

Reactions of complex ligands 74¹. Alkyne carbene chromium chelates: Synthesis, structure and carbene dimerization²

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Abstract

An alkyne-carbene chromium chelate **2**, a model complex for the first intermediate of the benzannulation reaction, is generated by low-temperature photodecarbonylation of pentacarbonyl[(*tert*-butylethynylphenyl)methoxycarbene]chromium **1**. X-ray structure determinations and ¹³C NMR studies on both compounds indicate only a weak coordination of the alkyne both in the solid state and in solution. Whereas thermal dimerization of the carbene ligand is directed by less bulky alkyne substituents to give chrysenes, pentacarbonyl complex **1** affords a mixture of stilbene diastereomers. © 1997 Elsevier Science S.A.

Keywords: Alkyne complexes; Carbene complexes; Chelate complexes; Chromium complexes; Stilbenes

1. Introduction

The chromium-mediated benzannulation [2] of Fischer-type metal carbenes [3] offers a direct access to densely functionalized arenes and has been applied to the synthesis of various natural products within the past two decades [4] (Scheme 1). A generally accepted mechanism of this reaction has been supported by the isolation and characterization of analogues of presumed intermediates such as the alkyne insertion product **B** [5] and vinyl ketene **C** [6] and by extended Hückel MO [7] and more recent quantum chemical calculations [8]. The first intermediate, the more trivial looking alkyne carbene complex **A**, however, generated by decarbonylation of the pentacarbonyl starting material and alkyne coordination, has even escaped reliable spectroscopic identification so far. Obviously, the lability of this species is due to the low barrier of activation for the alkyne insertion into the metal carbene bond [8].

We speculated whether the alkyne insertion could be blocked by connecting the alkyne and the carbene lig-

and by a rigid C₂–arene bridge. This strategy has been successfully applied to the isolation of a less reactive tetracarbonyl-η²-alkyne-carbene chelate complex of tungsten [9], but has failed in the chromium series; instead, an unprecedented chrysene formation based on a formal dimerization of the alkynylarylcarbene ligand has been observed [1] (Scheme 2). We found that the course of the carbene dimerization depends on the alkyne substitution pattern, and we now report on the synthesis and structure of non-chelated and chelated (*tert*-butylethynylphenyl)carbene complexes; these compounds provide insight into the nature of alkyne coordination which is relevant for the benzannulation reaction.

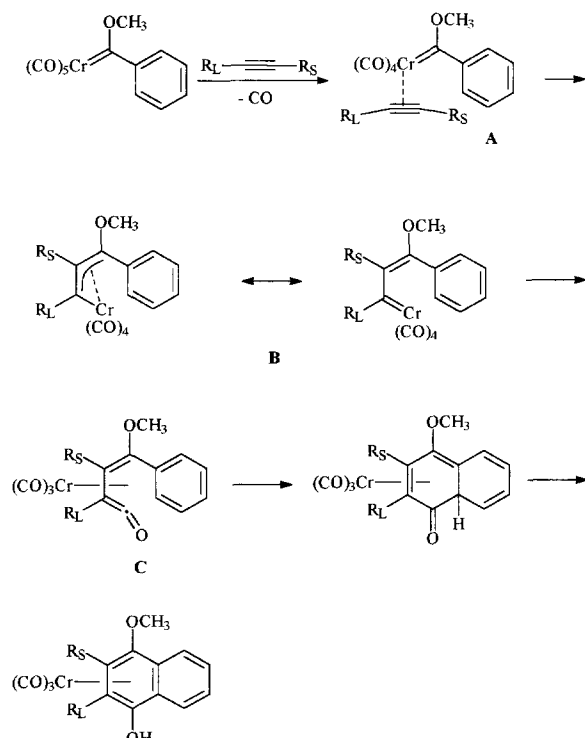
2. Results and discussion

The pentacarbonyl carbene complex **1** is accessible by standard methodology from 1-bromo-2-(3',3'-dimethyl-butyn-1'-yl)benzene in 89% yield after lithiation, addition to hexacarbonylchromium followed by alkylation. Low-temperature irradiation of an acetone solution of **1** – monitored by IR-spectroscopy – results in the regioselective substitution of a *cis*-CO ligand for the alkyne as indicated by a ν_{C=O} absorption pattern (2024m, 1947s, 1933s, 1897m) characteristic for *cis*-

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¹ For Part 73, see Ref. [1].

² Herrn Professor Dr. Gottfried Huttner zum 60. Geburtstag gewidmet.

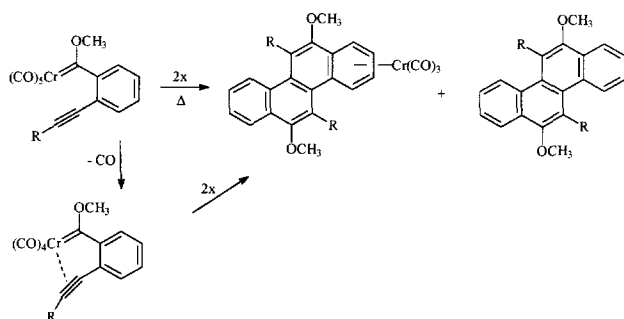


Scheme 1. Benzannulation reaction.

$L_2Cr(CO)_4$ complexes. After crystallization the alkyne carbene chelate **2** is isolated in 57% yield.

The comparison of the ^{13}C NMR spectra (Table 1) of pentacarbonyl complex **1** and alkyne carbene chelate complex **2** reveals an only moderate upfield coordination shift (10.8 and 5.8 ppm) for the alkyne carbon atoms. Additional spectroscopic support for the complexation of the alkyne may be derived from the sequence of the resonance absorptions of the tert-butyl group in both compounds: whereas in the non-chelated complex **1** the quaternary carbon atom is shielded as a consequence of the magnetic anisotropy of the adjacent uncoordinated $C\equiv C$ bond, and thus resonates upfield in comparison with the neighbouring methyl carbon atoms, this sequence is reversed in the alkyne carbene chelate **2**.

According to earlier observations [10] the formation of carbene chelate complexes affects the conformation



Scheme 2. Chrysene formation via carbene dimerization.

Table 1
Selected ^{13}C NMR data of alkyne carbene chelate **2** and its precursor **1** (in acetone- d_6)

	1 ^a	2	$\Delta\delta$
δ (Cr=C)	356.2	338.6	–17.6
δ (C $\equiv$ C–Ar)	103.8	93.0	–10.8
δ (C $\equiv$ C–Ar)	77.6	71.8	–5.8
δ (C(CH ₃) ₃)	29.0	32.5	3.5
δ (C(CH ₃) ₃)	31.4	29.4	–2.0

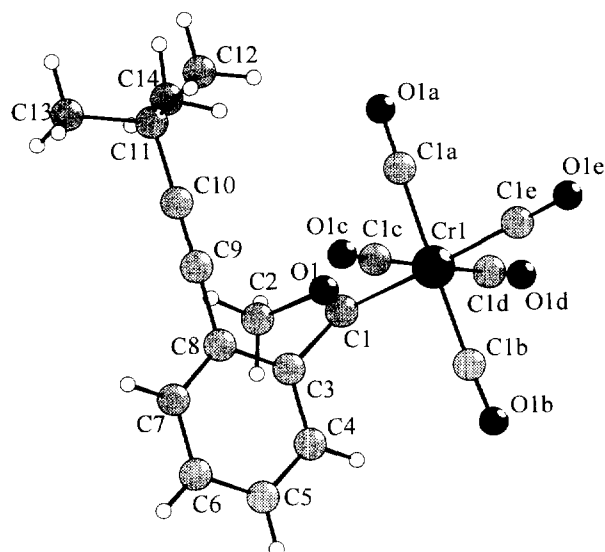
^a Resonances of the Z-isomer.

across the carbene to oxygen bond. At room temperature the ^{13}C NMR signals of the pentacarbonyl complex **1** are broadened indicating that the rate of rotation around this bond is close to the NMR time scale. The spectrum recorded at $-40^\circ C$ shows a double set of signals corresponding to a 4:1 mixture of *E/Z*-isomers; the alkyne carbene chelate **2**, however, adopts exclusively the *Z*-configuration. This result may be explained in terms of an increased electron density upon chelation, and thus the stereoelectronic repulsion between the oxygen lone pairs and the $Cr(CO)_4$ fragment favours the *Z*-configuration in chelate **2** [11].

3. Molecular structures of alkynylcarbene complexes **1** and **2**

In order to further elucidate the coordination of the alkyne, single crystals of complex analogues **1** and **2** were subjected to X-ray analysis. Their molecular structures are depicted in Figs. 1 and 2, and the relevant structural data are summarized in Table 2.

The most striking information is that the $C\equiv C$ bond does not reveal any significant elongation upon coordination (120.5(7) pm for **2** versus 119.2(4) pm for **1**). The Cr–C_{alkyne} bond lengths in chelate **2** are long and comparable to those observed for tungsten alkyne complexes [12]; moreover, the deviation of the alkyne skeleton from linearity is rather small (168.5(5) and 156.9(6) $^\circ$). All these structural features of chelate complex **2** indicate only a weak coordination of a two-electron donor alkyne ligand (for variable electron donor ability of alkyne ligands, see Ref. [13]), which is further supported by a remarkable *trans*-effect [14] observed for the *trans*-CO ligand (182.5(7) pm versus 188.6(6) pm as a mean value for the *cis*-CO ligands). A minor elongation of the chromium carbene bond upon chelation (204.0(5) pm for **2** versus 201.3(3) pm for **1**) as

Fig. 1. Molecular structure of **1**.

well as the decrease of the bond angles at the bridging arene carbon atoms C2 and C7 ($C1-C2-C7$: $114.6(5)^\circ$ and $C2-C7-C8$: $115.2(5)^\circ$) may be traced back to the steric strain in the rigid chelate geometry.

The chelation requires an adjustment of the carbene and alkynylarene planes. Whereas both planes are nearly orthogonal in the pentacarbonyl complex **1** (as evident from the dihedral angle $Cr(1)-C(1)-C(3)-C(8) = 97.7^\circ$), this angle is considerably decreased in the alkyne carbene chelate **2** ($Cr(1)-C(1)-C(2)-C(7) = 18.7^\circ$). There still remains a tilt between the alkyne and carbene planes, which is also evident from the dihedral angle $C(1)-Cr(1)-C(9)-C(8)$ of -24.8° .

The solid state configuration at the carbene to oxy-

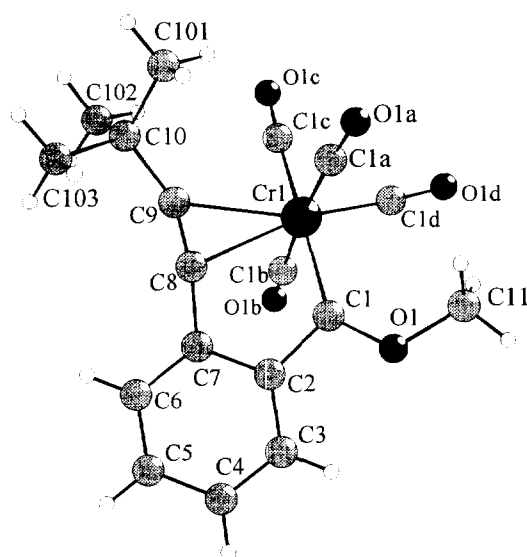
Fig. 2. Molecular structure of **2**.

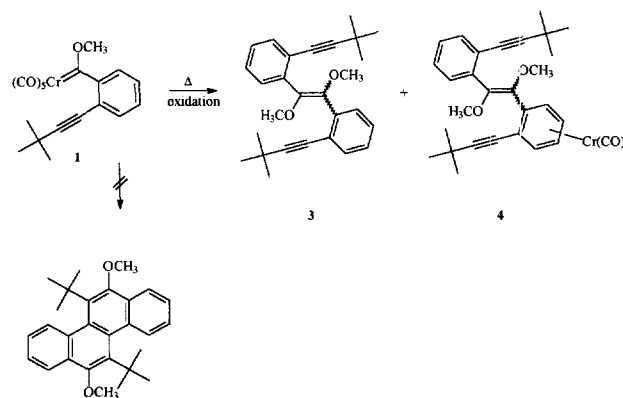
Table 2

Selected bond lengths, bond angles and dihedral angles of **1** and **2** (for atom numbering see Figs. 1 and 2)

	1	2
<i>Bond lengths (pm)</i>		
$C(9)-C(10)$	119.2(4)	$C(8)-C(9)$ 120.5(7)
$Cr(1)-C(1)$	201.3(3)	$Cr(1)-C(1)$ 204.0(5)
$Cr(1)-C(1a)$	189.2(4)	$Cr(1)-C(1a)$ 189.5(6)
$Cr(1)-C(1b)$	189.8(3)	$Cr(1)-C(1b)$ 188.9(6)
$Cr(1)-C(1c)$	190.7(3)	$Cr(1)-C(1d)$ 182.5(7)
$Cr(1)-C(1d)$	191.3(3)	
$Cr(1)-C(1e)$	188.5(3)	$Cr(1)-C(1e)$ 187.4(6)
		$Cr(1)-C(8)$ 231.5(5)
		$Cr(1)-C(9)$ 242.3(5)
<i>Bond angles ($^\circ$)</i>		
$C(9)-C(10)-C(11)$	179.4(3)	$C(8)-C(9)-C(10)$ 156.9(6)
$C(8)-C(9)-C(10)$	176.8(3)	$C(7)-C(8)-C(9)$ 168.5(6)
$C(1)-C(3)-C(8)$	120.3(2)	$C(1)-C(2)-C(7)$ 114.6(5)
$C(3)-C(8)-C(9)$	119.8(3)	$C(2)-C(7)-C(8)$ 115.2(5)
<i>Dihedral angles ($^\circ$)</i>		
$Cr(1)-C(1)-C(3)-C(8)$	97.7	$Cr(1)-C(1)-C(2)-C(7)$ 18.7
		$C(1)-Cr(1)-C(9)-C(8)$ -24.8

gen bond is reversed upon chelation: the pentacarbonyl complex **1** prefers to crystallize in the *E*-configuration whereas the alkyne carbene chelate **2** adopts the *Z*-configuration; this reflects the configurations prevailing in solution as determined by NMR spectroscopy.

Attempts to generate the alkyne carbene chelate **2** by a thermal decarbonylation of the pentacarbonyl precursor **1** failed; moreover, no chrysene derivative – resulting from a formal dimerization of the alkynylcarbene ligand as observed for less bulky methoxy(alkynylphenyl)carbene complex analogues [9] – could be detected. Instead, a carbene dimerization process occurred to give a mixture of $Cr(CO)_3$ -coordinated and uncoordinated stilbene derivatives. Oxidative demetallation afforded 1,2-dimethoxystilbene **3** as a mixture of diastereomers resulting from *E/Z*-isomerism and re-

Scheme 3. Carbene dimerization of **1** to give stilbenes **3** and **4**.

stricted rotation around the C_{alkene}–C_{arene} bonds (Scheme 3). Apparently, the steric bulk of the tert-butyl substituent compared with unbranched alkyl groups and the shorter bond distance between the alkyne carbon atom and the tert-butyl moiety relative to that for the trimethylsilyl analogue (147.8(4) pm for **2** versus 183.6(8) pm for the TMS analogue [1]) inhibit the sterically demanding chrysene formation [1].

4. Experimental part

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 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. 1-Bromo-2-(3',3'-dimethylbutyn-1'-yl)benzene was synthesized by palladium-catalyzed coupling from commercially available 2-bromo-1-iodobenzene following a slightly modified literature procedure [15] and purified by column chromatography. Photochemical transformations were conducted with a mercury high-pressure lamp (Fa. Heraeus). IR spectra were recorded on a Nicolet Magna 550 spectrometer, NMR spectra on a Bruker AMX 500, AM 400 or AM 250 spectrometer. All chemical shifts are given in ppm 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, Fa. Heraeus.

4.1. X-ray crystallographic studies of **1** and **2**³

The structures were solved by direct methods (SHELXTL-PLUS [16]). The non-hydrogen atoms were refined anisotropically on F^2 (SHELXL-93 [17]). Hydrogen atoms were refined isotropically using a riding model. An extinction correction (**1**) and an absorption correction on the basis of Ψ -scans were applied (**1**: $T_{\max/\min} = 0.913/0.224$; **2**: $T_{\max/\min} = 0.962/0.490$). Further details are given in Table 3. Atomic coordinates and equivalent isotropic displacement parameters are given in Tables 4 and 5 respectively. Molecular diagrams were plotted with DIAMOND [18].

³ Further details of crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen on quoting the depository numbers CSD-406838 (**1**) and CSD-406837 (**2**), the publication and the names of the authors.

Table 3
Crystallographic data of **1** and **2**

	1	2
Formula	C ₁₉ H ₁₆ CrO ₆	C ₁₈ H ₁₆ CrO ₅
M_r	392.32	364.31
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	11.276(1)	8.325(1)
b (Å)	10.733(2)	14.198(2)
c (Å)	16.354(4)	14.467(2)
β (deg)	100.11(2)	97.30(1)
V (Å ³)	1948.5(7)	1696.1(4)
Z	4	4
Crystal size (mm ³)	0.48 × 0.40 × 0.38	0.40 × 0.20 × 0.18
ρ_{calc} (g cm ⁻³)	1.34	1.43
μ (mm ⁻¹)	5.10	5.77
$F(000)$	808	752
Diffractionmeter Enraf–Nonius CAD4		
Radiation	Cu K α	Cu K α
λ (Å)	1.54178	1.54178
T (K)	208(2)	200(2)
Scan type	$2\theta/\omega$	$2\theta/\omega$
Max 2θ (deg)	120	120
Index range	$-12 \leq h \leq 12$ $-12 \leq k \leq 0$ $0 \leq l \leq 18$	$-9 \leq h \leq 9$ $0 \leq k \leq 15$ $0 \leq l \leq 16$
No. of data	2992	2638
No. of unique data	2879	2524
Parameters	240	217
$R(F)$ for $I > 2\sigma(I)$	0.052	0.061
$wR_2(F^2)$ for all data	0.140	0.182
Goodness of fit on F^2	1.05	1.02

4.2. Pentacarbonyl[methoxy(2-(3',3'-dimethylbutyn-1'-yl)phenyl)carbene]chromium(0) **1**

n-Butyllithium (11 mmol, 6.9 ml of a 1.6 M solution in hexane) was added dropwise to a solution of 1-bromo-2-(3',3'-dimethylbutyn-1'-yl)benzene (10 mmol, 2.36 g) 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 during 1 h. The solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane (20 ml). Trimethyloxoni-umtetrafluoroborate (11 mmol, 1.63 g) was added and the suspension was stirred for a further 1 to 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).

Yield: 3.49 g (89%), orange solid.

Anal. Found: C, 58.37; H, 4.47. C₁₉H₁₆O₆Cr Calc.: C, 58.17; H, 4.11%. M.p. 75 °C. MS(EI): m/z 392 (9%, M⁺). FT-IR (petroleum ether): 2066 [m, ν (C=O), A₁], 1993 [w, ν (C=O), B₁], 1960 [s, ν (C=O), A₁], 1952 cm⁻¹ [s, ν (C=O), E]. ¹H NMR (250 MHz, acetone-*d*₆, 293 K): δ = 7.45 (m, 2H, Ar–H), 7.32 (m, 1H,

Table 4

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**

Atom	[x]	[y]	[z]	U_{eq}
Cr(1)	6363(1)	2266(1)	7953(1)	30(1)
C(1a)	4835(3)	2467(3)	8263(2)	41(1)
O(1a)	3926(2)	2592(3)	8463(2)	69(1)
C(1b)	7915(3)	2072(3)	7671(2)	40(1)
O(1b)	8862(2)	1944(2)	7528(2)	58(1)
C(1c)	5857(3)	732(3)	7413(2)	39(1)
O(1c)	5561(2)	–195(2)	7115(2)	59(1)
C(1d)	6822(3)	3828(3)	8478(2)	39(1)
O(1d)	7075(2)	4756(2)	8784(2)	58(1)
C(1e)	6897(3)	1377(3)	8944(2)	44(1)
O(1e)	7209(3)	811(2)	9541(2)	72(1)
C(1)	5752(2)	3176(2)	6887(2)	30(1)
O(1)	5162(2)	4222(2)	6898(1)	39(1)
C(2)	4668(3)	4916(3)	6146(2)	48(1)
C(3)	5902(2)	2724(2)	6046(2)	29(1)
C(4)	6983(3)	2885(3)	5774(2)	39(1)
C(5)	7139(3)	2432(3)	5008(2)	47(1)
C(6)	6228(3)	1786(3)	4516(2)	47(1)
C(7)	5152(3)	1607(3)	4778(2)	41(1)
C(8)	4958(2)	2079(2)	5538(2)	32(1)
C(9)	3822(3)	1931(3)	5806(2)	35(1)
C(10)	2870(3)	1870(3)	6026(2)	39(1)
C(11)	1688(3)	1801(3)	6295(2)	44(1)
C(12)	1756(4)	835(4)	6988(3)	74(1)
C(13)	737(3)	1412(7)	5568(3)	95(2)
C(14)	1393(4)	3066(4)	6619(4)	84(2)

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

Table 5

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

Atom	[x]	[y]	[z]	U_{eq}
Cr(1)	7055(1)	2703(1)	1484(1)	28(1)
C(1a)	5205(7)	2801(4)	2117(4)	34(1)
O(1a)	4046(5)	2793(3)	2486(3)	47(1)
C(1b)	8821(7)	2539(4)	798(4)	35(1)
O(1b)	9884(5)	2401(3)	384(3)	49(1)
C(1c)	8382(7)	2255(5)	2535(4)	39(1)
O(1c)	9208(6)	1912(4)	3148(3)	56(1)
C(1d)	6549(7)	1461(5)	1296(4)	38(1)
O(1d)	6313(6)	651(3)	1228(3)	50(1)
C(1)	5822(6)	3146(4)	251(3)	28(1)
O(1)	4603(4)	2795(3)	–328(2)	36(1)
C(11)	3688(7)	1994(5)	–84(4)	47(2)
C(2)	6393(6)	3996(4)	–201(3)	28(1)
C(3)	5984(6)	4259(4)	–1135(4)	33(1)
C(4)	6636(7)	5059(4)	–1456(4)	38(1)
C(5)	7687(7)	5621(4)	–867(4)	38(1)
C(6)	8074(7)	5387(4)	59(4)	34(1)
C(7)	7418(6)	4578(4)	390(3)	30(1)
C(8)	7688(6)	4281(4)	1351(3)	28(1)
C(9)	7910(6)	4200(4)	2186(4)	30(1)
C(10)	8313(7)	4511(4)	3179(4)	36(1)
C(101)	7239(8)	4062(5)	3835(4)	46(2)
C(102)	10109(8)	4294(5)	3494(4)	55(2)
C(103)	8046(9)	5591(5)	3164(5)	56(2)

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

Ar–H), 7.08 (d, 1H, $^3J_{HH} = 7.3$ Hz, Ar–H), 4.29 (brs, 3H, OCH₃), 1.30 ppm (s, 9H, C(CH₃)₃). ¹H NMR (250 MHz, acetone-*d*₆, 233 K): $\delta = 7.56$ – 7.27 (m, 3H, Ar–H), 7.22* (brd, 4H, $^3J_{HH} = 7.4$ Hz, Ar–H), 7.10 (d, 1H, $^3J_{HH} = 7.6$ Hz, Ar–H), 5.09*/4.23 (s, 3H, OCH₃), 1.27/1.25* ppm (s, 9H, C(CH₃)₃); ratio (OCH₃) *E/Z** 4:1. ¹³C NMR (125 MHz, CDCl₃, 298 K): $\delta = 354.5$ (br, Cr=C), 224.6 (br, CO_{trans}), 215.8 (br, CO_{cis}), 132.4 (Ar–C₂), 127.7 (br, Ar), 127.5 (br, Ar–C), 123.4 (br, Ar–C), 121.4 (br, Ar–C), 112.8 (Ar–C), 103.7 (br, C≡C), 74.9 (br, C≡C), 65.0 (br, OCH₃), 30.5 (C(CH₃)₃), 28.0 ppm (C(CH₃)₃). ¹³C NMR (62.5 MHz, acetone-*d*₆, 223 K): $\delta = 356.2^*/355.3$ (Cr=C), 226.3/225.5* (CO_{trans}), 217.8/216.9* (CO_{cis}), 158.1*/153.8 (Ar–C₁), 133.5*/133.4 (Ar–C), 129.5/128.1* (Ar–C), 129.3/128.5* (Ar–C), 123.4*/122.5 (Ar–C), 114.9*/112.9 (Ar–C₂), 104.7/103.8* (C≡C), 77.6*/76.9 (C≡C), 70.0*/67.3 (OCH₃), 31.4*/31.0 (C(CH₃)₃), 29.1/29.0* ppm (C(CH₃)₃).

The asterisk '*' denotes signals of the *Z*-isomers of the carbene oxygen bond.

4.3. Tetracarbonyl[*methoxy(2-(3',3'-dimethylbutyn-1'-yl)phenyl)carbene*]chromium(0) **2**

A solution of **1** (6.2 mmol, 2.43 g) in diethyl ether (80 ml) was cooled to -40°C and irradiated for 2 h while a slight 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 and -78°C yielded 1.29 g (57%) of black crystals. Anal. Found: C, 59.03; H, 4.67. C₁₈H₁₆O₅Cr Calc.: C, 59.34; H, 4.43%. FT-IR (n-hexane): 2024 [m, $\nu(\text{C}=\text{O})$, A₁], 1947 [s, $\nu(\text{C}=\text{O})$, A₁], 1933 [s, $\nu(\text{C}=\text{O})$, B₁], 1897 cm^{–1} [m, $\nu(\text{C}=\text{O})$, B₂]. ¹H NMR (250 MHz, acetone-*d*₆, 293 K): $\delta = 7.81$ (d, 1H, $^3J_{HH} = 7.4$ Hz, Ar–H), 7.59 (m, 2H, Ar–H), 7.41 (t, 1H, $^3J_{HH} = 7.3$ Hz, Ar–H), 5.04 (s, 3H, OCH₃), 1.56 ppm (s, 9H, C(CH₃)₃). ¹H NMR (250 MHz, acetone-*d*₆, 245 K): $\delta = 7.83$ (d, 1H, $^3J_{HH} = 7.9$ Hz, Ar–H), 7.60 (m, 2H, Ar–H), 7.43 (m, 1H, Ar–H), 5.01 (s, 3H, OCH₃), 1.52 ppm (s, 9H, C(CH₃)₃). ¹³C NMR (62.5 MHz, acetone-*d*₆, 235 K): $\delta = 338.6$ (br, Cr=C), 236.0 (CO_{trans}), 230.4 (CO_{trans}), 216.4 (CO_{all-cis}), 159.4 (Ar–C₁), 138.0 (Ar–C₂), 134.1, 131.2, 129.5, 119.1 (Ar–C), 93.0 (C≡C), 71.8 (C≡C), 69.0 (OCH₃), 32.5 (C(CH₃)₃), 29.4 ppm (C(CH₃)₃).

4.4. 1,2-Dimethoxy-1,2-[2'-(3'',3''-dimethylbutyn-1''-yl)phenyl]ethene **3**

A solution of **1** (1.32 mmol, 0.52 g) in *t*-butyl methyl ether (7 ml) was heated at reflux for 3 h. After removal

of the solvent under reduced pressure the reaction mixture was separated by column chromatography (silica gel, -10°C , dichloromethane/n-hexane 1:4). The red fraction contained a mixture of uncoordinated and $\text{Cr}(\text{CO})_3$ coordinated stilbenes **3** and **4** which was dissolved in acetone/ethanol. The solution was stirred in air at room temperature, the solvent was removed, the residue was adsorbed on silica gel and purified by chromatography using diethyl ether/n-hexane (1:1) as eluents.

Yield: 0.1 g (38%), colourless oil.

MS(ED): m/z 400 (100%, M^+). ^1H NMR (400 MHz, CDCl_3): δ = 7.25 (dd, 2H, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1$ Hz, Ar-H), 7.10 (dd, 2H, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1$ Hz, Ar-H), 7.03 (td, 2H, $^3J_{\text{HH}} = 7.6$ Hz, $J_{\text{HH}} = 1$ Hz, Ar-H), 6.93 (td, 2H, $^3J_{\text{HH}} = 7.6$ Hz, $^4J_{\text{HH}} = 1$ Hz, Ar-H), 3.81/3.56/3.49/3.28 (s, 6H, OCH_3), 1.53/1.36/1.29/1.06 ppm (s, 18H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (100 MHz, CDCl_3): δ = 167.8/155.0/154.0 ($\text{C}-\text{OCH}_3$), 142.3–116.6 ($\text{C}-\text{Ar}$), 102.1 ($\text{Ar}-\text{C}\equiv\text{C}$), 78.2 ($\text{Ar}-\text{C}\equiv\text{C}$), 68.0/60.4/57.2/54.7 (OCH_3), 31.8/31.0/30.5 ($\text{C}(\text{CH}_3)_3$), 30.2/29.6/28.8 ppm ($\text{C}(\text{CH}_3)_3$).

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