Palladium-Copper-Catalyzed Coupling of Tricarbonylchromium-Complexed Phenylacetylene with Iodoarenes – A Facile Access to Alkynyl-Bridged $Cr(CO)_3$-Complexed Benzenes

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The palladium-copper-catalyzed coupling of the tricarbonylchromium-complexed chlorobenzene **1** with (trimethylsilyl)acetylene gives tricarbonyl[η^6-[(trimethylsilyl)ethynyl]benzene}chromium(0) (**2**) in high yield. After desilylation of **2** tricarbonyl[η^6-(ethynylbenzene)]chromium(0) (**3**) is obtained quantitatively. Using the palladium-copper-catalyzed methodology, we can readily introduce $Cr(CO)_3$-complexed phenylethynyl units by a multifold coupling of **3** with iodobenzene, 1,2-, 1,3-, 1,4-di- and 1,3,5-tiiodobenzene (**4a–e**) or **1** to give polynuclear $Cr(CO)_3$-complexed (phenylethynyl)benzenes **5a–e** and doubly $Cr(CO)_3$-complexed tolane **6** in good to moderate yield. The crystal structure analyses of μ_3-{η^6:η^6:η^6[1,3,5-benzenetriyltris(2,1-ethynediyl)]tris(benzene)}tris[tricarbonylchromium(0)] (**5e**) and μ-{η^6:η^6-[1,2-ethynediylbis(benzene)]}bis[tricarbonylchromium(0)] (**6**) reveal that the tricarbonylchromium tripods in the same molecule are arranged in antiparallel *syn*-eclipsed conformations. The Eglington coupling of **3** affords a doubly $Cr(CO)_3$-complexed diphenylbutadiyne **7** in excellent yield.

Acetylenes have experienced a true renaissance as rigid bridging elements in π-conjugated polymers[1], dendrimers[2], and synthetic carbon allotropes[3] on the way to the architecture of nanostructures. In particular, alkynes have been of interest not only as bridges but also as transmitters of π-electron resonance in novel electro- and chromophores[4]. π-Conjugated systems fundamentally change their electronical behavior and reactivity on complexation with organometallic fragments[5]. Thus, the prospect of fine-tuning optical and electronical properties by attaching organometallic units to a conjugated chain or macrocycle[6] has had an important impact on the rapidly evolving search for syntheses and structures of novel organometallic conjugated target molecules. So far some oligo- and polymeric cyclobutadienylalkynyl complexes of cobalt and iron[7] have successfully been synthesized.

However, there is not much known about the synthesis and the chemistry of tricarbonylchromium-complexed alkynylarenes[8,9], interesting building blocks in the synthesis of $Cr(CO)_3$-complexed poly(phenylenealkynylenes) and oligo(arylenealkynyl)macrocycles. This has several reasons. The pyrolysis of hexacarbonylchromium in the presence of alkynylarenes is an unselective and inefficient force brute synthesis[8,9] that does not tolerate alkynes. $Cr(CO)_3$-transferring complexes like $(CH_3CN)_3Cr(CO)_3$[8] or $(NH_3)_3Cr(CO)_3$[10] can be used under milder conditions but the regioselectivity of complexation cannot be controlled. Therefore, coupling reactions offer chemo- and regioselective alternatives. The Stille coupling of alkynylstannanes and $Cr(CO)_3$-complexed chlorobenzenes proved to be a very efficient option and was successfully applied to the synthesis of $Cr(CO)_3$-complexed poly(phenylenealkynylenes)[11]. However, the inherent toxicity of tin compounds and the rather uneconomical application of alkynylstannanes require a catalytic mode of metalation and transmetalation of terminal alkynes. Here we report on an efficient synthesis of $Cr(CO)_3$-complexed phenylacetylene and a regioselective route to novel (arene)tricarbonylchromium(0) complexes.

Results and Discussion

The palladium-copper-catalyzed coupling of terminal acetylenes[12] with iodo- or bromoarenes is a well established methodology for the synthesis of alkynylarenes. $Cr(CO)_3$-complexed chlorobenzene was used in a coupling reaction with terminal alkynes[13]. Unfortunately, we were not able to reproduce the reported yields[13a], and we identified the major product as $Cr(CO)_3$-complexed benzene resulting from reductive dechlorination[9]. Therefore, the conditions for a catalytic[14] coupling of terminal alkynes with $Cr(CO)_3$-complexed chlorobenzene had to be adjusted.

We found that the successful formation of the alkynylbenzene complex **2** (90% yield) requires the slow addition of (trimethylsilyl)acetylene to a mixture of tricarbonyl[η^6-(chlorobenzene)]chromium(0) (**1**), 5 mol-% of bis(triphenylphosphane)palladium dichloride, and 5 mol-% of copper(I) iodide in triethylamine/THF and rapid heating to boiling temperature. The direct complexation[8] furnished only a 4% yield. Desilylation with 2 N NaOH in methanol gives the yellow crystalline complex **3** quantitatively (see Scheme 1).

The electronic spectra of **2** and **3** are almost identical and display strong absorption bands at 323 and 390 nm. These

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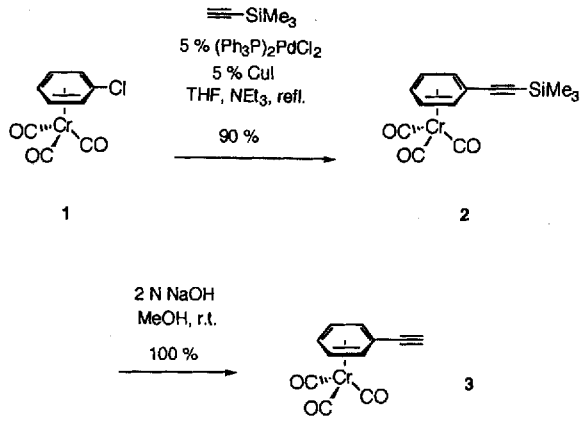
Scheme 1. Synthesis of the phenylacetylene complex **3**



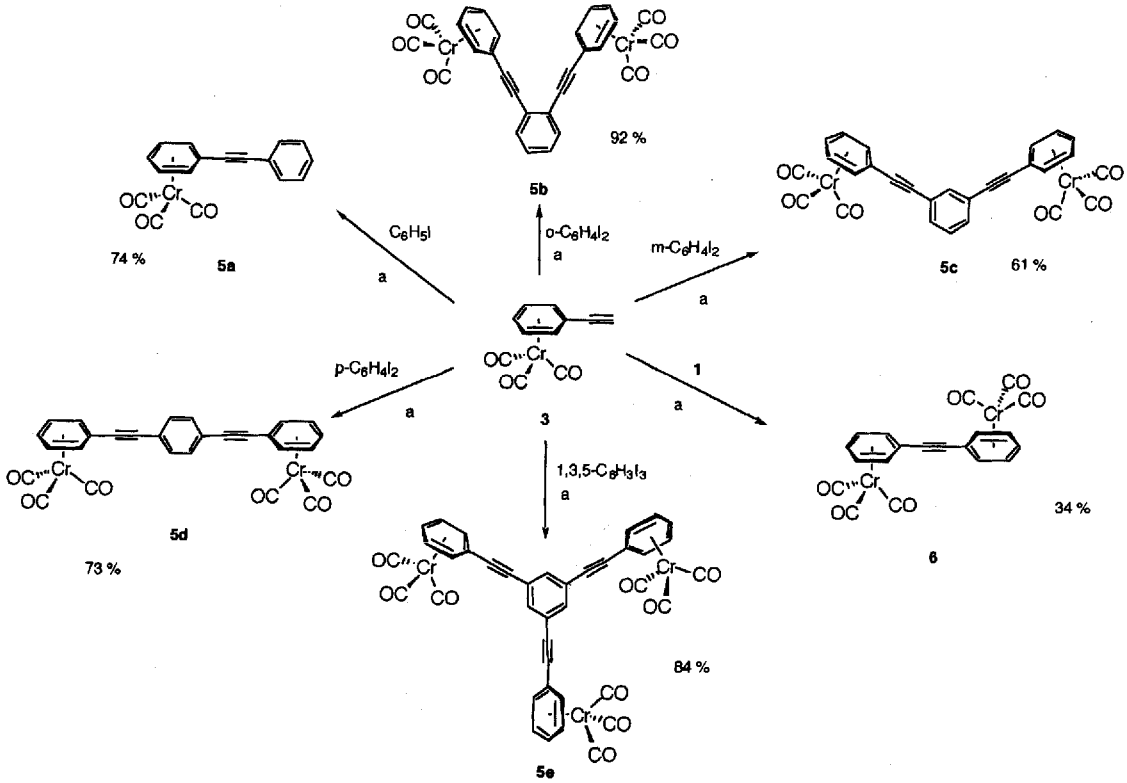
absorption maxima can be assigned to metal-to-ligand (ML) and ligand-to-metal (LM) charge transfer (CT) bands in accordance with the calculated and experimental electronic spectra[5b,15] of tricarbonyl(η^6-benzene)chromium(0), the most simple $Cr(CO)_3$-complexed arene.

The phenylacetylene complex **3** can be coupled with iodinated benzenes **4** at room temperature in the presence of 3% tetrakis(triphenylphosphane)palladium(0) and copper(I) iodide in an amine as solvent (see Scheme 2). Two or three $Cr(CO)_3$-complexed alkynylarene units are readily introduced in a one-pot reaction by the multifold coupling of **3** with 1,2-, 1,3-, 1,4-di- and 1,3,5-triiodobenzene (**4b–e**) to give new $Cr(CO)_3$-complexed (phenylethynyl)arenes **5** as yellow to orange crystalline solids. The reaction of **3** with **1** results in the formation of the doubly complexed tolane **6**. The formation of **6** was not observed in the direct complexation of tolane with $(NH_3)_3Cr(CO)_3$[10].

IC_6H_5	$1,2\text{-}I_2C_6H_4$	$1,3\text{-}I_2C_6H_4$	$1,4\text{-}I_2C_6H_4$	$1,3,5\text{-}I_3C_6H_3$
4a	**4b**	**4c**	**4d**	**4e**

The dominant IR peaks are broad carbonyl stretching vibrations between 1944 and 1985 and between 1858 and 1919 cm^{-1}. The carbon-carbon stretching vibrations of the carbon-carbon triple bonds between 2150 and 2220 cm^{-1} are generally fairly weak. In the ^{1}H-NMR spectra the set of signals for the protons of the complexed phenyl groups can be easily identified by their upfield shift to the region between δ = 5.7 and 6.0. The resonances attributed to the protons of the uncomplexed benzene rings appear as expected between δ = 7.3 and 7.7. Characteristic signals between δ = 90.0 and 97.2 in the ^{13}C-NMR spectra can be assigned to the carbon atoms of the complexed phenyl groups, and the carbonyl carbon resonances appear between δ = 232.9 and 233.5. In several studies of electronic effects of substituted ligands on the chromium atom the position of the carbonyl carbon signal can be used as a probe for the electron density on the metal[16]. The chemical shifts of the carbonyl carbon nuclei increase (i.e. the CO ligands are deshielded) with increasing electron richness on the metal center, presumably due to the dominance of the paramagnetic term in the chemical shift tensor. Although the effect is fairly small it states that the highest electron density on the chromium atoms is found in complex **5d**

Scheme 2. Coupling reactions of **3** with iodinated benzenes **4** and **1** (a: 2% $(Ph_3)P_4Pd$, 1% CuI, iPr_2NH or NEt_3, room temp. or reflux)



where the two complexed phenylacetylene units are connected by a conjugating *para*-substituted benzene ring. The fragmentation pattern in the mass spectra is similar for all complexes **5** and **6**. The main fragments result from the loss of two and three molecules of carbon monoxide, a $Cr(CO)_3$ tripod and the chromium cation.

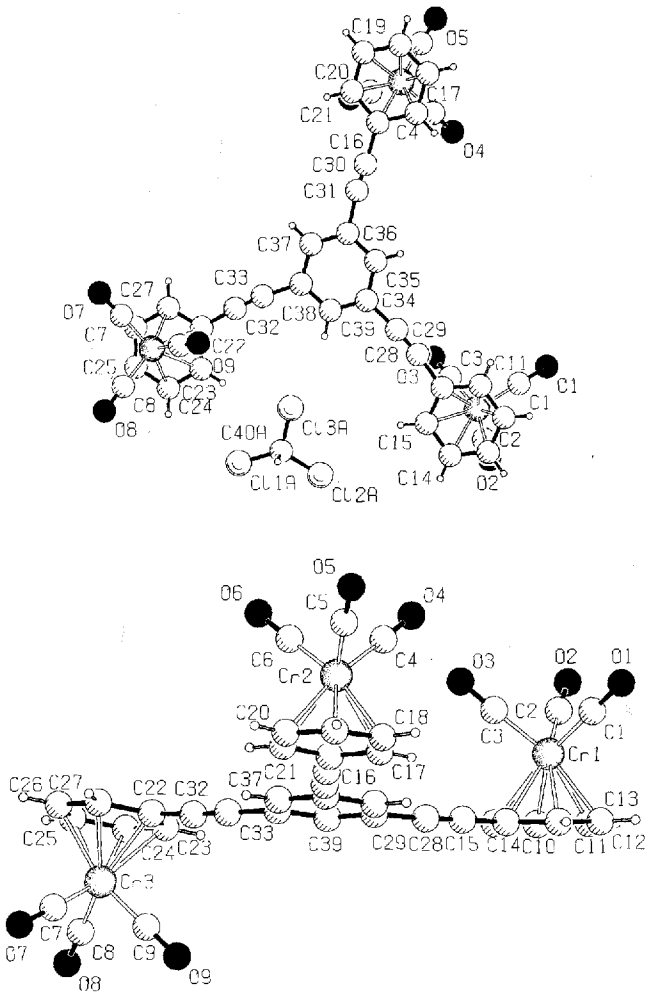
The electronic spectra display more distinct differences between the complexes. All UV/Vis spectra show two maxima in the range from 304 to 329 and from 399 to 416 nm. The latter absorption maxima can be interpreted as metal-to-ligand charge transfer bands (MLCT). Interestingly, only the MLCT band is influenced when a complexed phenylacetylene unit is introduced to a benzene ring in *meta* position. In the spectra of the complexes **5a**, **5c**, and **5e** the MLCT band is shifted bathochromically with increasing number of complexed phenylacetylene units whereas the shorter wave length maxima do not change their position (see Table 1). The successive downfield shift of the signal of the quaternary carbon atom of the uncomplexed phenyl ring in the ^{13}C-NMR spectra indicates a reduction of electron density in the ligands with each addition of a $Cr(CO)_3$ tripod.

Table 1. Comparison of the UV/Vis absorption maxima of **5a**, **5c**, and **5e**; λ_{max} in nm (ε) (recorded in DMSO)

	5a	**5c**	**5e**
π–π^*	275 (20800)	275 (38500)	276 (64500)
LMCT and π–π^*	325 (10100)	324 (18900)	325 (28900)
MLCT	390 (3570)	401 (7390)	410 (12300)

Besides the information obtained from the structure in solution, the solid-state structure of [tricarbonyl-η^6-phenylacetylene-chromium(0)]arenes provides additional insight into the mutual arrangement of molecular units in a crystal lattice. Single crystals for an X-ray analysis of **5e** were obtained by crystallization from trichloromethane. **5e** crystallizes together with one molecule of trichloromethane per complex molecule. The crystal structure determination[17] of the triply coordinated hydrocarbon shows that two $Cr(CO)_3$ units occupy the same face of the ligand and the third tripod is attached in an antiparallel manner on the opposite side, presumably due to crystal packing (see Figure 1). The deviation from coplanarity is only small (average 3–5°). The $Cr(CO)_3$ fragments are almost symmetrically bound with respect to the carbon atom plane of the phenyl rings. The two tripods on the same side of the ligand adopt *syn*-eclipsed conformations, typical of arene complexes bearing electron-releasing substituents[18]; i.e., the carbonyl ligands are aligned with the *meta* and *ipso* carbon atoms of the phenyl rings. The third $Cr(CO)_3$ group is arranged in an *anti*-eclipsed conformation with respect to the alkynyl substituent. The distance of a chromium atom from a phenyl ring plane is 170 pm as expected for $Cr(CO)_3$-complexed benzenes[19]. The carbon-carbon distances display the same characteristics as tolane[20], a comparable hydrocarbon.

Figure 1. Crystal structure of **5e** (view perpendicular to the plane of the central phenyl ring) and side-on view[a]

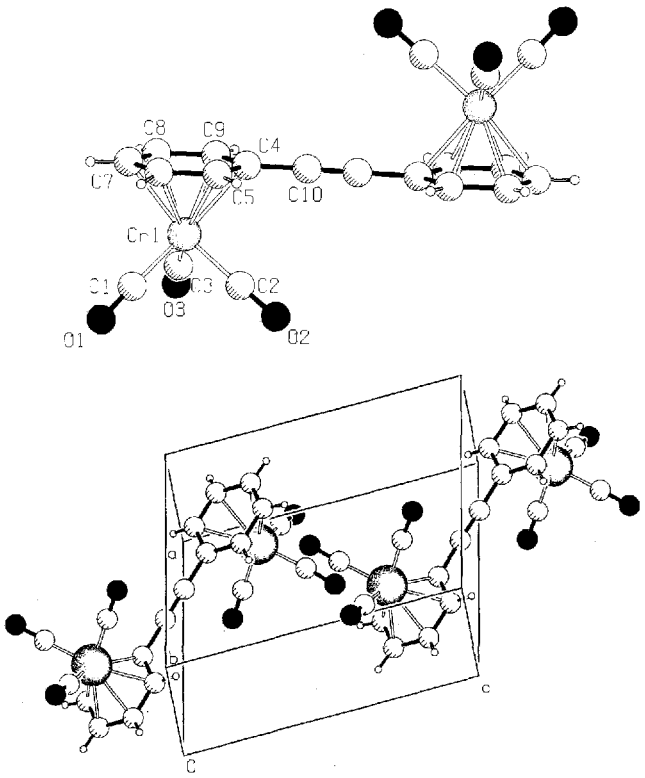


[a] Selected bond lengths [pm] and angles [°]: Cr(2)–C(6) 174.2(2), C(6)–O(6) 116.0(2), Cr(2)–C(12) 218.0(12), C(10)–C(28) 143.0(2), C(28)–C(29) 114.0(2), C(29)–C(34) 147.0(2), C(34)–C(35) 142.0(2), C(12)–C(13) 138.0(2); C(29)–C(28)–C(10) 176.1(14), C(28)–C(29)–C(34) 172.5(14).

Suitable crystals for an X-ray analysis of **6** were obtained by crystallization from trichloromethane. The crystal structure determination[17] reveals that the $Cr(CO)_3$ units are almost perfectly arranged antiparallel to each other (see Figure 2). The $Cr(CO)_3$ fragments are symmetrically bound to the carbon atoms of the phenyl rings and adopt *syn*-eclipsed conformations which are typical of arene complexes bearing electron-releasing substituents[18]. The distance of the chromium atom from the phenyl ring plane is 171 pm as expected for $Cr(CO)_3$-complexed benzenes[19]. The carbon-carbon distances are similar to those in noncoordinated tolane[20]. The intramolecular distance of the chromium atoms is 767 pm. Interestingly, the molecules of **6** lie in a zig-zag arrangement in the elementary cell. The $Cr(CO)_3$ tripods face each other in a staggered orientation.

The complex **3** dimerizes in the presence of stoichiometric amounts of copper(II) acetate[21] (Eglington coupling) to give **7** in 96% yield (see Scheme 3). Due to the

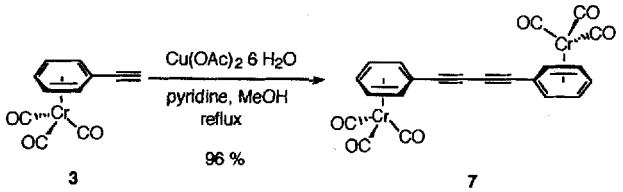
Figure 2. Crystal structure of **6** with elementary cell[a]



[a] Selected bond lengths [pm] and angles [°]: Cr(1)–C(2) 183.5(3), C(2)–O(2) 114.4(4), Cr(1)–C(4) 220.8(3), C(4)–C(10) 143.6(4), C(10)–C(10′) 118.8(5), C(8)–C(9) 140.6(4); C(10)–C(4)–Cr(1) 127.8(2), C(10′)–C(10)–C(4) 178.4(4).

sensitivity of **3** to oxidation with atmospheric oxygen, the Glaser coupling carried out in solution was not successful. Copper(II) acetate proved to be a mild and selective reagent for the oxidative dimerization. In the UV/Vis spectrum the MLCT band appears at 433 nm, the longest wavelength maximum in this series of complexes.

Scheme 3. Eglington coupling of **3**



Conclusion

The palladium-copper-catalyzed coupling reaction of tricarbonylchromium-complexed alkynylarenes **3** with iodoarenes offers a facile and selective access to tricarbonyl-η^6-phenylacetylene-chromium(0) arenes **5** and **6** in a one-pot procedure. This methodology is superior to a direct complexation since it allows us to introduce complexed phenylacetylene fragments regioselectively. In the solid state these complexes tend to adopt an antiparallel *syn*-eclipsed arrangement of the tricarbonylchromium tripods in the same molecule. The electronic spectra can be qualitatively interpreted by assuming that the net effect of $Cr(CO)_3$ is an electron-withdrawing one. $Cr(CO)_3$-complexed alkynylarenes can be interesting new chromophores. Further studies will address the reactions and electronic properties of complexed alkynylbenzenes, and the syntheses of polyalkynylbenzene complexes, ultimate building blocks in tricarbonylchromium-complexed polymeric and macrocyclic structures, are currently under way.

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Experimental

All reactions involving tricarbonylchromium complexes were carried out in flame-dried Schlenk flasks under argon by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures[22]. – Column chromatography: silica gel 60 (Macherey-Nagel, Düren), mesh 64–200, or basic alumina activity B II–III (ICN Biomedicals, Eschwege). – TLC: silica gel plates (60 F_{254} Merck, Darmstadt). – Melting points (uncorrected values): Büchi SMP-20. – The chlorobenzene complex **1**[23] and (trimethylsilyl)acetylene[24] (as a 40 wt-% soluton in THF) were prepared by literature methods. Hexacarbonylchromium, bis(triphenylphosphane)palladium(II) dichloride, tetrakis(triphenylphosphane)palladium(0), copper(I) iodide, **4a**, **4b**, **4d**, and copper(II) acetate hexahydrate were purchased from Merck, Aldrich or Fluka and used without further purification. The polyiodobenzenes **4c** and **4e** were synthesized in analogy to literature procedures for the synthesis of dibromobenzenes in two steps from aniline and iodine[25,26]. – ^{1}H and ^{13}C NMR: Bruker WM 300 or Bruker AC 300, $CDCl_3$ and [D_6]DMSO. – IR: Beckman IR 5 A, KBr. – UV/Vis: Beckman DK-2-A or Beckman UV 5240. – MS: Finnigan MAT 311-A/100 MS. – Elemental analyses: Microanalytical laboratory of the Institut für Organische Chemie, Technische Hochschule Darmstadt.

X-ray Structure Determination of Compound **5e**[17]: $C_{39}H_{18}Cr_3O_9 \cdot HCCl_3$, M = 905.94, triclinic, space group $P\bar{1}$, a = 1124.2(3), b = 1264.0(3), c = 1585.5(2) pm, α = 72.59(2), β = 85.98(2), γ = 65.47(2)°, V = 1.9519(7) mm^3, Z = 2, λ(Mo-K_α) = 0.71069 Å, μ = 1.06 mm^{-1}, D_x = 1.541 Mgm^{-3}, F(000) = 908, T = 298 K. A yellow platelet with the dimensions 0.375 × 0.2 × 0.125 mm was mounted on a capillary and transferred to an Enraf-Nonius CAD4 diffractometer. A total of 5093 intensities (4161 unique, R_{int} = 0.1003) were measured in a Θ range from 1.35 to 20.97°. The structure was solved by direct methods and refined anisotropically on F^2 (programs SHELXS-86, SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were geometrically positioned. The final $wR(F^2)$ for all reflections was 0.2883, with a conventional $R(F)$ [$I > 2\sigma(I)$] of 0.0847 for 533 parameters.

X-ray Structure Determination of Compound **6**[17]: $C_{20}H_{10}Cr_2O_6$, M = 450.28, triclinic, space group $P\bar{1}$, a = 704.9(1), b = 719.3(2), c = 1030.8(2) pm, α = 78.94(2), β = 75.56(1), γ = 66.1(2)°, V = 0.4605(2) nm^3, Z = 1, λ(Mo-K_α) = 0.71069 Å, μ = 1.214 mm^{-1}, D_x = 1.624 Mgm^{-3}, F(000) = 226, T = 299 K. An orange platelet with the dimensions 0.375 × 0.2 × 0.075 mm was mounted on a capillary and transferred to an Enraf-Nonius CAD4 diffractometer. A total of 2356 intensities (1276 unique, R_{int} = 0.0210) were measured in a Θ range from 2.05 to 22.97°. The structure was solved by direct methods and refined anisotropically on F^2 (programs SHELXLS-86, SHELXL-93, G. M. Sheldrick, Univer-

sity of Göttingen). Hydrogen atoms were found from differential Fourier synthesis and refined. The final $wR(F^2)$ for all reflections was 0.0723, with a conventional $R(F)$ [$I > 2\sigma(I)$] of 0.0281 for 147 parameters.

Tricarbonyl{η^6-[(trimethylsilyl)ethynyl]benzene}chromium(0) (**2**): The chlorobenzene complex **1** (3.73 g, 15.0 mmol), bis(triphenylphosphane)palladium(II) dichloride (0.52 g, 0.74 mmol), and copper(I) iodide (0.14 g, 0.74 mmol) were dissolved at room temp. with stirring under argon in a deaerated mixture of 50 ml of THF and 25 ml of triethylamine. (Trimethylsilyl)acetylene (5.50 g of a 40 wt% solution in THF, 22.4 mmol) in 50 ml of THF was added dropwise at room temp. to the solution over a period of 1 h. The mixture soon became dark and cloudy. After the addition of the (trimethylsilyl)acetylene solution was finished the reaction mixture was immediately heated to reflux temp. under argon for 6 h. After cooling to room temp. under argon 50 ml of diethyl ether was added to the dark mixture. The suspension was filtered, and the solvents of the filtrate were removed in a rotary evaporator. The residue was chromatographed on silica gel (diethyl ether/pentane, 1:12), and the yellow-orange band was collected to give 4.20 g (90%) of **2** as yellow-orange crystals, m.p. 74–75°C (pentane) (ref.[8] 75–76°C). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.08 (s, 9H), 5.00 (m, 1H), 5.15 (m, 2H), 5.26 (m, 2H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = −0.26 (CH_3), 90.32 (CH, $C_{quat.}$), 91.57 (CH), 94.78 (CH), 95.74 ($C_{quat.}$), 100.49 ($C_{quat.}$), 232.01 ($C_{quat.}$, CO). – MS (70 eV, EI), *m/z* (%): 310 [M^+] (17), 254 [M^+ − 2 CO] (12), 226 [M^+ − 3 CO] (100), 159 (18), 52 [Cr^+] (50). – IR: $\tilde{\nu}$ = 2150 cm^{-1}, 1944, 1869, 1442, 1243, 1207, 839, 755, 670, 649. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 323 nm (9030), 390 (2270 sh). – $C_{14}H_{14}CrO_3Si$ (310.4): calcd. C 54.18, H 4.55; found C 54.02, H 4.31.

Tricarbonyl[η^6-(ethynylbenzene)]chromium(0) (**3**): The alkynylarene complex **2** (2.80 g, 9.02 mmol) was dissolved at room temp. under argon in 50 ml of deaerated methanol. 10 ml (20 mmol) of 2 N NaOH was added dropwise to this solution. The reaction mixture was stirred at room temp. for 3 h. Then the suspension was extracted with diethyl ether (3 × 50 ml). After the combined organic phases were dried with magnesium sulfate, the solvents were removed in a rotary evaporator to give 2.21 g (100%) of **3** as yellow-orange crystals, m.p. 68–69°C (hexane) (ref.[8] 70–71°C). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.95 (s, 1H), 5.30 (m, *J* = 5.5 Hz, 2H), 5.48 (m, *J* = 5.9 Hz, 3H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 77.42 (CH), 79.56 ($C_{quat.}$), 88.35 ($C_{quat.}$), 90.96 (CH), 91.08 (CH), 95.13 (CH), 231.70 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 238 [M^+] (20), 182 [M^+ − 2 CO] (11), 154 [M^+ − 3 CO] (49), 102 [M^+ − $Cr(CO)_3$] (6), 52 [Cr^+] (100). – IR: $\tilde{\nu}$ = 3256 cm^{-1}, 2114, 1950, 1858, 1145, 813, 672, 647. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 nm (9760 sh), 257 (6750 sh), 323 (9190), 390 (1930 sh). – $C_{11}H_6CrO_3$ (238.2): calcd. C 55.47, H 2.54; found C 55.58, H 2.43.

General Procedure (GP) for the Palladium-Copper-Catalyzed Coupling of Tricarbonyl[η^6-(ethynylbenzene)]chromium(0) (**3**): 1 mmol of **3** and the appropriate amount of **4** were dissolved in a deaerated amine under argon at room temp. 2–10 mol-% of bis(triphenylphosphane)palladium(II) dichloride or tetrakis(triphenylphosphane)palladium(0) and 1–7 mol-% of copper(I) iodide were added to the solution. The reaction mixture was then stirred at room temp. or heated at reflux temp. for the time indicated. To this suspension 50 ml of diethyl ether was added at room temp., and the mixture was filtered. The clear filtrate was evaporated to dryness in a rotary evaporator. The residue was chromatographed on silica or alumina, and the yellow to orange band was collected. Further purification was achieved by recrystallization.

Tricarbonyl{η^6-[(phenylethynyl)benzene]}chromium(0) (**5a**): Complex **3** (242 mg, 1.02 mmol) and **4a** (200 mg, 0.98 mmol) were allowed to react in the presence of bis(triphenylphosphane)palladium(II) dichloride (14 mg, 0.02 mmol) and copper(I) iodide (2 mg, 0.01 mmol) in 10 ml of triethylamine at reflux temp. for 5 h according to the GP. Subsequent chromatography on silica gel (ether/pentane, 1:8) afforded 227 mg (74%) of pure **5a** (R_f = 0.23) as yellow needles, m.p. 101–102°C (hexane). – ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 5.70 (m, *J* = 6.1 Hz, 1H), 5.80 (m, *J* = 6.1, 6.2 Hz, 2H), 5.95 (m, *J* = 6.2 Hz, 2H), 7.46 (m, 3H), 7.55 (m, 2H). – ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 85.43 ($C_{quat.}$), 88.94 ($C_{quat.}$), 91.15 ($C_{quat.}$), 93.25 (CH), 94.14 (CH), 96.47 (CH), 120.92 ($C_{quat.}$), 128.67 (CH), 129.45 (CH), 131.55 (CH), 233.10 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 314 [M^+] (6), 258 [M^+ − 2 CO] (9), 230 [M^+ − 3 CO] (29), 178 [M^+ − $Cr(CO)_3$] (100), 140 (19), 124 (18), 89 (11), 78 (11), 52 [Cr^+] (49). – IR: $\tilde{\nu}$ = 2225 cm^{-1}, 1979, 1963, 1893, 1873, 1488, 1451, 1442, 917, 814, 757, 690, 673, 656, 625, 615. – UV/Vis (DMSO): λ_{max} (ε) = 275 nm (20800), 325 (10100), 390 (3570). – $C_{17}H_{10}CrO_3$ (314.3): calcd. C 64.97, H 3.21; found C 65.16, H 3.15.

μ-{η^6:η^6-[1,2-Phenylenebis(2,1-ethynediyl)]bis(benzene)}bis[tricarbonylchromium(0)] (**5b**): Complex **3** (240 mg, 1.01 mmol) and **4b** (168 mg, 0.51 mmol) were allowed to react in the presence of tetrakis(triphenylphosphane)palladium(0) (29.6 mg, 0.026 mmol) and copper(I) iodide (2.8 mg, 0.015 mmol) in 20 ml of diisopropylamine at reflux temp. for 14 h according to the GP. Subsequent chromatography on silica gel (ether) yielded 257 mg (92%) of **5b** as brown microcrystals, m.p. 163–164°C (dec.) (trichloromethane). – ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 5.75 (m, 2H), 5.80 (m, 4H), 5.99 (m, 4H), 7.51 (m, 2H), 7.64 (m, 2H). – ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 87.19 ($C_{quat.}$), 90.03 ($C_{quat.}$), 90.75 ($C_{quat.}$), 94.04 (CH), 94.44 (CH), 97.03 (CH), 123.76 ($C_{quat.}$), 129.91 (CH), 132.73 (CH), 233.35 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 550 [M^+] (1), 466 [M^+ − 3 CO] (1), 382 [M^+ − 6 CO] (3), 330 [M^+ − $Cr(CO)_6$] (22), 278 [M^+ − 2 $Cr(CO)_3$] (8), 80 [$CrCO^+$] (28), 52 [Cr^+] (100). – IR: $\tilde{\nu}$ = 2224 cm^{-1}, 1985, 1919, 1481, 1457, 761, 672, 653, 631. – UV/Vis (DMSO): λ_{max} (ε) = 293 nm (21800 sh), 320 (18300 sh), 408 (6790). – $C_{28}H_{14}Cr_2O_6$ (550.4): calcd. C 61.10, H 2.56; found C 59.90, H 2.68.

μ-{η^6:η^6-[1,3-Phenylenebis(2,1-ethynediyl)]bis(benzene)}bis[tricarbonylchromium(0)] (**5c**): Complex **3** (213 mg, 0.89 mmol) and **4c** (145 mg, 0.44 mmol) were allowed to react in the presence of tetrakis(triphenylphosphane)palladium(0) (28 mg, 0.024 mmol) and copper(I) iodide (4.6 mg, 0.024 mmol) in 15 ml of diisopropylamine at room temp. for 14 h according to the GP. Subsequent chromatography on silica gel (ether/pentane, 1:2) furnished 148 mg (61%) of pure **5c** (R_f = 0.51) as yellow-orange microcrystals, m.p. 162–163°C (dec.) (dichloromethane/pentane). – ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 5.8–6.0 (br 10H), 7.4–7.7 (br 4H). – ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 86.81 ($C_{quat.}$), 87.87 ($C_{quat.}$), 90.79 ($C_{quat.}$), 94.03 (CH), 94.52 (CH), 97.11 (CH), 122.01 ($C_{quat.}$), 129.90 (CH), 132.63 (CH), 134.73 (CH), 233.32 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 550 [M^+] (8), 466 [M^+ − 3 CO] (11), 414 [M^+ − $Cr(CO)_3$] (10), 382 [M^+ − 6 CO] (19), 358 [M^+ − $Cr(CO)_5$] (14), 330 [M^+ − $Cr(CO)_6$] (52), 278 [M^+ − 2 $Cr(CO)_3$] (34), 108 [$Cr(CO)_2$] (11), 80 [$CrCO^+$] (19), 52 [Cr^+] (100). – IR: $\tilde{\nu}$ = 2221 cm^{-1}, 1970, 1889, 1593, 1571, 1523, 1477, 1451, 1409, 1151, 894, 816, 797, 671, 652, 629, 617. – UV/Vis (DMSO): λ_{max} (ε) = 275 nm (38500), 324 (18900), 401 (7390). – $C_{28}H_{14}Cr_2O_6$ (550.4): calcd. C 61.10, H 2.56; found C 59.50, H 2.45. – HRMS $C_{28}H_{14}Cr_2O_6$: calcd. 549.96; found 549.981.

μ-{η^6:η^6-[1,4-Phenylenebis(2,1-ethynediyl)]bis(benzene)}bis[tricarbonylchromium(0)] (**5d**): Complex **3** (236 mg, 0.99 mmol)

and **4d** (163 mg, 0.49 mmol) were allowed to react in the presence of tetrakis(triphenylphosphane)palladium(0) (27.7 mg, 0.024 mmol) and copper(I) iodide (3.1 mg, 0.016 mmol) in 15 ml of triethylamine at room temp. for 18 h according to the GP. Subsequent filtration through a short pad of alumina (ether/THF, 1:1), removal of the solvents in a rotary evaporator and recrystallization of residue from trichloromethane furnished 199 mg (74%) of pure **5d** as orange needles, m.p. 193–194°C (dec.). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.73 (m, 2H), 5.81 (m, 4H), 6.00 (m, 4H), 7.59 (s, 4H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 88.17 ($C_{quat.}$), 88.49 ($C_{quat.}$), 90.76 ($C_{quat.}$), 94.07 (CH), 94.52 (CH), 97.13 (CH), 122.06 ($C_{quat.}$), 132.28 (CH), 233.43 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 550 [M$^+$] (4), 466 [M$^+$ – 3 CO] (4), 382 [M$^+$ – 6 CO] (14), 330 [M$^+$ – Cr(CO)$_6$] (17), 80 [CrCO$^+$] (19), 52 [Cr$^+$] (100). – IR: $\tilde{\nu}$ = 2225 cm^{-1}, 1963, 1882, 1529, 1495, 1451, 1407, 842, 671, 652, 629, 617. – UV/Vis (DMSO): λ_{max} (ε) = 304 nm (41100), 416 (10300). – $C_{28}H_{14}Cr_2O_6$ (550.4): calcd. C 61.10, H 2.56; found C 60.51, H 2.34.

μ_3-{η^6:η^6:η^6-[1,3,5-Benzenetriyltris(2,1-ethynediyl)]tris(benzene)}tris[tricarbonylchromium(0)] (**5e**): Compound **3** (242 mg, 1.02 mmol) and **4e** (138 mg, 0.30 mmol) were allowed to react in the presence of tetrakis(triphenylphosphane)palladium(0) (31 mg, 0.027 mmol) and copper(I) iodide (4.0 mg, 0.021 mmol) in 20 ml of triethylamine at room temp. for 3 d according to the GP. Subsequent filtration through a short pad of alumina (dichloromethane), removal of the solvents in a rotary evaporator and recrystallization of residue from trichloromethane yielded 200 mg (84%) of pure **5e** as fine yellow needles, m.p. 170°C (dec.). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.8–6.0 (br 15H), 7.8 (br 3H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 86.62 ($C_{quat.}$), 87.74 ($C_{quat.}$), 89.98 ($C_{quat.}$), 94.09 (CH), 94.19 (CH), 97.11 (CH), 122.85 ($C_{quat.}$), 134.86 (CH), 233.19 ($C_{quat.}$, CO). – MS (FD), *m/z*: 758 [M$^+$ – CO], 378 [M$^+$ – 3 Cr(CO)$_3$]. – IR: $\tilde{\nu}$ = 2219 cm^{-1}, 1961, 1888, 1583, 1457, 1153, 880, 813, 671, 653, 629. – UV/Vis (DMSO): λ_{max} (ε) = 276 nm (64500), 325 (28900), 410 (12300). – $C_{39}H_{18}Cr_3O_9$ (786.6): calcd. C 59.55, H 2.31; found C 57.42, H 2.29.

μ-{η^6:η^6-[1,2-Ethynediylbis(benzene)]}bis[tricarbonylchromium(0)] (**6**): The chlorobenzene complex **1** (127 mg, 0.51 mmol), **3** (132 mg, 0.55 mmol), and cooper(I) iodide (5.4 mg, 0.028 mmol) were dissolved at room temp. with stirring under argon in a deaerated mixture of 10 ml of THF and 5 ml of triethylamine. Bis(triphenylphosphane)palladium(II) dichloride (18.4 mg, 0.026 mmol) was added at room temp., and the reaction mixture was immediately heated at reflux temp. under argon for 24 h. After cooling to room temp. under argon 50 ml of diethyl ether was added to the mixture. The suspension was filtered, and the solvents of the filtrate were removed in a rotary evaporator. The residue was filtered through a short pad of silica gel (diethyl ether). The ether was removed in a rotary evaporator, and the residue was recrystallized from trichloromethane to yield 77 mg (34%) of pure **6** as orange crystals, m.p. 180°C (dec.). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.76 (m, 6H), 5.92 (m, 4H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 85.45 ($C_{quat.}$), 89.25 ($C_{quat.}$), 94.01 (CH, br), 97.04 (CH), 232.99 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 450 [M$^+$] (12), 366 [M$^+$ – 3 CO] (11), 338 [M$^+$ – 4 CO] (9), 282 [M$^+$ – 6 CO] (55), 230 [M$^+$ – Cr(CO)$_6$] (23), 80 [CrCO$^+$] (12), 52 [Cr$^+$] (100). – IR: $\tilde{\nu}$ = 1959 cm^{-1}, 1875, 1462, 1158, 842, 816, 678, 657. – UV/Vis (DMSO): λ_{max} (ε) = 327 nm (17400), 415 (6280). – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 329 nm (14500), 417 (5380). – $C_{20}H_{10}Cr_2O_6$ (450.3): calcd. C 53.35, H 2.24; found C 52.95, H 2.08.

μ-{η^6:η^6-[1,4-Butadiynediylbis(benzene)]}bis[tricarbonylchromium(0)] (**7**): Complex **3** (147 mg, 0.62 mmol) was dissolved under argon in 10 ml of deaerated methanol. To this solution, a solution of copper(II) acetate hexahydrate (248 mg, 1.24 mmol) in a mixture of 10 ml of deaerated pyridine and 10 ml of deaerated methanol was added dropwise. The reaction mixture was heated at reflux for 15 min. After cooling to room temp. the mixture was poured into 50 ml of 2 N HCl. The aqueous suspension was extracted with diethyl ether (3 × 30 ml). The combined extracts were washed with 20 ml of water and then dried with magnesium sulfate. The solvents were removed in a rotary evaporator to give 140 mg (96%) of pure **7** as orange crystals, m.p. 180°C (dec.) (trichloromethane). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.72 (dd, *J* = 6.2, 6.3 Hz, 4H), 5.81 (t, *J* = 6.1 Hz, 2H), 6.08 (d, *J* = 6.3 Hz, 4H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 71.90 ($C_{quat.}$), 86.34 ($C_{quat.}$), 92.82 (CH), 93.04 ($C_{quat.}$), 94.73 (CH), 98.03 (CH), 232.45 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 474 [M$^+$] (5), 390 [M$^+$ – 3 CO] (7), 338 [M$^+$ – Cr(CO)$_3$] (8), 306 [M$^+$ – 6 CO] (25), 282 (11), 254 [M$^+$ – Cr(CO)$_6$] (47), 202 [M$^+$ – 2 Cr(CO)$_3$] (11), 52 [Cr$^+$] (100). – IR: $\tilde{\nu}$ = 1950 cm^{-1}, 1867, 1438, 812, 667, 646. – UV/Vis (DMSO): λ_{max} (ε) = 288 nm (15100), 313 (17100 sh), 325 (18700 sh), 330 (18900), 430 (8700). – $C_{22}H_{10}Cr_2O_6$ (474.3): calcd. C 55.71, H 2.13; found C 55.55, H 2.09.

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