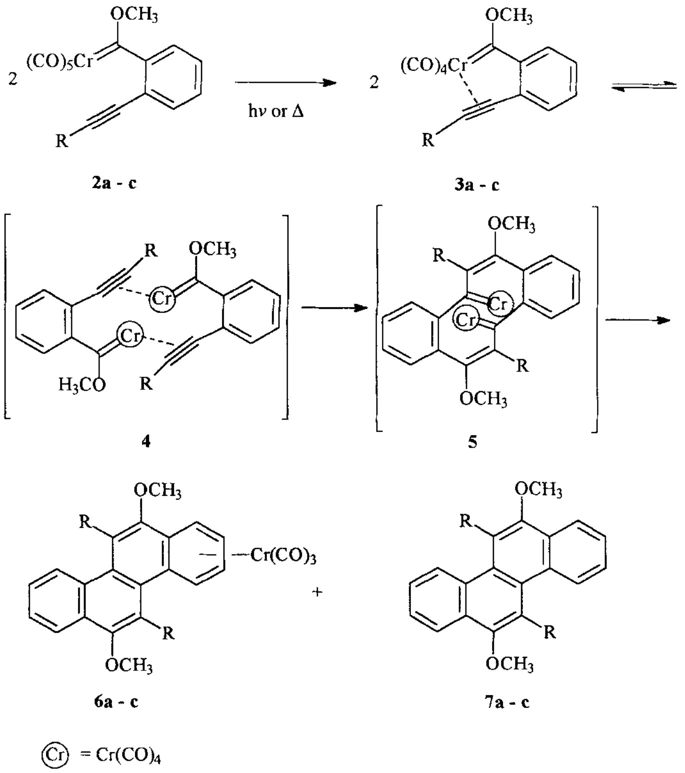
Figure 5. Structure of **8a**.

Table 3. Selected bond angles and dihedral angles (°) of **8a** (for atom numbering see Figure 5).

C1-C2-C7	119.2(3)	C8-C17-C18	119.2(3)
C2-C7-C8	118.0(3)	C1-C18-C17	119.2(3)
C7-C8-C17	117.0(3)	C2-C1-C18	117.7(3)
C17-C18-C19	124.7(3)	C1-C18-C19	116.0(3)
C16-C17-C8-C7	−152.2	C9-C8-C17-C18	−147.3
C9-C8-C17-C16	30.7	C7-C8-C17-C18	29.8

In order to test the scope and limitations of this unprecedented type of reaction we varied the substitution pattern at the alkyne moiety. A trimethylsilyl group attached to the alkyne terminus gave poor yields of chrysenes **6c** and **7c** under similar conditions. The ^1H NMR spectrum of the uncomplexed chrysene **7c** is complicated by gearing effects between the neighbouring groups that result in four signals for the methoxy group, two resonances for the trimethylsilyl group and additional signals for the aromatic protons at ambient temperature.

A possible mechanism for the chrysene formation (Scheme 5) involves an equilibrium of alkyne–carbene complex monomers **3** and dimers **4**. A double alkyne insertion into the chromium carbene bonds in dimer **4**—similar to the accepted mechanism for the benzannulation—is expected to generate the central ten-membered ring of **5** bearing two opposite metal carbene units. A formal carbene dimerization accompanied by partial or complete demetallation leads to the chrysene skeleton **6**/**7**. Steric strain in the aromatic skeleton seems to favour the loss of the $Cr(CO)_3$ fragment and haptotropic migration[22] to the angular ring.



Scheme 5. Suggested mechanism for chrysene formation.

Table 4. Experimental data for X-ray diffraction structure studies of **2c**, **3c**, **6b**·0.5 Et_2O, **7b** and **8a**.

	2c	**3c**	**6b**·0.5 Et_2O	**7b**	**8a**
formula	$C_{18}H_{16}CrO_6Si$	$C_{17}H_{16}CrO_5Si$	$C_{29}H_{28}CrO_5 \cdot 0.5\,Et_2O$	$C_{26}H_{28}O_2$	$C_{30}H_{18}O_2$
M_r	408.40	380.39	545.57	372.48	410.44
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$Pbca$ (no. 61)
a/pm	1108.3(1)	827.8(1)	1543.2(2)	1147.0(1)	939.4(1)
b/pm	1069.8(3)	1518.5(1)	1194.4(3)	1582.8(1)	2089.0(2)
c/pm	1802.2(2)	1464.1(1)	1549.1(2)	1163.9(1)	2136.1(2)
β/°	106.54(1)	95.82(1)	103.09(1)	96.94(1)	90
V/pm^3	$2.0484(6) \times 10^9$	$1.8322(2) \times 10^9$	$2.7811(9) \times 10^9$	$2.0975(3) \times 10^9$	$4.1919(7) \times 10^9$
Z	4	4	4	4	8
crystal size/mm^3	$0.35 \times 0.33 \times 0.10$	$0.40 \times 0.40 \times 0.20$	$0.30 \times 0.20 \times 0.10$	$0.68 \times 0.40 \times 0.18$	$0.25 \times 0.22 \times 0.10$
ρ_{calcd}/g cm^{-3}	1.32	1.38	1.30	1.18	1.30
T/K	200(2)	200(2)	293(2)	293(2)	200(2)
abs. coeff./mm^{-1}	5.41	5.97	3.71	0.57	0.63
F(000)	840	784	1148	800	1712
scan type	$2\theta/\omega$	$2\theta/\omega$	$2\theta/\omega$	$2\theta/\omega$	$2\theta/\omega$
θ_{max}/°	60	60	60	60	55
index range	$0 \le h \le 12$	$0 \le h \le 9$	$-17 \le h \le 0$	$-12 \le h \le 0$	$0 \le h \le 9$
	$0 \le k \le 12$	$0 \le k \le 17$	$-13 \le k \le 0$	$0 \le k \le 17$	$0 \le k \le 22$
	$-20 \le l \le 19$	$-16 \le l \le 16$	$-16 \le l \le 17$	$-12 \le l \le 13$	$-22 \le l \le 0$
total reflns	3215	2920	4291	3275	2626
unique reflns used in refinement	3039	2708	4114	3098	2624
parameters/restraints	231/30	221/0	337/9	254/0	290/0
R_1 (for $I > 2\sigma(I)$)	0.071	0.065	0.051	0.053	0.046
wR_2	0.227	0.169	0.171	0.149	0.150
GoF on F^2	1.09	1.06	1.03	1.11	1.01

Experimental Section

All operations were carried out in flame-dried glassware under an atmosphere of argon. Diethyl ether was dried over sodium hydride, dichloromethane, *tert*-butyl methyl ether, *n*-hexane and petroleum ether over calcium hydride. Acetone was reagent grade and was dried over molecular sieves. All solvents were saturated with argon and stored over molecular sieves. Silica gel (Merck, 0.063–0.200 mm) was degassed under vacuum and stored under argon. 2-Alkynyl-1-bromobenzenes **1a–c** were synthesized by palladium-catalyzed coupling reactions from commercially available 2-bromo-1-iodobenzene following a slightly modified literature procedure[16] and purified by column chromatography. Photochemical transformations were conducted with a mercury high-pressure lamp (Heraeus). IR spectra were recorded on a Nicolet Magna 550 spectrometer, NMR spectra on Bruker AMX500, AM400 or AM250 spectrometers. All chemical shifts are given relative to TMS as external standard. HR-MS were determined on a Kratos MS-50 spectrometer. Elemental analyses were carried out with an Elementaranalysator CHN-O-Rapid (Heraeus).

X-ray data were recorded on an Enraf-Nonius CAD4 diffractometer ($Cu_{K\alpha}$ radiation, $\lambda = 154.178$ pm, graphite monochromator). The structures were solved by direct methods (SHELXTL-Plus[23]). The non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined with a riding model (full-matrix least-squares refinement on F^2, SHELXL-93[24]). An extinction correction (**6b**, **7b**, **8a**) and an absorption correction on the basis of Ψ scans (**3c**, $T_{min/max} = 0.322/0.771$; **6b**, $T_{min/max} = 0.464/0.929$; **7b**, $T_{min/max} = 0.798/0.913$; **8a**, $T_{min/max} = 0.534/0.858$) or DIFABS[25] (**2c**) were applied. In **2c** the trimethylsilyl group and in **6b** the solvent were disordered. Further details of data collection and structure refinement are given in Table 4. The molecular diagrams were plotted with DIAMOND.[26] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-49. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

Synthesis of pentacarbonyl[methoxy(2-alkynylphenyl)carbene]chromium complexes (2b, 2c): *n*-Butyllithium (11 mmol, 6.9 mL of a 1.6 M solution in hexane) was added dropwise to a solution of 2-alkynyl-1-bromobenzenes **1b–c** (10 mmol) in diethyl ether (30 mL) at 0 °C. The mixture was stirred for 1 h, hexacarbonylchromium (11 mmol, 2.42 g) was added, and the solution was allowed to warm to ambient temperature over 1 h. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (20 mL). Trimethyloxoniumtetrafluoroborate (11 mmol, 1.63 g) was added and the suspension was stirred for a further 1–2 h. The solvent was removed and the product was purified by column chromatography (silica gel, −10 °C, *n*-hexane or petroleum ether/diethyl ether 8:1).

Pentacarbonyl[methoxy(2-pentyn-1′-ylphenyl)carbene]chromium(0) (2b):[27] Yield: 2.38 g (63%), dark red oil. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): $\delta = 7.8-6.6$ (m, 4H, Ar-H), 5.29* (the asterisk (*) denotes the signals of the (*Z*) isomer), 4.43, 4.41, 4.26 (br s, 3H, OCH_3), 2.44* (t, 2H, $^3J_{H,H} = 7.4$ Hz, $\text{-C}H_2\text{-CH}_2\text{-}$), 1.66 (br s, 2H, $\text{-C}H_2\text{-CH}_2\text{-}$), 1.45* (sxt, 2H, $^3J_{H,H} = 7.4$ Hz, $\text{-CH}_2\text{-C}H_2\text{-CH}_3$), 1.33 (br s, 2H, $\text{-CH}_2\text{-C}H_2\text{-CH}_3$), 1.00* (t, 3H, $^3J_{H,H} = 7.4$ Hz, $\text{-CH}_2\text{-C}H_3$), 0.93 (m, 3H, $\text{-CH}_2\text{-C}H_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 233 K): $\delta = 8.0-6.3$ (m, 4H, Ar-H), 5.31*, 5.00, 4.81, 4.50, 4.47, 4.43, 4.32, 3.98 (s, 3H, OCH_3), 2.41 (t, 2H, $^3J_{H,H} = 7.4$ Hz, $\text{-C}H_2\text{-CH}_2\text{-}$), 1.8–1.1 (br s, $\text{-C}H_2\text{-CH}_2\text{-}$, $\text{-CH}_2\text{-C}H_2\text{-CH}_3$), 1.02* (m, $\text{-CH}_2\text{-C}H_3$), 0.93 (m, $\text{-CH}_2\text{-C}H_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): $\delta = 355.9$, 355.1, 354.5 (Cr=C), 224.0, 223.7, 223.4 (CO_{trans}), 216.2, 216.1, 215.9 (CO_{cis}), 154.6 (br), 151.3 (C1), 141.7–139.2 (br, C2), 133.8–126.5 (26 signals, Ar-C), 123.2, 120.5 (br), 110.3 (Ar-C), 67.0, 66.9, 66.7 (OCH_3), 33.1, 32.8, 32.5 (br), 32.1, 29.6 ($\text{-CH}_2\text{-}C\text{H}_2\text{-CH}_3$), 22.8 ($\text{-}C\text{H}_2\text{-CH}_2\text{-}$), 13.8 ($\text{-CH}_2\text{-}C\text{H}_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 233 K): $\delta = 360.1$, 358.5, 357.7, 354.8, 354.6, 354.5, 354.4, 353.5 (Cr=C), 225.0, 224.9, 224.0, 223.9, 223.8 (CO_{trans}), 216.4, 216.3, 216.2, 216.1, 215.9, 215.7, 215.5, 215.2, 214.9 (CO_{cis}), 155.0, 154.9/154.5, 154.3, 151.3, 150.6, 149.6 (C1), 142.1, 141.1, 140.8, 140.7, 140.1, 139.8, 139.4, 139.3 (C2), 134.5–126.0 (26 signals, Ar-C), 126.0, 125.4, 123.4, 121.3, 119.5, 117.8, 117.7 (Ar-C), 67.9, 67.8, 67.7, 67.6, 67.4, 67.1, 66.8, 65.4 (OCH_3), 33.9, 33.0, 32.9, 32.2, 30.6, 30.0, 29.7, 29.2 ($-\text{CH}_2\text{-}C\text{H}_2\text{-CH}_3$), 23.1, 23.0, 22.9 ($\text{-}C\text{H}_2\text{-CH}_2\text{-}$), 14.7, 14.6, 14.3, 14.3 ($\text{-CH}_2\text{-}C\text{H}_3$); FT-IR (petroleum ether): $\tilde{\nu} = 2066$ [m, (C=O), A_1^1], 1954 [s, (C=O), E], 1941 [sh, (C=O), A_1^2] cm^{-1}; MS(FD): m/z (%): 378 (6) [M^+]; $C_{18}H_{14}O_6Cr$ (378.3): calcd C 57.15, H 3.73; found C 57.13, H, 3.62.

Pentacarbonyl[methoxy(2-trimethylsilylethynylphenyl)carbene]chromium(0) (2c): Yield: 3.26 g (80%), dark red solid. M.p. 62 °C; ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): $\delta = 7.48$ (d, 1H, $^3J_{H,H} = 7.7$ Hz, Ar-H), 7.41 (dd, 1H, $^3J_{H,H} = 7.7$ Hz, $^3J_{H,H} = 7.2$ Hz, Ar-H), 7.25 (dd, 1H, $^3J_{H,H} = 7.7$ Hz, $^3J_{H,H} = 7.2$ Hz, Ar-H), 6.99 (d, 1H, $^3J_{H,H} = 7.2$ Hz, Ar-H), 4.24 (s, 3H, OCH_3), 0.27 (s, 9H, $Si(CH_3)_3$); ^{1}H NMR (250 MHz, [D$_6$]acetone, 233 K): $\delta = 7.60-7.00$ (m, 4H, Ar-H), 5.08* (the asterisk (*) denotes the signals of the (*Z*) isomer), 4.22 (s, 3H, OCH_3), 0.20*, 0.18 (s, 9H, $Si(CH_3)_3$); ratio (OCH_3)

(*E*)/(*Z*)* = 2:1; ^{13}C NMR (125 MHz, $CDCl_3$, 298 K): δ = 353.3 (Cr=C), 224.6 (CO_{trans}), 215.8 (CO_{cis}), 132.7 (Ar-C 2), 128.4 (Ar-C), 127.8 (Ar-C), 121.2 (Ar-C), 112.3 (Ar-C), 101.4 (C≡C), 98.8 (C≡C), 65.3 (OCH_3), −0.45 ($Si(CH_3)_3$); ^{13}C NMR (62.5 MHz, [D_6]acetone, 223 K): δ = 355.1*/354.2 (Cr=C), 226.3, 225.6* (CO_{trans}), 217.3, 216.8* (CO_{cis}), 158.7*, 154.5 (Ar-C 1), 133.5 (Ar-C), 130.6, 129.8* (Ar-C), 129.6 /129.3* (Ar-C), 123.1*, 122.1 (Ar-C), 114.0*, 112.2 (Ar-C 2), 103.1*, 102.2 (C≡C), 101.2, 99.8* (C≡C), 70.0*, 67.5 (OCH_3), 0.19*/ − 0.04 ($Si(CH_3)_3$); FT-IR (petroleum ether): $\tilde{\nu}$ = 2161 [w, (C≡C)], 2067 [m, (C=O), A_1^1], 1993 [w, (C=O), B_1], 1963 [sh, (C=O), A_1^2], 1955 [s, (C=O), E] cm^{-1}; MS (EI): *m/z* (%): 408 (3) [M^+]; $C_{18}H_{16}O_6SiCr$ (408.4): calcd C 52.94, H 3.95; found C 53.03, H 4.08.

Tetracarbonyl[methoxy(2-pentyn-1′-ylphenyl)carbene]chromium(0) (3b): A solution of **2b** (6.2 mmol, 2.35 g) in diethyl ether (80 mL) was cooled to −40 °C and irradiated for 2 h while a light flow of argon was bubbled through the solution. In the course of the reaction the colour of the solution turned from red to brown. Then the solvent was removed under reduced pressure at −30 °C. Purification of the product by repeated crystallization from acetone between −30 °C and −78 °C yielded 1.17 g (52%) of black crystals. ^{1}H NMR (250 MHz, [D_6]acetone, 223 K): δ = 7.9–7.0 (m, 4H, Ar-H), 4.97 (brs, 3H, OCH_3), 2.97 (brs, 2H, $C\mathit{H}_2-CH_2$), 1.82 (brs, 2H; $CH_2-C\mathit{H}_2-CH_3$), 1.05 (brs, 3H, $CH_2-C\mathit{H}_3$); ^{13}C NMR (62.5 MHz, [D_6]acetone, 223 K): δ = 336.8 (Cr=C), 232.0 (CO_{trans}), 228.4 (CO_{trans}), 214.6 ($CO_{all-cis}$), 157.1 (C 1), 134.1 (C 2), 131.7, 128.9, 127.3, 116.6 (Ar-C), 79.4 (C≡C), 68.3 (C≡C), 66.8 (brs, OCH_3), 22.0 ($\mathit{C}H_2-CH_3$), 11.9 ($CH_2-\mathit{C}H_3$); ($\mathit{C}H_2-CH_2$) not observed; FT-IR (*n*-hexane): $\tilde{\nu}$ = 2024 [m, (C=O), A_1^1], 1948 [s, (C=O), A_1^2], 1931 [s, (C=O), B_1], 1894 [m, (C=O), B_2] cm^{-1}; MS (FAB, *m*NBA): *m/z* (%): 350 (10) [M^+]; $C_{17}H_{14}O_5Cr$ (350.3): calcd C 58.28, H 4.03; found C 58.09, H 4.10.

Tetracarbonyl[methoxy(2-trimethylsilylethynylphenyl)carbene]chromium(0) (3c): The title compound was synthesized from **2c** as for the preparation of **3b**. Yield: 1.77 g (75%), black crystals. ^{1}H NMR (250 MHz, [D_6]acetone, 223 K): δ = 7.90 (d, 1H, $^3J_{H,H}$ = 7.3 Hz, Ar-H), 7.65 (m, 2H, Ar-H), 7.50 (t, 1H, $^3J_{H,H}$ = 7.3 Hz, Ar-H), 5.00 (s, 3H, OCH_3), 0.50 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (62.5 MHz, [D_6]acetone, 223 K): δ = 336.3 (br, Cr=C), 233.4 (CO_{trans}), 228.8 (CO_{trans}), 214.1 ($CO_{all-cis}$), 158.5 (C 1), 133.3 (C 2), 131.8, 129.2, 128.2, 116.6 (Ar-C), 96.5 (C≡C), 76.5 (C≡C), 66.7 (OCH_3), −1.9 ($Si(CH_3)_3$); FT-IR (*n*-hexane): $\tilde{\nu}$ = 2029 [m, (C=O), A_1^1], 1948 [s, (C=O), A_1^2], 1935 [vs, (C=O), B_1], 1890 [s, (C=O), B_2] cm^{-1}; $C_{17}H_{16}O_5Cr$ (352.3): calcd C 53.68, H 4.24; found C 53.30, H 4.43.

1,2,3,4,4a,12a-η^6-Tricarbonyl(6,12-dimethoxy-5,11-diprop-1′-ylchrysene)-chromium(0) (6b) and **6,12-dimethoxy-5,11-diprop-1′-ylchrysene (7b)**: A solution of **2b** (4.5 mmol, 1.71 g) in *t*-butyl methyl ether (20 mL) was heated under reflux for 2 h. After removal of the solvent under reduced pressure, the reaction mixture was separated by column chromatography (silica gel, −10 °C, dichloromethane/*n*-hexane 6:1). The first fraction gave 0.25 g (15%) of recovered carbene complex **2b**. The subsequent red band yielded 0.60 g (60%) of a red solid containing chrysene complex **6b** and the uncoordinated chrysene **7b** in a 1:1 ratio (according to NMR). Complex **6b** was purified by crystallization from diethyl ether upon slow cooling to −20 °C. Decomplexation: A mixture of **6b** and **7b** was dissolved in acetone/ethanol and the solution was stirred in air at room temperature for 3 h. The decomplexation was monitored by TLC. The solvent was removed, the residue was adsorbed on silica gel and purified by chromatography with dichloromethane/*n*-hexane as eluents.

Complex 6b·0.5Et$_2$O: M.p. 95.5–96.0 °C; ^{1}H NMR (400 MHz, C_6D_6): δ = 8.23 (d, 1H, $^3J_{H,H}$ = 8.4 Hz, H10/H7), 8.13 (d, 1H, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1 Hz, H7/H10), 7.33 (m, 1H, H8/H9), 7.22 (m, H9/H8), 6.44 (d, 1H, $^3J_{H,H}$ = 6.3 Hz, H1/H4, Ar-H), 6.02 (d, 1H, $^3J_{H,H}$ = 6.0 Hz, H4/H1, Ar-H), 4.82 (m, 2H, H2/H3, Ar-H), 3.50 (s, 3H, OCH_3), 3.49 (s, 3H, OCH_3), 3.22 (m, 2H, $-C\mathit{H}_2-CH_2-$), 3.07 (m, 2H, $-C\mathit{H}_2-CH_2-$), 2.11 (m, 1H, $-CH_2-C\mathit{H}_2-CH_3$), 1.97 (m, 2H, $-CH_2-C\mathit{H}_2-CH_3$), 1.77 (m, 1H, $-CH_2-C\mathit{H}_2-CH_3$), 1.02 (t, 3H, $^3J_{H,H}$ = 7.3 Hz, $-CH_2-C\mathit{H}_3$), 0.86 (t, 3H, $^3J_{H,H}$ = 7.3 Hz, $-CH_2-C\mathit{H}_3$). Additional signals due to diethyl ether: δ = 3.25 (q, 2H), 1.12 (t, 3H); ^{13}C NMR (75 MHz, C_6D_6): δ = 232.6 (CO), 153.8, 151.1 ($\mathit{C}OCH_3$), 131.0, 130.4, 129.0, 127.9, 126.9, 126.7, 124.9, 122.5, 104.0, 98.7, 91.9, 90.3, 89.0, 85.7 (Ar-C), 60.5, 59.9 (OCH_3), 32.9, 31.9 ($-\mathit{C}H_2-CH_2-CH_3$), 23.9, 23.2 ($-CH_2-\mathit{C}H_2-CH_3$), 14.4, 14.1 ($-CH_2-CH_2-\mathit{C}H_3$). Additional signals due to diethyl ether: δ = 65.5, 15.2; $C_{31}H_{33}O_{5.5}Cr$ (545.2): calcd C 68.24, H 6.10; found C 67.84, H 5.88.

Chrysene 7b: R_f = 0.55 (SiO_2, hexane/Et_2O 4:1); ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.37 (d, 2H, $^3J_{H,H}$ = 8.3 Hz, Ar-H), 8.18 (d, 2H, $^3J_{H,H}$ = 7.7 Hz, Ar-H), 7.60 (m, 2H, Ar-H), 7.51 (m, 2H, Ar-H), 3.90 (s, 6H, OCH_3), 3.22 (m, 4H, $-C\mathit{H}_2-CH_2$), 2.03 (m, 4H, $-CH_2-C\mathit{H}_2-CH_3$), 1.12 (t, 6H, $^3J_{H,H}$ = 7.3 Hz, $-CH_2-C\mathit{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.4 (C 6/C 12), 130.7, 129.3, 128.3, 127.5, 127.4, 127.0, 126.0, 124.4, 122.3 (Ar-C), 60.9 (OCH_3), 32.9 ($-\mathit{C}H_2-CH_2-CH_3$), 23.8 ($-CH_2-\mathit{C}H_2-CH_3$), 14.7 ($-CH_2-CH_2-\mathit{C}H_3$); FT-IR (KBr): $\tilde{\nu}$ = 3072 w, 2956 vs, 2931 s, 2873 m, 2840 m, 1737 w, 1698 w, 1647 m, 1583 m, 1518 m, 1473 m, 1371 s, 1242 s, 1133 s, 1101 s, 1011 m, 767 s cm^{-1}; HR-MS (EI): calcd for $C_{26}H_{28}O_2$ (372.5): 372.2089. Found: 372.2092 (100%, M^+).

5,11-Diphenylchrysene-6,12-dione (8a): Trimethylsilyliodide (3.30 mmol, 0.66 g) was added to a solution of **7a**[14] (0.84 mmol, 0.37 g) in dichloromethane (3 mL). After stirring for 79 h at ambient temperature the solvent was removed and the product was purified by column chromatography (silica gel, dichloromethane/*n*-hexane 1:1). Yield: 0.17 g (50%), orange solid. M.p. 247–248 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 294 K): δ = 8.13 (d, 2H, $^3J_{H,H}$ = 7.7 Hz), 7.38 (m, 8H), 7.19 (m, 4H), 7.15 (td, 2H, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.3 Hz), 6.93 (d, 2H, $^3J_{H,H}$ = 7.7 Hz); ^{13}C NMR (62.5 MHz, $CDCl_3$, 294 K): δ = 185.1 (C=O), 141.9, 138.1, 135.8, 135.0, 131.6, 131.2, 131.0, 130.2, 129.5, 128.6, 126.9 (Ar-C); FT-IR (KBr): $\tilde{\nu}$ = 3068 w, 1644 vs, 1597 m, 1331 m, 1309 m, 1293 m, 1118 w, 1076 w, 757 w, 720 w, 700 w cm^{-1}; HR-MS (EI): calcd for $C_{30}H_{18}O_2$ (410.1): 410.1307; found 410.1310 (100%, M^+).

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[27] The NMR spectra of **2b** were complicated owing to hindered rotation of the *n*-propyl group around the carbene oxygen bond in the (*E*) isomer.