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Dialkynylated and functionalized alkynylated areneCr(CO)$_3$-complexes—syntheses and structures of carbon rich chromium-complexed benzenes

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Abstract

The dialkynylated η^6-(arene)Cr(CO)$_3$-complexes **2** and **4** can be synthesized: (a) by *Sonogashira coupling* of alkynes with dihalo areneCr(CO)$_3$-complexes; or (b) very efficiently by a Horner–Emmons–Wadsworth related acetylene synthesis with readily available Cr(CO)$_3$-complexed aryl aldehydes. The structural constitution of two novel difunctional alkynyl arene complexes (**2a** and **6**) was confirmed by X-ray crystal structure analyses. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkynes; Arene complexes; Catalysis; Chromium; Copper; Palladium

1. Introduction

Carbon rich organic and organometallic compounds have recently aroused considerable interest, in particular, as suitable precursors for the construction of new all-carbon networks [1] with potentially interesting material properties such as electrical conductivity [2], liquid crystallinity [3] or large optical nonlinearities [4]. Especially, the stabilization of polyalkynylated cyclobutadienes or cyclopentadienides by transition metal fragments by Bunz [5] has opened new paths towards the synthesis of novel carbon allotropes. Surprisingly, the most obvious six-membered ring building blocks for carbon rich organometallic arrays, i.e. alkynylated benzeneCr(CO)$_3$-complexes have not thoroughly been investigated. Several aspects in arene–chromium–carbonyl chemistry have hampered the development of this class of compound. A major handicap is that the facile direct complexation of alkynylated arenes is very inefficient due to the electron withdrawing nature of the alkynyl substituents. Another disadvantage of the thermal complexation is the low regioselectivity if more than one benzene ring is present in an alkynyl bridged substrate. Therefore, we sought for a general, selective synthesis of alkynyl substituted areneCr(CO)$_3$-complexes taking advantage of the rich methodological repertoire of organic synthesis. Here we wish to communicate our first results on the syntheses and structural features of difunctional alkynylated benzeneCr(CO)$_3$-complexes.

2. Results and discussion

Initially, we first tested the feasibility of the direct complexation of 1,4-bis(trimethylsilylethynyl)benzene (**1**) with chromium hexacarbonyl under thermal conditions [6] (path a, Scheme 1) and in boiling THF with *Kündig's reagent* [7] (path b, Scheme 1). Both complexation procedures give the desired complex **2a** in 10 and 22%, respectively. The structure of the bisalkynylated complex **2a** was confirmed by X-ray crystal structure analysis (Fig. 1, Table 1) indicating a staggered arrangement of the chromium carbonyl tripod with the

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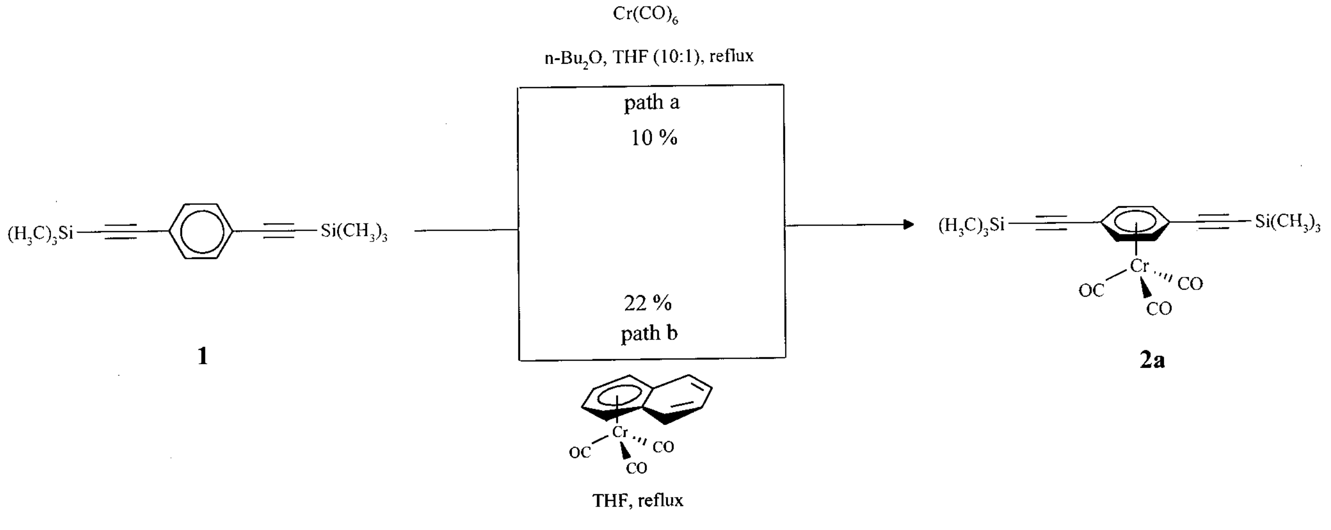


Scheme 1.

alkynyl substituents in the solid state. For further synthetic studies this path to **2a** did not seem very promising and was therefore abandonned.

Recently, we have reported a straightforward path to alkynyl substituted $Cr(CO)_3$-complexed arenes by applying *Sonogashira coupling* [8,9] to chloroarene complexes [10]. This process is general and gives rise to monoalkynylated complexes in good to excellent yields. Therefore, this methodology was extended to the synthesis of polyalkynylated complexes also with respect to the synthesis of suitable monomers for organometallic polymers. Sonogashira couplings with the complexes of 1,4- and 1,3-dichloro benzene **3a** and **3b** worked out nicely to give the dialkynylated complexes **2a**, **2b** and **2c** in moderate to excellent yields (see Scheme 2). Subsequent desilylation of **2a** and **2b** give rise to the bisethynyl substituted complexes **4a** and **4b**. Additionally, the coupling of TMS acetylene with the 2-iodo benzaldehyde dimethylacetal complex **5** furnishes the interesting bisprotected, difunctional, planar chiral arene complex **6** that can be selectively desilylated to give the ethynyl complex **7**. The crystal structure analysis of **6** (Fig. 2, Table 1) reveals that the lowest energy conformer adopts a *syn* orientation of the sterically least demanding acetal hydrogen atom (dihedral angle of the plane H(15)–C(15)–C(5)–C(4) 39.577°) with the alkynyl substituent. According to MM2 calculations [11] this conformation is 0.6 kcal mol^{-1} lower in energy than the corresponding *anti* orientation.

Although, Sonogashira coupling allows reliable access to polyalkynylated chromium arene complexes we became aware in the course of our studies that the limiting factor is the availability of polychloroarene complexes. In the case of 1,4- and 1,3-dichloro benzene

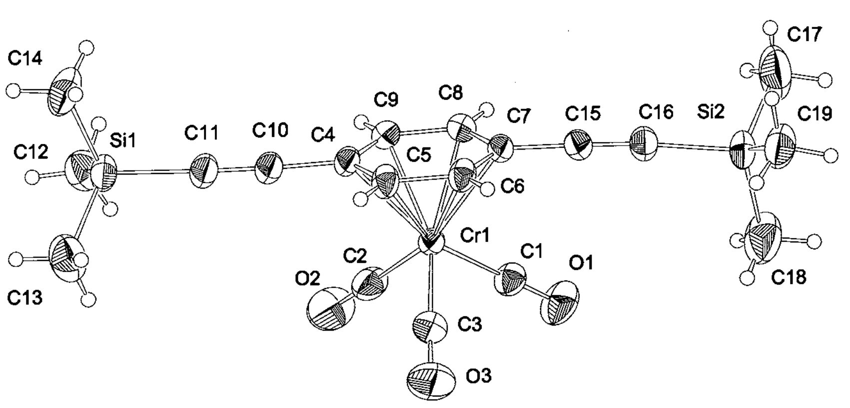


Fig. 1. Crystal structure of **2a**. Selected bond lengths (Å) and angles (°):Cr(1)-arene(centroid) 1.697, C(4)–C(10) 1.443(4), C(7)–C(15) 1.435(4), C(10)–C(11) 1.191(5), C(15)–C(16) 1.195(4), Si(1)–C(11) 1.846(4), Si(2)–C(16) 1.847(4), C(11)–C(10)–C(4) 177.1(4), C(10)–C(11)–Si(1) 177.8(4), C(16)–C(15)–C(7) 177.7(4), C(15)–C(16)–Si(2) 175.0(3).

Table 1
Crystal data and structure refinements for **2a** and **6**

	2a	**6**
Empirical formula	$C_{19}H_{22}CrO_3Si_2$	$C_{17}H_{20}CrO_5Si$
Color, form	Orange blocks	Yellow plates
Formula weight	406.6	384.4
Temperature (K)	293(2)	293(2)
Wavelength (Å), radiation	0.71073 (Mo–K_α)	0.71073 (Mo–K_α)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	20.024(3)	9.3.2(3)
b (Å)	19.752(2)	10.413(2)
c (Å)	11.778(2)	11.417(4)
α (°)		94.38(2)
β (°)	106.954(11)	105.85(3)
γ (°)		108.43(2)
V (Å^3)	4456.2(10)	995.2(5)
Z	8	2
$D_{calc.}$ (g cm^{-3})	1.212	1.283
Absorption coefficient (mm^{-1})	0.634	0.655
$F(000)$	1696	400
Crystal size (mm)	$0.6\times0.3\times0.2$	$.53\times53\times30$
Theta range for data collection (°)	2.57–23.97	3.62–23.98
Index ranges	$-22\le h\le 0$, $0\le k\le 22$, $-12\le l\le 13$	$-10\le h\le 10$, $-11\le k\le 11$, $-13\le l\le 0$
Reflections collected	7174	3277
Reflections observed [$I/2\sigma(I)$]	5231	2066
Independent reflections	6959 [$R_{int}=0.0142$]	3101 [$R_{int}=0.0307$]
Absorption correction	Semi-empirical from psi-scans	Semi-empirical from psi-scans
Max/min transmission	0.9999, 0.9880	0.9982, 0.8616
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6959/18/504	3101/0/222
Goodness-of-fit on F^2	1.092	1.126
Final R indices [$I>2\sigma(I)$]	$R_1=0.0429$, $wR_2=0.0919$	$R_1=0.0603$, $wR_2=0.1185$
R indices (all data)	$R_1=0.0667$, $wR_2=0.1041$	$R_1=0.1016$, $wR_2=0.1429$
Largest difference peak and hole (e Å^{-3})	0.265 and $-$0.238	0.307 and $-$0.259

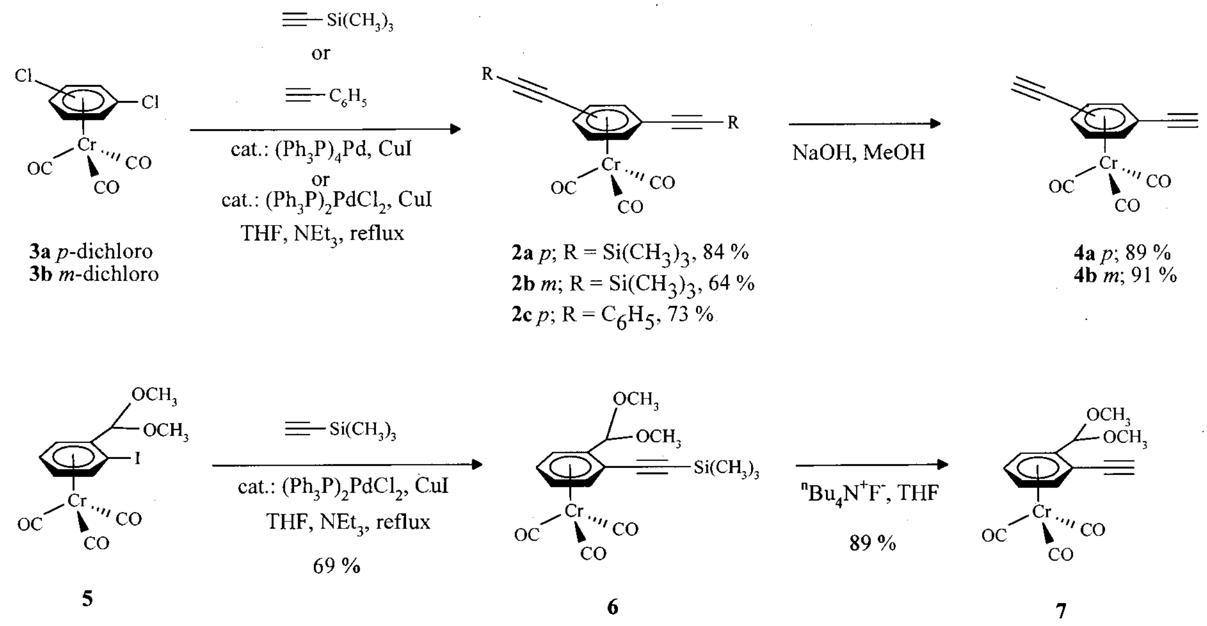
the yield of the thermal tricarbonyl chromium complexation in our hands was between 10 and 20%. To circumvent this severe limitation we suggest a recently published Horner–Emmons–Wadsworth related alkynylation [12] of the readily available terephthalic aldehyde complex **8** [13] as a suitable alternative for the synthesis of **4a**. Other standard transformations of aldehydes to alkynes [14] failed in our hands. Indeed, **4a** was obtained as orange–red crystals in 70% yield from **8** and 1-diazo-2-oxopropyl dimethylphosphonate (**9**) in the presence of four equivalents of potassium carbonate in methanol at room temperature (Scheme 3). Analogous to the complexed phenyl acetylene, the diethynyl benzene complex **4a** can be successfully coupled with iodobenzene to furnish the 1,4-bis(phenylethynyl)benzene complex **2c** in good yield as orange crystals. Now the stage is set for the synthesis of polymeric chromium–carbonyl complexed phenylethynylenes.

3. Conclusion

The direct complexation of polyalkynylated arenes with chromium hexacarbonyl under thermal conditions or with tricarbonyl chromium transferring agents under mild conditions is not a general and satisfactory path to polyalkynylated arene$Cr(CO)_3$-complexes. An efficient solution to this synthetic problem is a Horner–Emmons–Wadsworth related acetylene synthesis with readily available $Cr(CO)_3$-complexed benzaldehydes. Difunctional alkynyl arene complexes for highly sophisticated sidechain functionalizations can also be readily synthesized by Sonogashira coupling from *ortho*-halobenzene complexes. Further studies directed towards the synthesis of oligo- and polymeric organometallic poly(phenylene)ethynylenes and the investigation of their electronic (nonlinear optical activity) as well as their material properties (e.g. liquid crystallinity) are currently underway.

4. Experimental

All reactions involving tricarbonylchromium complexes were carried out in flame-dried Schlenk flasks under nitrogen by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures. [15]—Column chromatography: silica gel 60 (0.063–0.2 mm/70–230 mesh, Firma Merck Darmstadt). TLC: silica gel plates (60 F_{254} Merck, Darmstadt).—Melting points (uncorrected values): Reichert–Jung Thermovar.—The dichloro benzene complexes **3a** and **3b**, the benzaldehyde dimethylacetal complex and the terephthalic aldehyde complex **8** were prepared according to standard conditions [6]. The alkynes and catalysts were purchased from Merck, Aldrich or Fluka, and used without further purification, bis(trimethylsilylethynyl) benzene (**1**) [8d], 1-diazo 2-oxopropyl dimethylphosphonate (**9**) [16] and Kündig's reagent [7] were synthesized according to literature procedures.—^{1}H- and ^{13}C-spectra: Bruker WM 300, Bruker AC 300, Bruker ARX 300 or Varian VXR 400S $CDCl_3$, [D_6]DMSO.—IR: Perkin Elmer FT-IR spectrometer 1000 or Perkin Elmer FT-IR Paragon 1000 PC. The samples were pressed into KBr pellets or dissolved in CCl_4 and recorded as films on NaCl plates.—UV/vis: Beckman DK-2-A, Beckman UV 5240



Scheme 2.

and Perkin Elmer Lambda 16.—MS: Finnigan MAT 311-A/100MS, Finnigan MAT 90 and MAT 95 Q.—Elemental analyses were carried out in the Microanalytical Laboratories of the Institut für Organische Chemie, Technische Universität Darmstadt, and Institut für Organische Chemie, Ludwig-Maximilians-Universität München.

4.1. 1,4-$[(H_3C)_3SiC{\equiv}C]_2(\eta^6\text{-}C_6H_4)Cr(CO)_3$ (**2a**)

4.1.1. *Direct complexation of **1** (path a)*

A degassed solution of 1.32 g (6.00 mmol) of chromium hexacarbonyl and 1.35 g (5.00 mmol) of **1** in a mixture of 50 ml of *n*-dibutyl ether and 5 ml of THF was heated to reflux temperature (oil bath 140°C) for 36 h. After cooling the reaction mixture was filtered through a short pad of celite and the solvents were removed in vacuo. The residue was chromatographed on silica gel with pentane as eluent and the yellow–orange band was collected to give 194 mg (10%) of pure **2a**. Suitable crystals for the X-ray analysis were grown by cooling a concentrated pentane solution of **2a** in the refridgerator to −20°C for a week.

4.1.2. *Direct complexation **1** (path b)*

To a degassed solution of 522 mg (1.93 mmol) of **1** in 10 ml of THF was added 255 mg (0.97 mmol) of Kündig's reagent. The mixture was heated to reflux temperature (oil bath 80°C) for 36 h. After cooling the solvent was removed in vacuo and the residue was chromatographed on silica gel with pentane as eluent. The yellow–orange band was collected to give 88 mg (22% referring to Kündigs reagent) of pure **2a**.

4.1.3. *Sonogashira coupling of **3a** and (trimethylsilyl) acetylene*

To a degassed solution of 541 mg (1.91 mmol) of **3a**, 111 mg (0.10 mmol) of tetrakis(triphenylphosphane)palladium(0) and 25 mg (0.13 mmol) of copper(I) iodide in a mixture of 10 ml of THF and 5 ml of NEt_3 was added dropwise to a solution of 1.50 g (6.11 mmol) of (trimethylsilyl) acetylene in 10 ml of THF over a period of 60 min. The reaction mixture was then heated to reflux temperature for 5 h. After cooling to

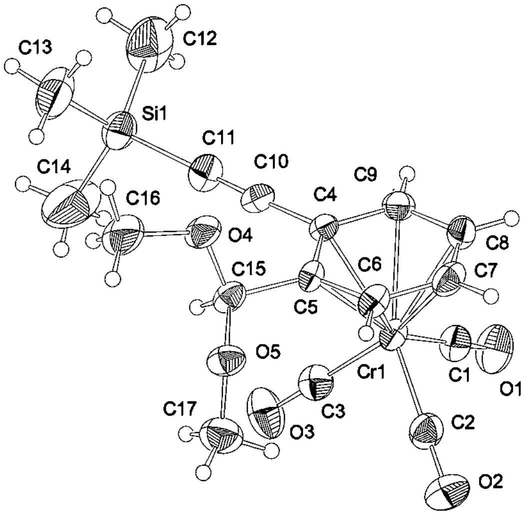
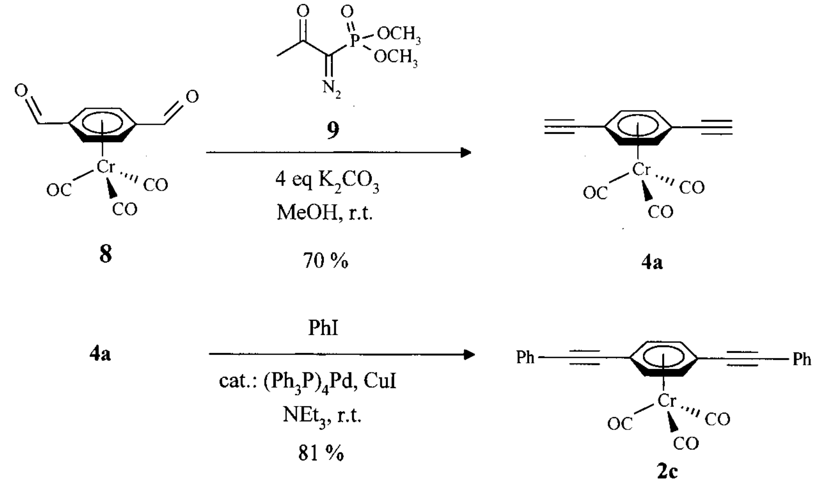


Fig. 2. Crystal structure of **6**. Selected bond lengths [Å] and angles [°]: Cr(1)–Centroid) 1.711, C(4)–C(10) 1.452(7), C(5)–C(15) 1.515(6), C(10)–C(11) 1.164(7), Si(1)–C(11) 1.856(6), C(11)–C(10)–C(4) 177.2(6), C(10)–C(11)–Si(1) 175.8(5).



Scheme 3.

room temperature 30 ml of diethyl ether was added, the mixture was filtered and the solvents of the filtrate were evaporated in vacuo. The residue was chromatographed on silica gel with pentane as eluent to give 650 mg (84%) of pure **2a** as yellow–orange crystals.—M.p. 116 – 117°C (pentane).—^{1}H-NMR (CDCl$_3$, 300 MHz): δ/0.07 (s, 18 H), 5.27 (s, 4 H).—^{13}C-NMR (CDCl$_3$, 75 MHz): δ/ – 0.3 (CH$_3$), 88.0 (C$_{\text{quat.}}$), 93.8 (CH), 96.2 (C$_{\text{quat.}}$), 100.3 (C$_{\text{quat.}}$), 231.2 (C$_{\text{quat.}}$, CO).—MS (EI), *m*/*z* (%): 406 (M^+, 8), 350 (M^+-2 CO, 10), 322 (M^+-3 CO, 100), 52 (Cr$^+$, 94).—IR (CCl$_4$): $\nu = 2150$, 1975, 1915, 1571, 1245, 1107, 854, 841, 744, 721, 651 cm^{-1}.—UV/vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (nm) (ε, M^{-1} cm^{-1}): 254 (26700), 266 (20800), 286 (8600), 292 (13600), 328 (8000), 421 (2100).—$C_{19}H_{22}CrO_3Si_2$ (406.57). Anal. Calc. C 56.13, H 5.45. Found C 55.94, H 5.68.

4.2. 1,3-[(H$_3$C)$_3$SiC≡C]$_2$(η^6-C$_6$H$_4$)Cr(CO)$_3$ (**2b**)

To a degassed solution of 315 mg (1.11 mmol) of **3b**, 64 mg (0.06 mmol) of tetrakis(triphenylphosphane) palladium(0) and 12 mg (0.07 mmol) of copper(I) iodide in a mixture of 10 ml of THF and 5 ml of NEt$_3$ was added dropwise to a solution of 0.82 g (3.34 mmol) of (trimethylsilyl) acetylene in 10 ml of THF over a period of 60 min. The reaction mixture was then heated to reflux temperature for 8 h. After cooling to room temperature 30 ml of diethyl ether was added, the mixture was filtered and the solvents of the filtrate were evaporated in vacuo. The residue was chromatographed on silica gel with pentane as eluent to give 290 mg (64%) of pure **2b** as yellow–orange crystals.

M.p. 73–74°C (pentane).—^{1}H-NMR (CDCl$_3$, 300 MHz): δ/0.08 (s, 18 H), 5.15 (br, 3 H), 5.42 (s, 1 H).—^{13}C-NMR (CDCl$_3$, 75 MHz): δ/ – 0.31 (CH$_3$), 89.37 (C$_{\text{quat.}}$), 90.63 (CH), 92.41 (CH), 96.03 (C$_{\text{quat.}}$), 96.65 (CH), 100.08 (C$_{\text{quat.}}$), 231.35 (C$_{\text{quat.}}$, CO).—MS (EI), *m*/*z* (%): 406 (M^+, 8), 350 ($M^+ - 2$ CO, 10), 322 ($M^+ - 3$ CO, 100), 52 (Cr$^+$, 78).—IR (KBr): $\nu = 2150$, 1981, 1915, 1889, 1248, 1151, 921, 841, 756, 672, 642 cm^{-1}.—UV/vis (CH$_2$Cl$_2$) $\lambda_{\max}$ (nm) (ε, M^{-1} cm^{-1}): 34 (9600), 407 (2300, sh).—$C_{19}H_{22}CrO_3Si_2$ (406.57). Anal. Calc. C 56.13, H 5.45. Found C 56.61, H 5.42.

4.3. 1,4-(H$_5$C$_6$C≡C)$_2$(η^6-C$_6$H$_4$)Cr(CO)$_3$ (**2c**)

4.3.1. Sonogashira coupling of **3a** and phenyl acetylene

To a degassed solution of 191 mg (0.68 mmol) of **3a**, 26 mg (0.04 mmol) of bis(triphenylphosphane) palladium dichloride and 9 mg (0.05 mmol) of copper(I) iodide in a mixture of 10 ml of THF and 5 ml of NEt$_3$ was added dropwise to a solution of 0.21 g (2.06 mmol) of phenyl acetylene in 10 ml of THF over a period of 60 min. The reaction mixture was then heated to reflux temperature for 8 h. After cooling to room temperature 30 ml of diethyl ether was added, the mixture was filtered and the solvents of the filtrate were evaporated in vacuo. The residue was chromatographed on silica gel with a 1:20 mixture of ether and pentane as eluent to give 180 mg (64%) of pure **2c** as orange powder.

4.3.2. Sonogashira coupling of **4a** and iodobenzene

To a degassed solution of 77 mg (0.30 mmol) of **4a** and 150 mg (0.74 mmol) iodobenzene in a mixture of 10 ml of THF and 5 ml of NEt$_3$ were added 20 mg (0.03 mmol) of bis(triphenylphosphane) palladium dichloride and 6 mg (0.03 mmol) of copper(I) iodide. The reaction mixture was then heated to reflux temperature for 15 h. After cooling to room temperature 30 ml of diethyl ether was added, the mixture was filtered and the solvents of the filtrate were evaporated in vacuo. The residue was chromatographed on silica gel with a 1:20 mixture of ether and pentane as eluent to give 100 mg (81%) of pure **2c** as an orange powder.—M.p. 161–162°C (dec.).—^{1}H-NMR ($CDCl_3$, 300 MHz): δ/5.59 (s, 4 H), 7.37 (m, 6 H), 7.51 (m, 4 H).—^{13}C-NMR ($CDCl_3$, 75 MHz): δ/85.0 ($C_{quat.}$), 88.7 ($C_{quat.}$), 90.3 ($C_{quat.}$), 93.8 (CH), 121.7 ($C_{quat.}$), 128.5 (CH), 129.2 (CH), 131.9 (CH), 231.6 ($C_{quat.}$, CO).—MS (EI), m/z (%): 414 (M^+, 8), 358 ($M^+ - 2$ CO, 17), 325 (64), 52 (Cr^+, 100).—IR (CCl_4): $\nu =$ 1975 , 1915, 1571, 1500, 1121, 683, 650 cm^{-1}.—UV/vis (CH_2Cl_2) λ_{max} (nm) (ε, M^{-1} cm^{-1}): 247 nm (23600, sh), 300 (45000), 338 (16000, sh), 427 (2600).—$C_{25}H_{14}CrO_3$ (414.39). Anal. Calc. C 72.46, H 3.41. Found C 71.86, H 3.38.

4.4. 1,4-$(HC{\equiv}C)_2(\eta^6\text{-}C_6H_4)Cr(CO)_3$ (**4a**)

4.4.1. Deprotection of **2a**

To a degassed solution of 650 mg (1.59 mmol) of **2a** in 40 ml of methanol was added 3 ml (6 mmol) of 2*N* NaOH and the reaction mixture was stirred at room temperature for 7 h. The suspension was extracted three times with portions of 30 ml of ether. After extraction of the combined organic phases with 10 ml of water the etheral phase was dried over sodium sulfate. The solvents were removed in vacuo to give 370 mg (89%) of pure **4a** as orange crystals.

4.4.2. Horner–Emmons–Wadsworth related alkyne synthesis with **8** and **9**

To a suspension of 1.27 g (9.19 mmol) of anhydrous potassium carbonate in 40 ml of degassed anhydrous methanol was added 622 mg (2.30 mmol) of **8**. After stirring for 15 min at ambient temperature a solution of 1.06 g (5.52 mmol) of **9** in 5 ml of anhydrous methanol was added dropwise over a period of 20 min to the suspension. After 15 h of stirring at room temperature the reaction mixture was extracted three times with portions of 50 ml of ether. After extraction of the combined organic phases with 20 ml of water the etheral phase was dried over sodium sulfate. The solvents were removed in vacuo and the residue was chromatographed on silica gel with pentane and pentane/ether (10:1) to give 420 mg (70%) of pure **4a** as orange crystals.—M.p. 124–125°C (pentane).—^{1}H-NMR ($CDCl_3$, 300 MHz): δ/2.97 (s, 2 H), 5.47 (s, 4 H); ([D_6]DMSO, 300 MHz): δ/4.29 (s, 2H), 5.92 (s, 4 H).—^{13}C-NMR ($CDCl_3$, 75 MHz): δ/78.35 (CH), 79.23 ($C_{quat.}$), 86.90 ($C_{quat.}$), 93.68 (CH), 230.74 ($C_{quat.}$, CO); ([D_6]DMSO, 75 MHz): δ/79.37 (CH), 82.10 ($C_{quat.}$), 89.16 ($C_{quat.}$), 96.18 (CH), 232.25 ($C_{quat.}$, CO).—MS (EI), m/z (%): 262 (M^+, 15), 206 ($M^+ -$ 2CO, 11), 178 ($M^+ - 3$ CO, 44), 52 (Cr^+, 100).—IR (KBr): $\nu = 1947$, 1875, 839, 651 cm^{-1}.—UV/vis (CH_2Cl_2) λ_{max} (nm) (ε, M^{-1} cm^{-1}): 272 nm (6400), 326 (9500), 417 (2200).—$C_{13}H_6CrO_3$ (262.19). Anal. Calc. C 59.55, H 2.31. Found C 59.55, H 2.27.

4.5. 1,3-$(HC{\equiv}C)_2(\eta^6\text{-}C_6H_4)Cr(CO)_3$ (**4b**)

To a degassed solution of 290 mg (0.71 mmol) of **2b** in 20 ml of methanol was added 1.5 ml (3 mmol) of 2*N* NaOH and the reaction mixture was stirred at room temperature for 9 h. The suspension was extracted three times with portions of 30 ml of ether. After extraction of the combined organic phases with 10 ml of water the etheral phase was dried over sodium sulfate. The solvents were removed in vacuo to give 170 mg (91%) of pure **4b** as orange crystals.—M.p. 97–98°C (pentane).—^{1}H-NMR ($CDCl_3$, 300 MHz): δ/2.78 (s, 2 H), 5.12 (t, J/6.4 Hz, 1 H), 5.25 (d, J/6.2 Hz, 2 H), 5.46 (s, 1 H).—^{13}C-NMR ($CDCl_3$, 75 MHz): δ/77.92 (CH), 79.07 ($C_{quat.}$), 87.20 ($C_{quat.}$), 89.71 (CH), 93.39 (CH), 97.19 (CH), 230.64 ($C_{quat.}$, CO).—MS (EI), m/z (%): 262 (M^+, 16), 206 ($M^+ - 2$ CO, 12), 178 ($M^+ - 3$ CO, 45), 52 (Cr^+, 100).—IR (KBr): $\nu = 1967$, 1880, 1443, 998, 873, 834, 699, 679, 647 cm^{-1}.—UV/vis (CH_2Cl_2) λ_{max} (nm) (ε, M^{-1} cm^{-1}): 252 nm (9900, sh), 260 (6900, sh), 336 (9600), 405 (1900, sh).—$C_{13}H_6CrO_3$ (262.19). Anal. Calc. C 59.55, H 2.31. Found C 59.42, H 2.32.

4.6. 1-2-$[(H_3CO)_2CH](\eta^6\text{-}C_6H_4)Cr(CO)_3$ (**5**)

To a degassed solution of 1.16 g (4.02 mmol) of the tricarbonyl(η^6-benzaldehyde dimethylacetal)chromium(0) in 20 ml of dry THF, cooled to −78°C, 2.6 ml (4.2 mmol) of a 1.6 M solution of BuLi in hexane is added dropwise over a period of one minute. The mixture is stirred at that temperature for 2 h then a solution of 1.06 g (4.18 mmol) of iodine in 10 ml THF is added dropwise. After stirring at −78°C for 30 min the mixture is allowed to come to room temperature over a period of 2.5 h. After evaporation of the solvent in vacuo at room temperature the residue was chromatographed on basic alumina with diethyl ether/pentane (1:1) as eluent to afford 1.30 g (78%) of crude **5**. After recrystallization from diethyl ether/pentane yellow crystals with melting point 77°C were obtained.—^{1}H-NMR ([D_6]DMSO, 300 MHz): δ/3.35 (s, 3 H), 3.63 (s, 3 H), 5.09 (s, 1 H), 5.23 (m, 2 H), 5.69 (d, J/5.0 Hz, 1 H), 5.79 (d, J/4.7 Hz, 1 H).—^{13}C-NMR ([D_6]DMSO, 75 MHz): δ/52.41 (CH_3), 57.46 (CH_3), 65.21 (C_{quat}), 89.55 (CH), 90.89 (CH), 93.66 (CH), 100.70 (CH), 105.06 (CH), 106.65 (C_{quat}), 231.63 (C_{quat}, CO).—MS (70 eV), m/z (%): 414 (M^+, 17), 383 ($M^+ -$ OMe, 7), 358 ($M^+ - 2$ CO, 10), 330 ($M^+ - 3$ CO, 43), 52 (Cr^+, 100).—IR (KBr): $\nu =$ 1967, 1891, 1196, 1109, 1051, 902, 819, 661, 625 cm^{-1}.—UV/vis (DMSO) λ_{max} (nm) (ε, M^{-1} cm^{-1}): 320 (9640).—$C_{12}H_{11}CrIO_5$ (414.12). Anal. Calc. C 34.80, H 2.68. Found C 35.65, H 2.58.

4.7. 1-[$(H_3C)_3SiC{\equiv}C$]-2-[$(H_3CO)_2CH$](η^6-C_6H_4)$Cr(CO)_3$ (**6**)

To a degassed solution of 500 mg (1.21 mmol) of **5**, 17 mg (0.02 mmol) of bis(triphenylphosphane) palladium dichloride and 3 mg (0.02 mmol) of copper(I) iodide in a mixture of 10 ml of THF and 4 ml of NEt_3 was added a solution of 0.27 ml (1.93 mmol) of (trimethylsilyl) acetylene in 5 ml of THF, dropwise over a period of 40 min. The reaction mixture was then heated to reflux temperature for 6 h. After cooling to room temperature 30 ml of diethyl ether was added, the mixture was filtered and the solvents of the filtrate were evaporated in vacuo. The residue was chromatographed on silica gel with a 1:4 mixture of diethyl ether and pentane as eluent to give 320 mg (69%) of pure **6** as yellow–orange crystals.—M.p. 66–67°C (pentane).—^{1}H-NMR ([D_6]DMSO, 300 MHz): δ/0.22 (s, 9 H), 3.33 (s, 3 H), 3.52 (s, 3 H), 5.19 (s, 1 H), 5.68 (dd, J/6.1, 6.4 Hz, 1 H), 5.75 (dd, J/6.2, 6.2 Hz, 1 H), 5.82 (d, J/7.5 Hz, 1 H), 5.84 (d, J/7.2 Hz, 1 H).—^{13}C-NMR ([D_6]DMSO,75 MHz): δ/0.20 (CH_3), 54.27 (CH_3), 57.27 (CH_3), 89.70 ($C_{quat.}$), 91.59 (CH), 92.50 (CH), 94.39 (CH), 96.41 (CH), 98.88 ($C_{quat.}$), 99.08 ($C_{quat.}$), 101.86 (CH), 109.35 ($C_{quat.}$), 232.86 ($C_{quat.}$, CO).—MS (EI), m/z (%): 384 (M^+, 5), 328 ($M^+ - 2$ CO, 25), 300 ($M^+ - 3$ CO, 56), 253($M^+ - CH_3O - 3$ CO $- CH_4$, 100), 52 (Cr^+, 46).—IR (KBr): $\nu = 2166$, 1964, 1989, 1636, 1342, 1251, 1089, 848, 662, 625 cm^{-1}.—UV/vis (DMSO): λ_{max} (nm) (ε, M^{-1} cm^{-1}): 326 (10100).—$C_{17}H_{20}CrO_5Si$ (384.42). Anal. Calc. C 53.11, H 5.24. Found C 53.39, H 5.42.

4.8. 1-($HC{\equiv}C$)-2-[$(H_3CO)_2CH$](η^6-C_6H_4)$Cr(CO)_3$ (**7**)

To a degassed solution of 200 mg (0.52 mmol) of **6** in 10 ml of THF was added 165 mg (0.52 mmol) of tetrabutyl ammonium fluoride trihydrate. The reaction mixture was stirred at room temperature for 2 h and then filtered over silica gel with ether as eluent to give 140 mg (86%) of pure **7** as yellow crystals.—M.p. 38–40°C (pentane).—^{1}H-NMR ([D_6]DMSO, 300 MHz): δ/3.26 (s, 3 H), 3.51 (s, 3 H), 4.41 (s, 1 H), 5.27 (s, 1 H), 5.73 (m, 2 H), 5.82 (m, 1 H), 5.88 (m, 1 H).—^{13}C-NMR ($CDCl_3$, 75 MHz): δ/52.69 (CH_3), 56.83 (CH_3), 77.71 (CH), 84.55 ($C_{quat.}$), 88.98 ($C_{quat.}$), 91.33 (CH), 93.09 (CH), 93.91 (CH), 97.30 (CH), 100.86 (CH), 109.72 ($C_{quat.}$), 232.76 ($C_{quat.}$, CO).—MS (EI), m/z (%): 312 (M^+, 16), 284 ($M^+ -$ CO, 6), 256 ($M^+ - 2$ CO, 51), 228 ($M^+ - 3$ CO, 54), 52 (Cr^+, 100).—IR (KBr): $\nu = 3295$, 1971, 1987, 1629, 1344, 1200, 1111, 1072, 662, 625 cm^{-1}.—UV/vis (DMSO): λ_{max} (nm) (ε, M^{-1} cm^{-1}): 324 (9800).—$C_{14}H_{12}CrO_5$ (312.25). Anal. Calc. C 53.85, H 3.87. Found C 54.48, H 4.03.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 102932 (**2a**), 102933 (**6**). Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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