Synthesis and Substituent Interactions of Tricarbonylchromium-Complexed Arylalkynylbenzenes – Novel Organometallic Push-Pull Chromophores☆

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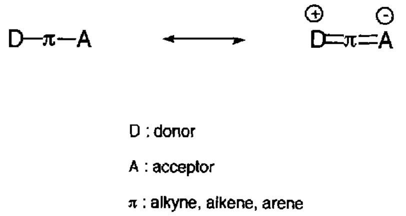
The tricarbonylchromium complexes chlorobenzene **1** reacts with terminal alkynes **2** through a palladium-copper-catalyzed coupling to give a variety of $Cr(CO)_3$-complexed phenylethynyl arenes, heteroarenes and ferrocene **3** in good to excellent yield. Due to the electron-withdrawing nature of the $Cr(CO)_3$ group these novel complexes can be regarded as organometallic push-pull chromophores. Analogously, the corresponding free ligands **4** (phenylethynyl arenes, heteroarenes and ferrocene) were synthesized by coupling iodobenzene and **2**. The crystal structure analysis of the singly $Cr(CO)_3$-complexed tolane **3e** reveals a strong deviation from coplanarity of both phenyl rings by an angle of 50.9(2)° presumably due to crystal packing. Correlations are established between selected substituent parameters (σ_P, σ_I, σ_R, σ_{P+} and Δ_π) and the carbonyl carbon resonances in the ^{13}C-NMR spectra for the complexes **3**. The overall electronic substituent effect is transmitted to the carbonyl groups by both mesomeric and inductive mechanisms. The push-pull complexes **3** display relatively small negative solvochromicities of longest wavelength absorption band (MLCT band).

Introduction

A remarkable number of organic chromophores have been investigated for their nonlinear optical (NLO) properties[1]. The common features of NLO chromophores are an electron-donating group, a bridging conjugated π-system (alkyne, alkene or arene) and an electron-accepting group (Scheme 1), generally refered to as a push-pull system. Especially, extended conjugated π systems like donor-acceptor α,ω-diaryl polyenes and polyines are classes of organic molecules that display considerable NLO responses[2]. Many transition metal π complexes are also known to exhibit high polarizabilities, facile excitation upon irradiation with visible light and stable specimens of higher oxidation states; nevertheless, the synthesis of extended organometallic π-systems possibly showing NLO properties is a rapidly expanding field[1a].

Scheme 1. Idealized donor-acceptor π systems



The tricarbonyl-η^6-benzenechromium(0) unit, a well-known organometallic fragment, behaves as a net electron-withdrawing group[3]. Therefore, $Cr(CO)_3$-benzene fragments can be interesting building blocks in extended organic-organometallic chromophores. Furthermore, due to their ability to stabilize negative as well as positive charges in benzylic positions[3], $Cr(CO)_3$-arene complexes with conjugated side chains could also display an intriguing reactivity. Theoretical[4] and NLO studies[5] on simple $Cr(CO)_3$-complexed arenes also support this view although the NLO responses of some (arene)chromium tricarbonyls are fairly small, which is partially due to pseudo symmetrical electron distribution around the metal. However, the stilbene complex (E)-$(C_6H_5CH{=}CHC_6H_5)Cr(CO)_3$ displayed a β value larger than any other comparable system in that series[5]. As a consequence complexes with extended π-systems behave as good NLO materials.

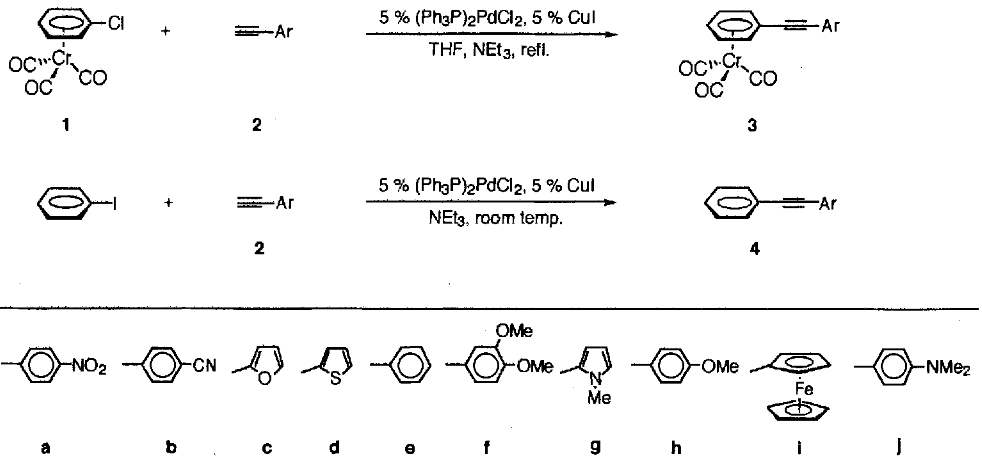
Alkynes represent rotational symmetric π-bridges and form the back-bone of a rigid-rod molecular architecture. Thus, tricarbonylchromium-complexed arylalkynylbenzenes that can be regarded as organometallic donor-acceptor alkynes are intriguing synthetic targets. Furthermore, the question arises how the influence of a remote substituent is transmitted through the alkyne bridge and the coordinated arene on the tricarbonylchromium moiety. In principle, regression analyses of correlations[6] of spectral data and substituent parameters can disclose an insight into the mechanisms of substituent effect transmission in organometallic chromophores.

Recently, we have found a facile access to $Cr(CO)_3$-complexed phenylethynyl benzenes using a palladium-copper-catalyzed coupling[7]. This methodology offers a superior chemo- and regioselective alternative over the direct complexation (pyrolysis of hexacarbonyl chromium in presence of the ligand). Here we report on the synthesis of a variety of $Cr(CO)_3$-complexed phenylethynyl arenes. In addition we want to describe the quantification of the substituent effects on the chromium atom as established by correlations between Hammett substituent parameters, resonances of the carbonyl carbon atoms in the ^{13}C-NMR spectra and the longest wave length absorption bands in the UV/Vis spectra.

Results and Discussion

The palladium-copper catalyzed coupling of the chlorobenzene complex **1** with trimethylsilyl acetylene turned out to be an efficient method for the preparation of the $Cr(CO)_3$-complexed phenylacetylene[7]. We could extend this facile synthesis using a plethora of terminal aryl, heteroaryl and organometallic acetylenes **2**. The reaction of **1** with **2** in the presence of 5 mol% of bis(triphenylphosphane)palladium(II) dichloride and 5 mol% copper(I) iodide in a refluxing mixture of THF and triethylamine furnishes under mild conditions the tricarbonyl{η^6-[(arylethynyl)benzene]}chromium(0) complexes **3** as yellow to orange solids in good to excellent yields (Scheme 2). For comparison the free ligands **4** were synthesized analogously by the palladium-copper-catalyzed coupling of iodobenzene with the corresponding alkynes[8].

Scheme 2. Syntheses of the complexes **3** and the free ligands **4**



	a	b	c	d	e	f	g	h	i	j
3	77 %	82 %	76 %	91 %	85 %	67 %	72 %	63 %	88 %	78 %
4	85 %	89 %	78 %	77 %	86 %	61 %	82 %	60 %	80 %	58 %

The infrared spectra of the complexes exhibit the expected pairs of carbonyl stretching frequencies due to the A_1 and E bands of the $Cr(CO)_3$ groups (assuming a pseudo C_{3v} symmetry). Unfortunately, the A_1 bands in the region between 1950 and 1978 cm^{-1} and the E bands in the region between 1867 and 1907 cm^{-1} are split in some spectra presumably due to a significant deviation from the idealized C_{3v} symmetry. Therefore, the CO stretching frequencies can not be considered for correlations. In the ^1H-NMR spectra of the complexes **3** the signals of complexed arene protons can be easily identified by their upfield shift to the region between $\delta = 5.5$ and 6.0. These protons are assigned by the characteristic splitting pattern (triplet, pseudotriplet and doublet). The uncomplexed arene protons give rise to the expected sets of signals and multiplicity. The carbon resonances (see Table 1) of the C_1 to C_4 atoms (complexed phenyl rings of **3**) assigned by CH correlation spectroscopy are shifted to higher field compared to those of the free ligands **4** and appear in the region between $\delta = 89$ and 94 [for complexing chemical shifts (CCS), i.e. shifts on complexation see Table 2]. More difficult is the unambiguous assignment of the resonances of the alkyne carbon atoms C_5 and C_6. A comparison of the CCS of the C_5 signals reveals that they are shifted upfield by 4 ppm. The upfield shift can be plausibly rationalized by the electronic back-donation exerted by the chromium carbonyl tripod, which is in direct proximity. The CCS of the C_6 resonances do not behave similarly.

Interestingly, the carbonyl carbon resonances appearing in the region between $\delta = 232.6$ and 233.6 are arranged according to increasing donating ability of the remote arene substituent (*vide infra*). The chemical shifts of the carbonyl carbon nuclei increase, i.e. the CO ligands are deshielded, with increasing electron richness[9] of the metal center, presumably due to the dominance of the paramagnetic term in the chemical shift tensor. In the mass spectra, the fragmentation pattern is similar for all complexes. 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 two characteristic main absorption bands in the electronic spectra appear in the region between 308 and 338 nm and in the region between 377 and 433 nm. These absorption maxima can be assigned[4a,10] to π-π^* transitions, metal-to-ligand (ML) and ligand-to-metal (LM) charge transfer (CT) bands, respectively.

Additional structural information on the complexes **3**, especially on conformational aspects of the mutual arrangement of the substituents and the $Cr(CO)_3$-complexed phenyl rings in solid state, can be obtained from X-ray crystal analysis. Suitable crystals for an X-ray analysis of **3e** were obtained by crystallization from hexanes. The crystal structure determination[11] of singly coordinated tolane re-

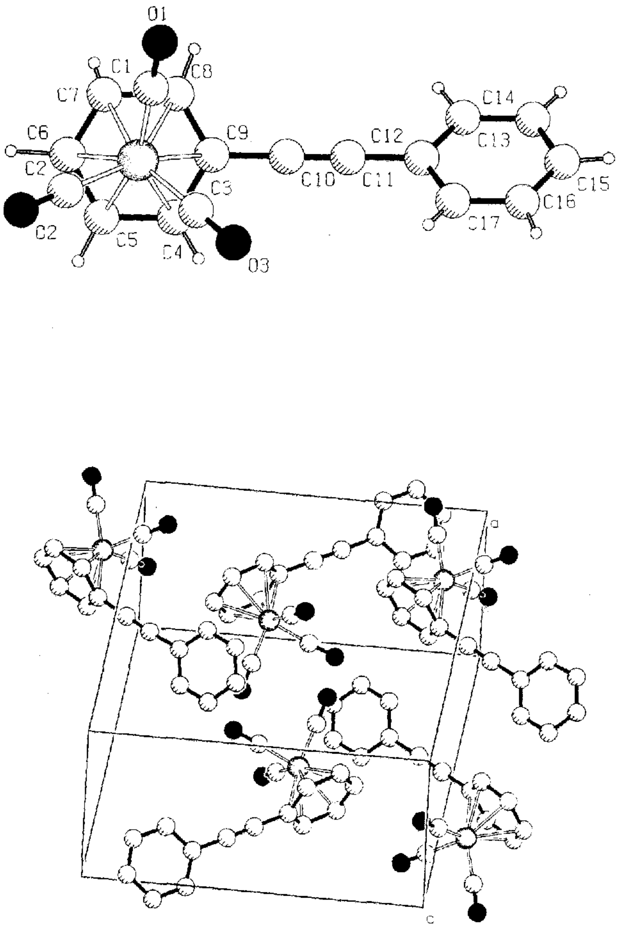
Table 1. Selected ^{13}C-NMR data of the complexes **3** and free ligands **4** and Hammett-Taft parameters of the corresponding substituents

Compnd	C_1	C_2	C_3	C_4	C_5	C_6	CO	$\Delta\pi$	σ_P	σ_I	σ_R	σ_{P+}
3a	91.15	91.07	94.94	87.85	90.34	87.26	231.66	0.08	0.78	0.63	0.15	0.79
4a	129.25	128.45	131.82	122.11	94.69	87.53		0.80				
3b	91.14	91.06	94.87	88.19	89.46	87.50	231.71	0.08	0.66	0.59	0.07	0.66
4b	129.07	128.45	131.72	122.13	93.71	87.67		0.62				
3c	90.90	91.04	94.57	89.38	88.87	79.46	231.82	-0.14	0.02	0.17	-0.15	-0.39
4c	128.66	128.36	131.40	122.25	93.22	79.37		0.30				
3d	90.66	91.33	94.58	90.01	88.85	82.97	232.01	-0.67	0.05	0.19	-0.14	-0.43
4d	128.34	128.36	131.37	122.86	93.00	82.58		-0.02				
3e	90.56	91.64	94.75	90.62	85.14	89.71	232.16	-1.08	-0.01	0.10	-0.11	-0.18
4e	128.24	128.32	131.58	123.22	89.34	89.34		-0.08				
3f	90.40	91.73	94.63	91.27	83.77	90.05	232.27	-1.33	-0.24	0.23	-0.47	-0.73
4f	128.00	128.30	131.45	123.47	87.95	89.47		-0.30				
3g	90.31	91.82	94.38	91.30	89.08	81.91	232.27	-1.51	-0.30	0.17	-0.47	-1.40
4g	127.81	128.25	130.99	123.36	92.98	81.27		-0.44				
3h	90.36	91.95	94.62	91.54	83.88	89.96	232.32	-1.59	-0.27	0.23	-0.50	-0.78
4h	127.91	128.28	131.43	123.56	88.04	89.34		-0.37				
3i	89.95	92.05	94.31	92.45	81.54	89.85	232.40	-2.10	-0.30	0.12	-0.42	-1.00
4i	127.63	128.25	131.38	123.93	85.70	88.28		-0.62				
3j	89.99	92.03	94.46	92.97	83.22	91.68	232.53	-2.04	-0.83	0.10	-0.93	-1.70
4j	127.42	128.20	131.24	124.09	87.30	90.56		-0.78				

Table 2. Complexing Chemical Shifts (CCS) of C_1, C_2, C_3, C_4, C_5 and C_6

Substituent	C_1	C_2	C_3	C_4	C_5	C_6
a	-38.10	-37.38	-36.88	-34.26	-4.35	-0.27
b	-37.93	-37.39	-36.85	-33.94	-4.25	-0.17
c	-37.76	-37.32	-36.83	-32.87	-4.35	0.09
d	-37.68	-37.03	-36.79	-32.85	-4.15	0.39
e	-37.68	-36.68	-36.83	-32.60	-4.20	0.37
f	-37.60	-36.57	-36.82	-32.20	-4.18	0.58
g	-37.50	-36.43	-36.61	-32.06	-3.90	0.64
h	-37.55	-36.33	-36.81	-32.02	-4.16	0.62
i	-37.68	-36.20	-37.07	-31.48	-4.16	1.57
j	-37.43	-36.17	-36.78	-31.12	-4.08	1.12

Figure 1. Crystal structure of **3e** with elementary cell; selected bond lengths [pm]: Cr(1)–C(1) 184.0(7), C(1)–O(1) 114.2(7), Cr(1)–C(9) 220.0(6), C(9)–C(10) 145.5(10), C(10)–C(11) 116.7(9), C(4)–C(9) 141.7(9), C(11)–C(12) 144.6(10), C(12)–C(17) 138.7(10); bond angles [°]: C(10)–C(9)–Cr(1) 127.4(4), C(9)–C(10)–C(11) 179.3(7)



veals some significant differences in comparison to the doubly complexed tolane[7]. The coordinated and the noncoordinated phenyl rings of **3e** (see Figure 1) are mutually arranged with a dihedral angle of 50.9(2)°. If this conformation has also a strong preference in solution the substituent effect on the carbonyl ligands is expected to be fairly small due to a weak orbital overlap. Interestingly, the $Cr(CO)_3$ group is arranged in an *anti*-eclipsed conformation with respect to the alkynyl substituent, which is typical for arene complexes bearing electron-withdrawing substituents. We tend to attribute this somewhat puzzling orientation of the phenylethynyl substituent to the crystal packing of **3e** (see Figure 1). This observation is also in agreement with a low rotational barrier around the sp-sp^2 single bond in tolane[12]. Nevertheless, a remote substituent seems to exert an electronical influence on the $Cr(CO)_3$ group.

However, in solution the correlation of independent parameters offers a more quantitative treatment of substituent effects. Among the parameters to establish correlations with a detection center, the Hammett σ values[13] (σ_P, σ_I, σ_R and σ_{P+}) are the most common ones. But often more convenient are Δ_π values[14] derived from ^{13}C-NMR spectra as a measure of π-donor or π-acceptor character of substituents on aromatic rings. In general, Δ_π is defined as the difference (in ppm) between the measured chemical shifts of the para- and meta-substituted carbon atoms in monosubstituted benzene rings, i.e. $\Delta_\pi = \delta_{para} - \delta_{meta}$, which places both π-donor or π-acceptor interactions on the same scale. The same is true for (η^6-arene)$Cr(CO)_3$ complexes. First, we tested for the free ligands **4** the correlation between the carbon resonances of C_1 to C_4 and σ_P, σ_I, σ_R and σ_{P+} and Δ_π, respectively. The results of the linear regression analyses are summarized in Table 3. The carbon resonances of C_1

and C_2 correlate strongly with the Hammett parameter σ_P and Δ_π, respectively. The signals of C_3 correlate only poorly with σ_P and Δ_π. Surprisingly, the resonances of C_4 correlate strongly only with Δ_π. Correlations with σ_P can be interpreted on the basis that a substituent effect is transmitted by resonance and inductive mechanisms[6b]. The consistency of the correlation of the C_1 and C_2 resonances with Δ_π also establishes a measure of π-donor or π-acceptor influence of the corresponding substituent. The nitrophenyl substituent in the complex **3a** ($\Delta_\pi = 0.08$) is a weak acceptor and the *p*-dimethylaminophenyl group in the complex **3j** ($\Delta_\pi = -2.04$) is a moderate donor.

Table 3. Regression analyses of the correlations of the carbon resonances of C_1 to C_4 (free ligands **4**) and σ_P, σ_I, σ_R and σ_{P+} and Δ_π (**4**)

Correlation $\delta(C_n)$ - parameter	$\delta(C_{n1})$ [ppm]	$\delta(C_{n0})$ [ppm]	standard deviation s [ppm]	correlation coefficent
$\delta(C_1)$ - σ_P	128.29	1.23	0.055	0.962
$\delta(C_1)$ - σ_I	127.58	2.58	0.193	0.828
$\delta(C_1)$ - σ_R	128.75	1.73	0.111	0.919
$\delta(C_1)$ -σ_{P+}	128.60	0.72	0.075	0.951
$\delta(C_1)$ - Δ_π	128.34	1.16	0.006	0.9996
$\delta(C_2)$ - σ_P	128.33	0.17	0.007	0.973
$\delta(C_2)$ - σ_I	128.23	0.36	0.026	0.833
$\delta(C_2)$ - σ_R	128.39	0.24	0.014	0.932
$\delta(C_2)$ -σ_{P+}	128.37	0.10	0.009	0.968
$\delta(C_2)$ - Δ_π	128.34	0.16	0.005	0.981
$\delta(C_3)$ - σ_P	131.46	0.39	0.048	0.792
$\delta(C_3)$ - σ_I	131.21	0.88	0.091	0.732
$\delta(C_3)$ - σ_R	131.60	0.530	0.075	0.727
$\delta(C_3)$ -σ_{P+}	131.57	0.26	0.041	0.904
$\delta(C_3)$ - Δ_π	131.47	0.34	0.051	0.767
$\delta(C_4)$ - σ_P	123.04	-1.38	0.108	0.899
$\delta(C_4)$ - σ_I	123.80	-2.76	0.283	0.733
$\delta(C_4)$ - σ_R	122.50	-2.00	0.160	0.884
$\delta(C_4)$ -σ_{P+}	122.69	-0.79	0.151	0.861
$\delta(C_4)$ - Δ_π	122.98	-1.36	0.058	0.972

The results of the regression analyses of the complexes **3** are summarized in Table 4. Only the resonances of C_4 and the carbonyl carbon atom correlate satisfyingly ($r > 0.92$) with σ_P. For consistency the correlation of C_1, C_2 and C_4 with Δ_π was examined and found to be excellent. In particular, the correlation (see Figure 2) of the carbonyl signals (the chemical shift of the carbonyl resonance can be regarded as a probe for the electron density[9] on the chromium atoms as stated above) with σ_P and Δ_π supports a mechanistic rationale of the transmission of a substituent effect over a conjugated system and the metal to the carbonyl carbon atom. The substituent effect is transmitted to the carbonyl groups by a mechanism that largely operates through π-electron resonance and to a minor extend through the σ framework[6b]. The inductive contribution is reflected by the additive nature of σ_P ($\sigma_P = \sigma_I + \sigma_R$). Additionally, this view is supported by the strong correlation of carbonyl carbon resonances with Δ_π. These findings are also in agreement with correlation analyses on simple monosubstituted (η^6-arene)$Cr(CO)_3$ complexes[6b,6d].

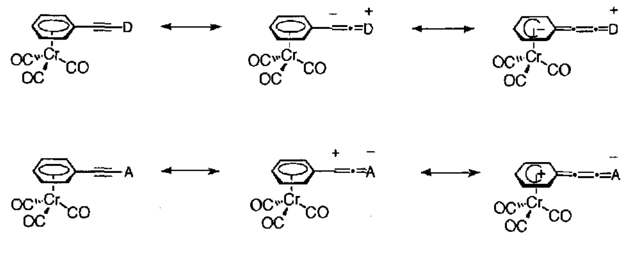
Table 4. Selected regression analyses of the correlations of the carbon resonances of C_1 to C_6 and CO (complexes **3**) and σ_P, σ_I, σ_R and σ_{P+} and Δ_π (**3**)

Correlation $\delta(C_n)$ - parameter	$\delta(C_{n1})$ [ppm]	$\delta(C_{n0})$ [ppm]	standard deviation s [ppm]	correlation coefficent
$\delta(C_1)$ - σ_P	90.58	0.82	0.057	0.918
$\delta(C_2)$ - σ_P	91.54	-0.74	0.074	0.847
$\delta(C_3)$ - σ_P	94.63	0.35	0.039	0.816
$\delta(C_4)$ - σ_P	90.41	-3.43	0.166	0.957
$\delta(C_5)$ - σ_P	86.63	4.88	0.749	0.721
$\delta(C_6)$ - σ_P	86.94	-2.26	1.350	0.258
$\delta(CO)$ - σ_P	232.09	-0.59	0.036	0.936
$\delta(CO)$ - σ_I	232.42	-1.20	0.109	0.773
$\delta(CO)$ - σ_R	231.86	-0.85	0.057	0.914
$\delta(CO)$ - σ_{P+}	231.94	-0.340	0.052	0.903
$\delta(C_1)$ -Δ_π	91.07	0.51	0.033	0.990
$\delta(C_2)$ - Δ_π	91.07	-0.49	0.033	0.989
$\delta(C_3)$ - Δ_π	94.81	0.19	0.069	0.781
$\delta(C_4)$ - Δ_π	88.48	-2.01	0.179	0.982
$\delta(CO)$ - Δ_π	231.75	-0.36	0.026	0.987

The electronic spectra were recorded in dichloromethane and acetonitrile. The longest wave length absorptions have small extinction coefficients and are assigned[4a,10] to the MLCT bands; higher energy absorptions immediately adjacent have higher extinction coefficients and can be regarded as intra ligand (IL) transition bands. According to the perpendicular orientation of the transition dipole moment to the molecular main dipole axis the MLCT transition band is expected to be smaller in its intensity[4a]. The strong absorption bands in the region between 300 and 340 nm presumably arise from π-π* as well as from LM and ILCT transitions. As for the carbonyl resonances, there exists a strong correlation between the MLCT bands and the Hammett parameter σ_P as a consequence of a strong substituent interaction through the σ- and the π-framework (see Figure 3). Surprisingly, the correlations with the Δ_π values are fairly poor.

A major criterion of potential NLO materials is the existence of solvochromicity[15], i.e. the solvent dependent shift of the absorption bands in the UV/Vis spectra. The complexes **3** display weak negative solvochromicities of the longest wavelength absorption band ranging from −70 to −520 cm⁻¹ (see Table 5). Negative solvochromicities can be attributed to the stabilization of polar ground states in polar solvents. As a consequence of the ability of the $Cr(CO)_3$-arene moiety to stabilize negative as well as positive charges and partial charges in positions that are a to the complexed

Scheme 3. Resonance structures of (top) donor- and (bottom) acceptor-substituted tricarbonylchromium-complexed arylalkynylbenzenes **3**



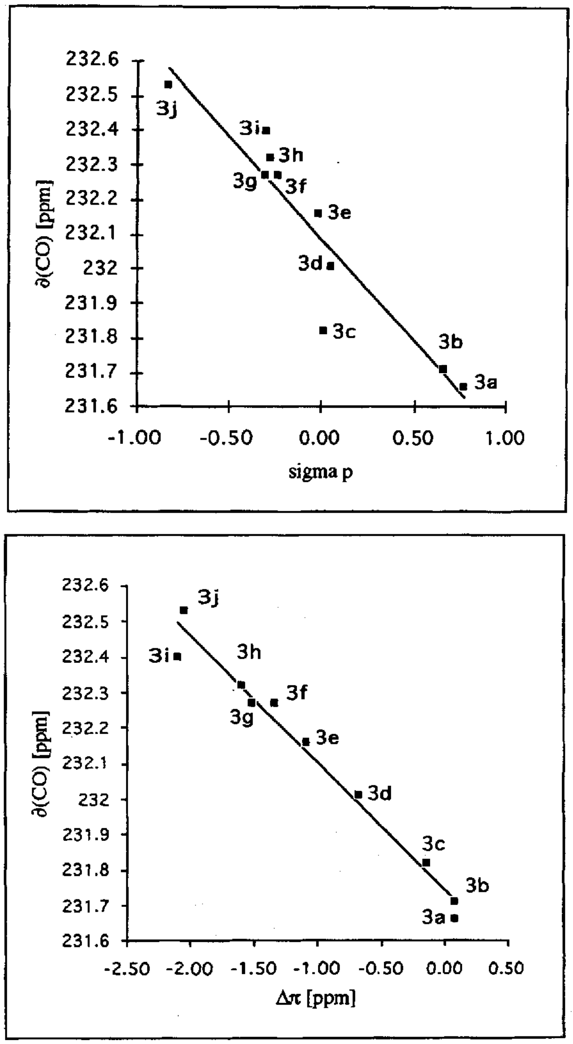


Figure 2. (top) δ(CO) – σ_P plot (r = 0.936; s = 0.036 ppm) and (bottom) δ(CO) – Δ_π plot (r = 0.987; s = 0.026 ppm); (top) regression line δ(CO) = 232.09–0.59 σ_P [ppm]; (bottom) regression line δ(CO) = 231.75–0.36 Δ_π [ppm]

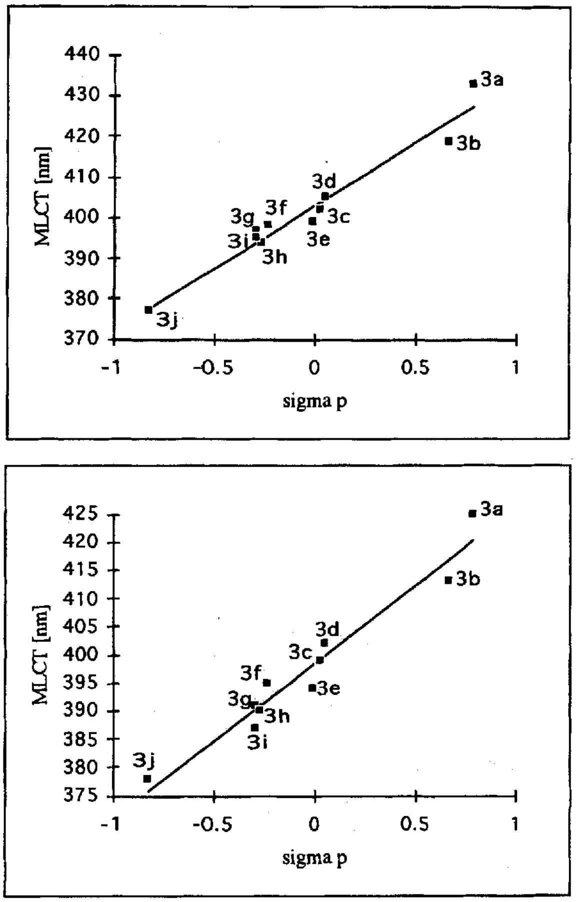


Figure 3. (top) λ_{max} (MLCT, CH_2Cl_2) – σ_P plot (r = 0.978; s = 1.057 nm) and (bottom) λ_{max} (MLCT, CH_3CN) – σ_P plot (r = 0.972; s = 1.056 nm); (top) regression line λ_{max} (MLCT, CH_2Cl_2) = 403 + 31.1 σ_P [nm]; (bottom) regression line λ_{max} (MLCT, CH_3CN) = 399 + 27.6 σ_P [nm]

phenyl ring, the negative solvochromicity of both, donor- and acceptor, alkynylarene complexes can be rationalized quite well (see Scheme 3). Although, the experimentally determined solvochromicities are fairly small, complexes like **3** are still good candidates for NLO chromophores due to their strong CT absorption bands.

Conclusion

Tricarbonyl{η^6-[(arylethynyl)benzene]}chromium(0) complexes **3** can be prepared easily and in good yield using a palladium-copper catalyzed coupling reaction. Assuming a net electron withdrawing effect of the $Cr(CO)_3$-phenyl fragment, complexes with electron-donating aryl substituents can be regarded as organometallic push-pull systems; the nitrophenyl- and the cyanophenyl alkynyl substituents behave as acceptor groups. The regression analysis of correlations between the carbon resonances of the *para*- and *meta*-phenyl carbon atoms and of the carbonyl carbon atoms of the complexes **3** and the σ_P and Δ_π values reveal that substituent effects are transmitted by a combination of resonance and inductive mechanisms through the π and σ framework of the molecule. Thus, electronic information from a remote substituent is conveyed through the conjugating bridge to the complexed phenyl ring and finally to

Table 5. Selected UV/Vis data of **3** in dichloromethane and acetonitrile and solvochromicities

	3a	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**3j**
λ_{max} (MLCT) [cm^{-1}] in CH_2Cl_2	23100	23870	24880	24690	25060	25130	25190	25380	25320	26460
λ_{max} (MLCT) [cm^{-1}] in CH_3CN	23530	24210	25060	24880	25380	25320	25580	25640	25840	26530
Δ_{MLCT} (CH_2Cl_2-CH_3CN) [cm^{-1}]	-430	-340	-180	-190	-320	-190	-390	-260	-520	-70

the chromium atom. A strong correlation between the longest wave length absorption band (MLCT) and the σ_P values also supports this rationale. The complexes **3** display small solvochromicities of the MLCT bands and are potential candidates for organometallic NLO substances. Future studies will be directed towards the investigation of nonlinear optical effects of complexes like **3**, and the syntheses of longer conjugated organometallic systems 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[16]. – 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**[17] was prepared by literature methods. Hexacarbonylchromium, bis(triphenylphosphane)palladium(II) dichloride, copper(I) iodide and phenylacetylene (**2e**) were purchased from Merck, and used without further purification. The alkynes **2a**[8], **2b**[8], **2c**[18], **2d**[18] and **2i**[19] were prepared by literature procedures. The acetylenes **2f** and **2h** were synthesized in analogy to literature procedures in two steps from the corresponding aldehydes[20]; the compounds **2g** and **2j** were obtained in one step from the corresponding aldehyde following a recently published protocol[21]. The free ligands **4** were prepared in analogy to literature methods[8] by palladium-copper-catalyzed coupling of iodobenzene, and the alkynes **2** and were only characterized by NMR spectroscopy. – ^{1}H- and ^{13}C-NMR spectra: Bruker WM 300 or Bruker AC 300, $CDCl_3$. – IR: Perkin Elmer FT-IR Paragon 1000 PC. The samples were pressed into KBr pellets. – UV/Vis: Beckman DK-2-A or Beckman UV 5240. – MS: Finnigan MAT 311-A/100 MS. – Elemental analyses were carried out in the microanalytical laboratory of the Institut für Organische Chemie, Technische Hochschule Darmstadt.

X-ray Structure Determination of Compound **3e**[11]: $C_{17}H_{10}CrO_3$, M = 314.27, monoclinic, space group $P2_1/n$, a = 610.5(1), b = 1292.5(2), c = 1836.2(4) pm, $\alpha = 90$, $\beta = 94.99(2)$, $\gamma = 90°$, V = 1.4434(5) nm^3, Z = 4, $\lambda(\text{Mo-}K_\alpha)$ = 0.71069 Å, μ = 0.78 mm^{-1}, D_x = 1.446 Mgm^{-3}, $F(000)$ = 640, T = 298(2) K. A yellow platelet with the dimensions 0.225 × 0.125 × 0.05 mm was mounted on a capillary and transferred to an Enraf-Nonius CAD4 diffractometer. A total of 2744 intensities ($-6 \leqslant h \leqslant 2$, $0 \leqslant k \leqslant \mathrm{k} \leqslant 14$, $-20 \leqslant l \leqslant 20$; $\omega/2\Theta$ scan, 2007 unique, R_{int} = 0.0578) were measured in a Θ range from 1.93 to 22.97°. 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 $w\mathrm{R}(\mathrm{F}^2)$ for all reflections was 0.1320, with a conventional $\mathrm{R}(F)$ [$\mathrm{I} > 2\sigma(I)$] of 0.0506 for 230 parameters.

General Procedure (GP) for the Palladium-Copper-Catalyzed Coupling of Tricarbonyl(η^6-chlorobenzene)chromium(0) (**1**) *with Terminal Arylacetylenes:* 0.248 g (1.00 mmol) of **1**, 35 mg (0.05 mmol) of bis(triphenylphosphane)palladium(II) dichloride and 9.5 mg (0.05 mmol) of copper(I) iodide were dissolved in a degassed mixture of 10 ml of THF and 5 ml of triethylamine under argon at room temp. 1.1 to 1.5 mmol of the corresponding terminal arylacetylene **2** dissolved in 10 ml of THF was added dropwise at room temp. to this solution over a period of 1 h. After the addition of the solution of **2** was finished, the reaction mixture was immediately heated to reflux temperature under argon for 4 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 basic alumina activity B II–III or silica gel and the intense yellow to orange band was collected. Further purification was achieved by recrystallization.

Tricarbonyl{η^6-[(4-nitrophenylethynyl)benzene]}chromium(0) (**3a**): According to the *GP* the reaction was carried out with 0.236 g (1.61 mmol) of 4-nitrophenylacetylene (**2a**). Subsequent chromatography on silica gel (ether/pentane, 1:3) afforded 280 mg (77%) of pure **3a** (R_f = 0.30, silica gel, ether/pentane 1:1) as orange red crystals, m.p. 150 °C (dec.) (trichloromethane/pentane). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.36 (m, 3H), 5.57 (m, 2H), 7.65 (d, J = 8.3 Hz, 2H), 8.22 (d, J = 8.3 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 87.26 ($C_{quat.}$), 87.85 ($C_{quat.}$), 90.34 ($C_{quat.}$), 91.07 (CH), 91.15 (CH), 94.94 (CH), 123.65 (CH), 128.61 ($C_{quat.}$), 132.64 (CH), 147.40 ($C_{quat.}$), 231.66 ($C_{quat.}$, CO). – MS (EI), m/z (%): 359 (M^+, 17), 303 (M^+ – 2 CO, 10), 275 (M^+ – 3 CO, 29), 223 [M^+ – $Cr(CO)_3$, 24], 52 (Cr^+, 100). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2219 cm^{-1}, 1967, 1890, 1594, 1516, 1343, 1107, 854, 810, 749, 687, 653, 620. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 308 nm (22000), 433 (4340). – (CH_3CN): λ_{max} (qual.) = 304 nm, 425. – $C_{17}H_9CrNO_5$: calcd. C 56.83, H 2.53, N 3.90; found C 57.21, H 2.85, N 3.87.

Tricarbonyl{η^6-[(4-cyanophenylethynyl)benzene]}chromium(0) (**3b**): According to the *GP* the reaction was carried out with 0.186 g (1.49 mmol) of 4-cyanophenylacetylene (**2b**). Subsequent chromatography on silica gel (ether/pentane, 1:3) afforded 278 mg (82%) of pure **3b** (R_f = 0.33, silica gel, ether/pentane 1:1) as orange needles, m.p. 151 °C (trichloromethane/pentane). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.35 (m, 2H), 5.37 (m, 1H), 5.55 (m, 2H), 7.59 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.0 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 87.50 ($C_{quat.}$), 88.19 ($C_{quat.}$), 89.46 ($C_{quat.}$), 91.06 (CH), 91.14 (CH), 94.87 (CH), 112.23 ($C_{quat.}$), 118.24 ($C_{quat.}$), 126.63 ($C_{quat.}$), 132.05 (CH), 132.34 (CH), 231.71 ($C_{quat.}$, CO). – MS (EI), m/z (%): 339 (M^+, 15), 283 (M^+ – 2 CO, 7), 255 (M^+ – 3 CO, 84), 203 [M^+ – $Cr(CO)_3$, 10], 80 [$Cr(CO)^+$, 10], 52 (Cr^+, 100). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2229 cm^{-1}, 1978, 1907, 1605, 1529, 1501, 841, 814, 651, 619. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 270 nm (28200), 280 (27400 sh), 292 (22200 sh), 325 (11300), 419 (4430). – (CH_3CN): λ_{max} (qual.) = 268 nm, 279, 290, 325, 413. – $C_{18}H_9CrNO_3$: calcd. C 63.72, H 2.67, N 4.13; found C 63.45, H 2.49, N 4.11.

Tricarbonyl{η^6-[(2-furylethynyl)benzene]}chromium(0) (**3c**): According to the *GP* the reaction was carried out with 0.138 g (1.10 mmol) of 2-ethynylfurane (**2c**). Subsequent chromatography on basic alumina activity B II–III (ether/pentane, 1:8) afforded 230 mg (76%) of pure **3c** (R_f = 0.44, silica gel, ether/pentane 1:2) as orange crystals, m.p. 80–82 °C (ether/pentane). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.32 (m, 3H), 5.53 (m, 2H), 6.44 (m, 1H), 6.71 (m, 1H), 7.44 (m, 1H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 79.46 ($C_{quat.}$), 88.87 ($C_{quat.}$), 89.38 ($C_{quat.}$), 90.90 (CH), 91.04 (CH), 94.57 (CH), 111.19 (CH), 116.39 (CH), 135.91 ($C_{quat.}$), 144.38 (CH), 231.82 ($C_{quat.}$, CO). – MS (EI), m/z (%): 304 (M^+, 18), 248 (M^+ – 2 CO, 11), 220 (M^+ – 3 CO, 60), 168 [M^+ – $Cr(CO)_3$, 5], 80 [$Cr(CO)^+$, 8], 52 (Cr^+, 100). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2221 cm^{-1}, 1971, 1897, 1574, 1497, 1215, 1165, 1074, 1014, 926, 885, 815, 754, 744, 690, 652, 626, 619. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 255 nm (15100), 290 (17600), 310 (14200), 325 (12700), 402 (3720). – (CH_3CN): λ_{max} (qual.) = 252 nm, 285, 305, 318, 399. – $C_{15}H_8CrO_4$: calcd. C 59.22, H 2.65; found C 59.23, H 2.65.

Tricarbonyl{η^6-[(2-thienylethynyl)benzene]}chromium(0) (**3d**): According to the *GP* the reaction was carried out with 0.160 g (1.48 mmol) of 2-ethynylthiophene (**2d**). Subsequent chromatography on basic alumina activity B II–III (ether/pentane, 1:8) afforded 290 mg (91%) of pure **3d** (R_f = 0.45, silica gel, ether/pentane 1:2) as orange crystals, m.p. 72–75 °C (ether/pentane). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.28 (m, 1 H), 5.35 (m, 2 H), 5.51 (m, 2 H), 7.02 (m, 1 H), 7.32 (m, 2 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 82.97 ($C_{quat.}$), 88.85 ($C_{quat.}$), 90.01 ($C_{quat.}$), 90.66 (CH), 91.33 (CH), 94.58 (CH), 121.63 ($C_{quat.}$), 127.21 (CH), 128.37 (CH), 133.25 (CH), 232.01 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 320 (M^+, 23), 264 (M^+ – 2 CO, 27), 236 (M^+ – 3 CO, 86), 208 [M^+ – $Cr(CO)_3$, 15], 80 [$Cr(CO)^+$, 18], 52 (Cr^+, 100). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2204 cm^{-1}, 1971, 1900, 1597, 1576, 1571, 1559, 1488, 1425, 1215, 853, 829, 755, 700, 689, 673. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 252 nm (15200), 264 (13900), 296 (19300), 315 (16100), 405 (3530). – (CH_3CN): λ_{max} (qual.) = 250 nm, 262, 294, 313, 402. – $C_{15}H_8CrO_3S$: calcd. C 56.25, H 2.52; found C 56.77, H 2.80.

Tricarbonyl{η^6-[(phenylethynyl)benzene]}chromium(0) (**3e**): According to the *GP* the reaction was carried out with 0.140 g (1.37 mmol) of phenylacetylene (**2e**). Subsequent chromatography on silica gel (ether/pentane, 1:12) afforded 267 mg (85%) of pure **3e** (R_f = 0.17, silica gel, ether/pentane 1:12) as yellow needles, m.p. 103–104 °C (ether/pentane) (ref.[7]: 101–102 °C). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 5.26 (t, *J* = 6.1 Hz, 1 H), 5.36 (pt, *J* = 6.2, 6.3 Hz, 2 H), 5.54 (d, *J* = 6.1 Hz, 2 H), 7.37 (m, 2 H), 7.52 (m, 2 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 85.14 ($C_{quat.}$), 89.71 ($C_{quat.}$), 90.56 (CH), 90.62 (CH), 91.64 ($C_{quat.}$), 94.75 (CH), 121.74 ($C_{quat.}$), 128.41 (CH), 129.08 (CH), 131.90 (CH), 232.16 ($C_{quat.}$, CO). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2224 cm^{-1}, 1988, 1890, 1598, 1576, 1570, 1559, 1489, 1443, 756, 690, 651, 617. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 nm (17200 sh), 267 (20500 sh), 275 (21600), 297 (9730 sh), 327 (10400), 399 (3180). – (CH_3CN): λ_{max} (qual.) = 273 nm, 325, 394.

Tricarbonyl{η^6-[(3,4-dimethoxyphenylethynyl)benzene]}chromium(0) (**3f**): According to the *GP* the reaction was carried out with 0.178 g (1.10 mmol) of 3,4-dimethoxyphenylacetylene (**2f**). Subsequent chromatography on basic alumina activity B II–III (ether/pentane, 1:1) afforded 250 mg (67%) of pure **3f** (R_f = 0.16, silica gel, ether/pentane 1:2) as orange crystals, m.p. 132–134 °C (ether/pentane). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.90 (s, 6 H), 5.26 (m, 1 H), 5.36 (m, 2 H), 5.52 (m, 2 H), 6.83 (m, *J* = 8.0 Hz, 1 H), 6.99 (m, 1 H), 7.12 (m, *J* = 8.0 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 55.91 (CH_3), 83.77 ($C_{quat.}$), 90.05 ($C_{quat.}$), 90.40 (CH), 91.27 ($C_{quat.}$), 91.73 (CH), 94.63 (CH), 110.95 (CH), 113.80 ($C_{quat.}$), 114.34 (CH), 125.48 (CH), 148.63 ($C_{quat.}$), 150.12 ($C_{quat.}$), 232.27 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 374 (M^+, 25), 318 (M^+ – 2 CO, 16), 290 (M^+ – 3 CO, 100), 238 [M^+ – $Cr(CO)_3$, 10], 80 [$Cr(CO)^+$, 11], 52 (Cr^+, 94). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2213 cm^{-1}, 1949, 1884, 1867, 1600, 1577, 1529, 1513, 1469, 1442, 1413, 1331, 1279, 1252, 1226, 1125, 1036, 1020, 864, 810, 762, 676, 658, 627. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 nm (16400), 289 (19400), 314 (21200), 398 (4000). – (CH_3CN): λ_{max} (qual.) = 242 nm, 287, 311, 395. – $C_{19}H_{14}CrO_5$: calcd. C 60.96, H 3.77; found C 61.09, H 3.80.

Tricarbonyl{η^6-[(N-methylpyrrol-2-ylethynyl)benzene]}chromium(0) (**3g**): According to the *GP* the reaction was carried out with 0.157 g (1.50 mmol) of 2-N-methylpyrrylacetylene (**2g**). Subsequent chromatography on basic alumina activity B II–III (ether/pentane, 1:8) afforded 230 mg (72%) of pure **3g** (R_f = 0.38, silica gel, ether/pentane 1:2) as yellow needles, m.p. 104–106 °C (ether/pentane). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.71 (s, 3 H), 5.25 (m, 1 H), 5.37 (m, 2 H), 5.50 (m, 2 H), 6.11 (m, 1 H), 6.50 (m, 1 H), 6.69 (m, 1 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 34.67 (CH_3), 81.91 ($C_{quat.}$), 89.08 ($C_{quat.}$), 90.31 (CH), 91.30 ($C_{quat.}$), 91.82 (CH), 94.38 (CH), 108.39 (CH), 114.19 ($C_{quat.}$), 116.22 (CH), 124.69 (CH), 232.27 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 317 (M^+, 15), 261 (M^+ – 2 CO, 12), 233 (M^+ – 3 CO, 67), 181 [M^+ – $Cr(CO)_3$, 10], 80 [$Cr(CO)^+$, 12], 52 (Cr^+, 100). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2207 cm^{-1}, 1966, 1891, 1576, 1473, 1421, 1323, 1256, 1052, 756, 724, 691, 670, 654, 627, 602. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 232 nm (16500), 250 (14700), 312 (18700), 322 (20300), 397 (3830). – (CH_3CN): λ_{max} (ε) = 232 nm (16500), 250 (14700), 312 (18700), 322 (20300), 397 (3830). – (CH_3CN): λ_{max} (qual.) = 252 nm, 321, 391. – $C_{16}H_{11}CrNO_3$: calcd.C 60.57, H 3.49, N 4.41; found C 60.36, H 3.49, N 4.40.

Tricarbonyl{η^6-[(4-methoxyphenylethynyl)benzene]}chromium(0) (**3h**): According to the *GP* the reaction was carried out with 0.145 g (1.10 mmol) of 4-methoxyphenylacetylene (**2h**). Subsequent chromatography on basic alumina activity B II–III (ether/pentane, 1:4) afforded 217 mg (63%) of pure **3h** (R_f = 0.37, silica gel, ether/pentane 1:2) as lightyellow needles, m.p. 128–130 °C (ether/pentane). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.74 (s, 3 H), 5.16 (m, 1 H), 5.28 (m, 2 H), 5.42 (m, 2 H), 6.79 (m, *J* = 8.0 Hz, 2 H), 7.37 (m, *J* = 8.0 Hz, 2 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 55.30 (CH_3), 83.88 ($C_{quat.}$), 89.96 ($C_{quat.}$), 90.36 (CH), 91.54 ($C_{quat.}$), 91.85 (CH), 94.62 (CH), 113.70 ($C_{quat.}$), 114.05 (CH), 133.45 (CH), 160.20 ($C_{quat.}$), 232.20 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 344 (M^+, 19), 288 (M^+ – 2 CO, 16), 260 (M^+ – 3 CO, 86), 208 [M^+ – $Cr(CO)_3$, 7], 80 [$Cr(CO)^+$, 6], 52 (Cr^+, 100). – IR (CH_2Cl_2): $\tilde{\nu}$ = 2223 cm^{-1}, 1967, 1884, 1877, 1604, 1530, 1508, 1288, 1250, 1174, 1137, 1026, 830, 673, 656, 629, 618. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 255 nm (16700), 289 (23700), 306 (18600), 323 (12300), 394 (3500). – (CH_3CN): λ_{max} (qual.) = 254 nm, 287, 322, 390. – $C_{18}H_{12}CrO_4$: calcd. C 62.79, H 3.51; found C 61.91, H 3.42.

Tricarbonyl{η^6-[(ferrocenylethynyl)benzene]}chromium(0) (**3i**): According to the *GP* the reaction was carried out with 0.315 g (1.50 mmol) of ethynylferrocene (**2i**). Subsequent chromatography on basic alumina activity B II–III (ether/pentane, 1:4) afforded 370 mg (88%) of pure **3i** (R_f = 0.48, silica gel, ether/pentane 1:2) as orange platelets, m.p. > 168 °C (dec.) (trichloromethane/pentane). – ^1H NMR ($CDCl_3$, 300 MHz): δ = 4.18 (m, 7 H), 4.42 (m, 2 H), 5.13 (m, 1 H), 5.29 (m, 2 H), 5.40 (m, 2 H). – ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 63.28 ($C_{quat.}$), 69.29 (CH), 70.19 (CH), 71.75 (CH), 81.54 ($C_{quat.}$), 89.85 ($C_{quat.}$), 89.95 (CH), 92.05 (CH), 92.45 ($C_{quat.}$), 94.31 (CH), 232.40 ($C_{quat.}$, CO). – MS (EI), *m/z* (%): 422 (M^+, 26), 338 (M^+ – 3 CO, 77), 282 [M^+ – $Cr(CO)_3$, 100], 217 (M^+ – 3 CO – FeCp, 5), 165 [M^+ – $Cr(CO)_3$ – FeCp, 13], 121 ($FeCp^+$, 15), 117 ($CrCp^*$, 12), 80 [$Cr(CO)^+$, 28], 54 (Fe^+, 24, 52 (Cr^+, 82). – IR (CH_2Cl_29: $\tilde{\nu}$ = 2223, 2211 cm^{-1}, 1959, 1880, 1868, 1533, 1441, 1410, 1162, 1104, 1001, 833, 810, 671, 656, 629, 622. – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 252 nm (19700), 296 (13300), 327 (10900), 395 (3810). – (CH_3CN): λ_{max} (qual.) = 294 nm, 325, 387. – $C_{21}H_{14}CrFeO_3$: calcd. C 59.74, H 3.34; found C 60.02, H 3.45.

Tricarbonyl{η^6-[(4-dimethylaminophenylethynyl)benzene]}chromium(0) (**3j**): According to the *GP* the reaction was carried out with 0.217 g (1.50 mmol) of 4-*N*,*N*-dimethylaminophenylacetylene (**2j**). Subsequent chromatography on basic alumina activity B II–III (ether/pentane, 1:2) afforded 280 mg (78%) of pure **3j** (R_f =

0.34, silica gel, ether/pentane 1:2) as yellow platelets, m.p. 158−161 °C (ether/pentane). − ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 2.82 (s, 6H), 5.03 (m, 1H), 5.18 (m, 2H), 5.32 (m, 2H), 6.46 (m, J = 8.0 Hz, 2H), 7.20 (m, J = 8.0 Hz, 2H). − ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 40.09 (CH$_3$), 83.22 (C$_{quat.}$), 89.99 (CH), 91.68 (C$_{quat.}$), 92.03 (CH), 92.97 (C$_{quat.}$), 94.46 (CH), 108.21 (C$_{quat.}$), 111.69 (CH), 133.14 (CH), 150.62 (C$_{quat.}$), 232.53 (C$_{quat.}$, CO). − MS (EI), *m/z* (%): 357 (M$^+$, 19), 301 (M$^+$ − 2 CO, 15), 273 (M$^+$ − 3 CO, 100), 221 [M$^+$ − Cr(CO)$_3$, 30], 80 [Cr(CO)$^+$, 9], 52 (Cr$^+$, 82). − IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 2205 cm^{-1}, 1965, 1892, 1609, 1593, 1521, 1441, 1361, 1226, 1199, 1136, 817, 755, 690. − UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 288 (15100), 338 (33200), 378 (12800), 405 (6000). − (CH$_3$CN): λ_{max} (qual.) = 288 nm, 336, 377, 400. − C$_{19}$H$_{15}$CrNO$_3$: calcd. C 63.86, H 4.23, N 3.92; found C 64.12, H 4.27, N 4.02.

☆ Dedicated to Prof. Dr. *Rudolf Gompper* on the occasion of his 70th birthday.

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