



Synthesis, structure, electronic properties and thermal behavior of butadiynyl substituted phenylCr(CO)₃-complexes

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Abstract

Butadiynyl-substituted η^6 -benzeneCr(CO)₃ complexes **3** are very efficiently prepared by a copper catalyzed coupling of the phenylacetylene complex **1** and bromo alkynes **2**. The transmission of electronic effects through the butadiynyl bridge operates by resonance mechanisms as established by correlations between Hammett's σ_p , σ_R and σ_{P+} parameters. Most interestingly, however, is an unusual thermal behavior that leads to intractable paramagnetic polymers of unknown structure. According to thermal analyses (thermal gravimetric analysis, differential scanning calorimetry) the complexes **3** react in a thermal solid-state reaction under CO extrusion to give amorphous cross-linked polymers.

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1. Introduction

Carbon rich organic and organometallic compounds are suitable precursors and building blocks for novel carbon allotropes that are theoretically and from a materials science point of view highly interesting, yet, their syntheses remain an ongoing challenge [1]. In particular, the steady flow of ground breaking contributions in the chemistry of polyalkynylated η^4 -cyclobutadienyl and η^5 -cyclopentadienyl complexes by Bunz [2] has opened new pathways to novel topologies of carbon allotropes supported by transition metal fragments. Furthermore, these systems also showed remarkable materials properties such as liquid crystalline behavior [3]. Over the past years, we have investigated the chemistry of η^6 -arene chromiumtricarbonyl complexes bearing unsaturated side chains with respect to their syntheses, reactivity and photonic properties [4]. Most interestingly, in alkynylated and alkenylated chromium-

carbonyl arene complexes the organometallic auxochrome, i.e. the chromiumtricarbonyl phenyl fragment, behaves in an electronically amphoteric manner [4d]. In agreement with the electrochemical behavior [5,6] and depending on the electronic nature of the auxochrome at the other terminus the chromium complex fragment either acts as a donor or as an acceptor. Since butadiynes, the higher homologues of alkynes, can be polymerized thermally or photochemically in a topochemical solid-state reaction to give 1,4-disubstituted polydiacetylenes [7], butadiynes bearing chromiumcarbonyl fragments additionally appear to be suitable monomer precursors for polydiacetylenes with redox-switchable side chains [8]. Furthermore, the carbon monoxide ligands of chromium complexes can be exchanged photo- [9] and electrochemically [10] by suitable σ -donor ligands or labile donor solvent molecules that can easily be liberated and lead to cluster forming reactions [11]. Therefore, the triple bonds in butadiynyl substituted complexes could as well act as coordinating ligands [12]. Here, we wish to report the synthesis, structure and electronic properties and the thermal behavior of the butadiynyl substituted η^6 -phenyl chromiumtricarbonyl complexes.

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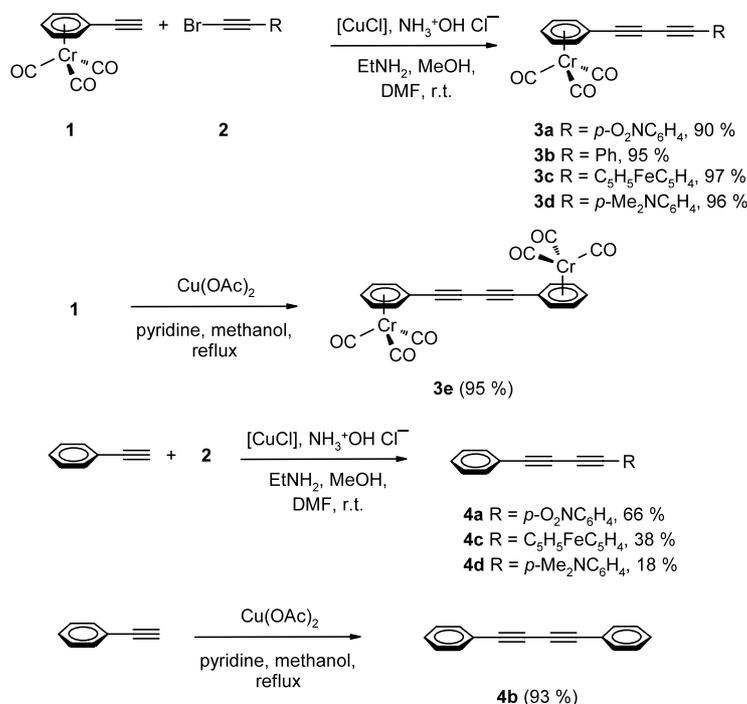
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2. Results and discussion

Retrosynthetically, the Cadiot–Chodkiewicz coupling [13] of ethynylated chromium complexes and bromo alkynes represents the logical and most flexible strategy to butadiynyl substituted complexes. Based upon our efficient route to alkynyl substituted (arene)Cr(CO)₃-complexes [4h,14] and starting from the chromiumtricarbonyl complexed phenyl acetylene (**1**) the Cadiot–Chodkiewicz coupling with bromo acetylenes **2** gives rise to the formation of butadiynylated complexes **3** in excellent yields as yellow orange to red crystalline solids (Scheme 1). Likewise and for comparison the free ligands **4** were synthesized analogously with phenyl acetylene as coupling partner. The copper-mediated Eglinton coupling of **1** or phenyl acetylene furnishes the doubly η⁶-complexed 1,4-diphenyl butadiyne **3e** [4h] and the free ligand 1,4-diphenyl butadiyne (**4b**) almost quantitatively as orange (**3e**) and colorless crystals (**4b**), respectively.

The structure of the complexes **3** is unambiguously supported by spectroscopic and combustion analytical data. In the ¹H-NMR spectra of the complexes **3** the signals of complexed arene protons can easily be identified by their upfield shift to the region between δ 5.5 and 6.0. In most cases these protons are reasonably well resolved and can be assigned by the characteristic splitting pattern (triplet, doublet of doublets, and doublet). The uncomplexed arene and ferrocenyl protons give rise to the expected sets of signals and

multiplicities. In the ¹³C-NMR spectra the most characteristic signals are the carbonyl resonances (Table 1) that appear in a small window between δ 232.8 and 233.3 in accord with the electronic nature of the remote substituent at C_δ. The correlation analysis (Table 2) of the carbonyl shifts with various Hammett parameters reveals excellent correlations for σ_p, σ_R and σ_{p+}, and a pretty poor correlation for σ_I (Table 2). This can be reasonably well interpreted as a dominant contribution of resonance mechanisms for the transmission of electronic effects through the butadiynyl bridge, i.e. by the stabilization of positive charge density. The carbon resonances of the complexed phenyl rings of **3** are assigned by CH correlation spectroscopy and they are considerably shifted to higher field as compared to those of the free ligands **4** and appear in the region between δ 86.5 and 98.5. Interestingly, as already found for the carbonyl resonances, good correlations can be established between σ_p or σ_{p+}, resp., and δ(C_{ipso}), δ(C_{para}), and the Δ_π values. As also reflected by the positive Δ_π values (Δ_π = δ_{para} – δ_{meta}) [15] the overall electronic effect of the butadiynyl fragment is moderately electron withdrawing in its nature. However, more difficult is the unambiguous assignment of the resonances of the four alkyne carbon atoms C_α to C_δ. A thorough comparison of the complexing chemical shifts (CCS) of the C_α and C_β signals, both in direct proximity to the complexed phenyl rings, reveals that they are shifted upfield by Δδ 3.0–3.4 and 0.5–0.8, respectively. This upfield shift can be rationalized by the electronic back-donation exerted



Scheme 1. Synthesis of butadiynyl substituted chromiumcarbonyl arene complexes **3** and their free ligands **4** by Cadiot–Chodkiewicz and Eglinton coupling.

Table 1

Selected ^{13}C -NMR data (recorded in the experimental $\text{Me}_2\text{SO}-d_6$, 75 MHz, 25 °C) of the complexes **3** and the free ligands **4**, complexing chemical shifts ($\text{CCS} = \delta_{\text{complex}} - \delta_{\text{ligand}}$), $\Delta\pi$ values ($\Delta\pi = \delta_{\text{para}} - \delta_{\text{meta}}$), and Hammett–Taft parameters of the corresponding substituents

| | CO | C_{para} | C_{meta} | C_{ortho} | C_{ipso} | $\Delta\pi$ | C_α | C_β | C_γ | C_δ | σ_{p} | σ_{I} | σ_{R} | σ_{P^+} |
|-----------|-------|-------------------|-------------------|--------------------|-------------------|-------------|------------|-----------|------------|------------|---------------------|---------------------|---------------------|-----------------------|
| 3a | 232.8 | 95.3 | 93.3 | 98.5 | 86.5 | 2.0 | 81.0 | 80.2 | 77.1 | 72.1 | 0.78 | 0.63 | 0.15 | 0.79 |
| 4a | – | 130.7 | 129.2 | 132.8 | 120.0 | 1.5 | 84.4 | 77.9 | 79.9 | 73.1 | | | | |
| CCS | – | –35.4 | –35.9 | –34.3 | –33.5 | –3.4 | –3.4 | –0.8 | –2.8 | –1.0 | | | | |
| 3b | 233.0 | 95.0 | 93.5 | 98.3 | 87.7 | 1.5 | 78.6 | 73.0 | 72.8 | 82.6 | –0.01 | 0.10 | –0.11 | –0.18 |
| 4b | – | 130.2 | 129.1 | 132.6 | 120.6 | 1.1 | 82.0 | 73.7 | 73.7 | 82.0 | | | | |
| CCS | – | –35.2 | –35.6 | –34.3 | –32.9 | –3.4 | –3.4 | –0.7 | –0.9 | 0.6 | | | | |
| 3c | 233.1 | 94.7 | 93.7 | 98.0 | 88.8 | 1.0 | 75.6 | 74.0 | 70.2 | 84.0 | –0.30 | 0.12 | –0.42 | –1.00 |
| 4c | – | 129.6 | 128.9 | 132.2 | 121.0 | 0.7 | 79.0 | 74.6 | 72.0 | 83.0 | | | | |
| CCS | – | –34.9 | –35.2 | –34.2 | –32.2 | –3.4 | –3.4 | –0.6 | –1.8 | 1.0 | | | | |
| 3d | 233.3 | 94.6 | 93.8 | 98.0 | 89.2 | 0.8 | 77.8 | 71.6 | 74.2 | 85.1 | –0.83 | 0.10 | –0.93 | –1.70 |
| 4d | – | 129.7 | 129.0 | 132.3 | 121.3 | 0.7 | 81.2 | 72.1 | 74.7 | 84.3 | | | | |
| CCS | – | –35.1 | –35.2 | –34.3 | –32.1 | –3.4 | –3.4 | –0.5 | –0.5 | 0.8 | | | | |
| 3e | 232.8 | 95.2 | 93.3 | 98.4 | 86.7 | 1.9 | 79.0 | 72.1 | 72.1 | 79.0 | – | – | – | – |
| 4b | – | 130.2 | 129.1 | 132.6 | 120.6 | 1.1 | 82.0 | 73.7 | 73.7 | 82.0 | | | | |
| CCS | – | –35.1 | –35.2 | –34.3 | –32.1 | –3.0 | –3.0 | –1.6 | –1.6 | –3.0 | | | | |

Table 2

Correlation coefficients r^2 of selected linear regression analyses between Hammett–Taft parameters and selected ^{13}C -NMR resonances of the complexes **3** (see Table 1)

| | $\delta(\text{CO})$ | C_{ipso} | C_{para} | C_δ | $\Delta\pi$ |
|-----------------------|---------------------|-------------------|-------------------|---------------|---------------|
| σ_{p} | $r^2 = 0.987$ | $r^2 = 0.952$ | $r^2 = 0.946$ | $r^2 = 0.873$ | $r^2 = 0.952$ |
| σ_{I} | $r^2 = 0.647$ | $r^2 = 0.717$ | $r^2 = 0.701$ | $r^2 = 0.967$ | $r^2 = 0.692$ |
| σ_{R} | $r^2 = 0.969$ | $r^2 = 0.873$ | $r^2 = 0.875$ | $r^2 = 0.635$ | $r^2 = 0.890$ |
| σ_{P^+} | $r^2 = 0.980$ | $r^2 = 0.981$ | $r^2 = 0.980$ | $r^2 = 0.814$ | $r^2 = 0.986$ |

by the proximal chromium carbonyl tripod. Furthermore, the remote substituent effect is almost parallel for complexed and free ligand systems. In contrast, the corresponding CCS of the C_γ and C_δ resonances more directly experience the electronic influence of the adjacent substituents at C_δ by mechanisms operating predominantly through inductive effects.

Besides solution NMR, solid-state NMR spectroscopy is nowadays a powerful method to investigate polycrystalline and amorphous materials. For example, recently both bis(benzene)chromium [16] and (arene)tricarbonylchromium [17] and materials derived thereof have been thoroughly investigated by ^{13}C and ^2H solid-state NMR spectroscopy. The solid-state ^{13}C -NMR spectrum of **3e**, recorded with optimized cross polarization (CP) [18] with 10 kHz rotational speed is displayed in Fig. 1. The rotational sidebands were distinguished from the isotropic lines by changing the spinning frequency to 4 kHz. The chemical shifts of the carbon

resonances in the solid-state correspond to the $\delta(^{13}\text{C})$ in solution very well, with maximal deviations of less than $\Delta\delta$ 0.5. Interestingly, the signals of the acetylene carbons at δ 71.8 and 78.5 (solution: δ 72.1 and 79.0) have very small halfwidths (79 and 59 Hz), as well as the quaternary carbon resonance at δ 87.1 (70 Hz) (solution: 86.7). In contrast to this, the non-quaternary carbon resonances of the phenyl moieties display a broad signal at about δ 96. This could be perhaps the result of some sort of disorder in the solid state. Alternatively, the effect could be due to an interference of the proton decoupling frequency with the frequency of a dynamic, out-of-plane wagging type process of the phenyl rings. This assumption is corroborated by the result that simple high-power decoupling gives the same appearance of the spectrum as the CP measurement. In the case of chromocenes this line-broadening effect of proton decoupling on non-quaternary carbon signals has been investigated and described before [19]. Unfortunately, with the obtained signal-to-noise ratio, the carbonyl resonances, which can also be expected to have low intensity because of their large chemical shift anisotropy [20] could not be assigned unequivocally. However, in addition to the expected ^{13}C resonances, there is one more isotropic line at δ 174.4 with a small halfwidth of 147 Hz. We tentatively assign the signal to free CO or CO attached to the solid by weak interactions, which might be liberated from **3e** by the slightly higher temperature in the rotor due to friction effects while spinning [19], or due to the mechanical stress. The

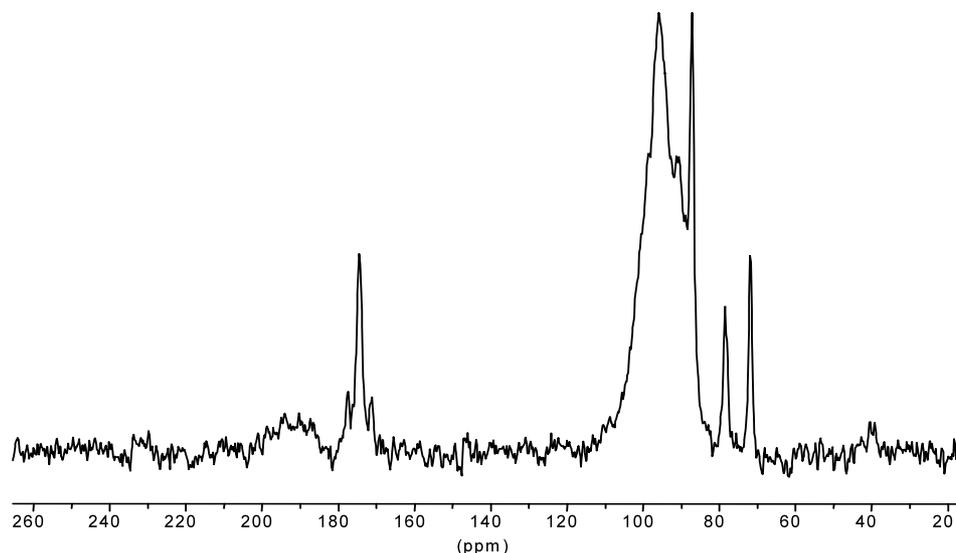


Fig. 1. 100.6 MHz ^{13}C CP/MAS-NMR spectrum of **3e**, recorded with a spinning speed of 10 kHz. The low-intensity peaks at δ 190, 177 and 171 are rotational sidebands. For further details of the measurement see text and experimental section.

^{13}C chemical shift of this CO resonance is not too far off from the value for solid CO with about δ 181 [20], and the narrow line indicates a high mobility of the species [21]. Furthermore, the thermal behavior of **3e** corroborates the assumption that traces of CO are liberated from the sample during the measurement.

According to the X-ray structure analysis of the symmetrical homometallic binuclear complex **3e** the chromiumtricarbyl tripods are almost perfectly arranged *anti* parallel to each other (Fig. 2). The $\text{Cr}(\text{CO})_3$ fragments adopt *syn*-eclipsed conformations and the intramolecular distance of the chromium atoms is 1011 pm. In the unit cell the molecules of **3e** (Fig. 3) display two different structural features. Along the *b*-axis the molecules are arranged *anti* parallel with respect to the chromium fragments, whereas they are oriented parallel along the *a*-axis. Thus, the intermolecular distance between adjacent molecules aligned on the *b*-axis is 360 pm, which lies within the margins required for topochemical polymerizations [7]. Most interestingly, the intermolecular chromium distances to the next

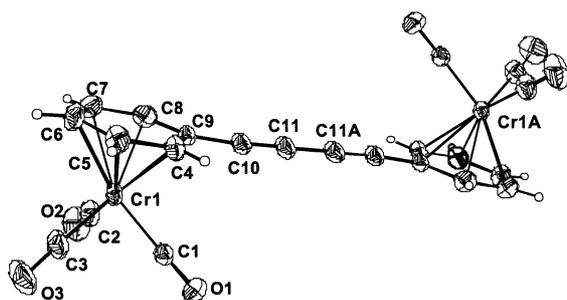


Fig. 2. ORTEP plot of **3e**. Selected bond lengths [pm]: Cr(1)–C(centroid) 172, C(4)–C(9) 142.1(7), C(8)–C(9) 137.5(8), C(9)–C(10) 143.1(6), C(10)–C(11) 118.1(7), C(11)–C(11A) 138.5(10), Cr(1)–Cr(1A) 1011(0).

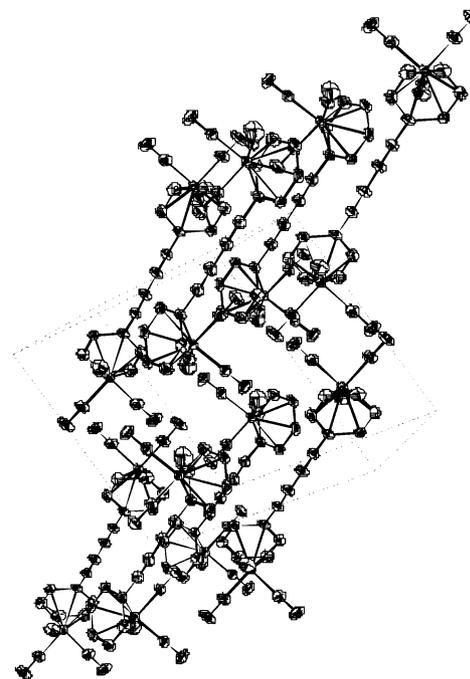


Fig. 3. Unit cell of **3e** (hydrogen atoms were omitted for clarity).

neighboring molecules range between 581 and 834 pm and places the chromiumcarbonyl tripods in a favorable proximity for cluster forming intermolecular solid-state reactions.

The electronic spectra of the butadiynyl substituted complexes **3** were recorded in dimethylsulfoxide. Most characteristically, the longest wavelength absorptions (Table 3) have small extinction coefficients and are assigned [22,23] to the metal-to-ligand charge transfer (MLCT) bands, whereas close-by higher energy absorptions have higher extinction coefficients and can be

Table 3

IL (intra ligand $\pi-\pi^*$) and MLCT (metal-to-ligand charge transfer) UV–vis transitions (recorded in DMSO at 20 °C) of the complexes **3** and selected linear regression analyses (correlation coefficients r^2) with Hammett–Taft parameters

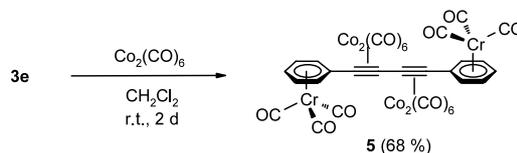
| | IL (cm ⁻¹) (nm) | MLCT (cm ⁻¹) (nm) | | IL | MLCT |
|-----------|-----------------------------|-------------------------------|-----------------------|---------------|---------------|
| 3a | 31 300 (320) | 23 000 (434) | σ_{P} | $r^2 = 0.591$ | $r^2 = 0.880$ |
| 3b | 31 300 (320) | 24 100 (415) | σ_{I} | $r^2 = 0.147$ | $r^2 = 0.959$ |
| 3c | 31 100 (322) | 24 300 (411) | σ_{R} | $r^2 = 0.805$ | $r^2 = 0.649$ |
| 3d | 28 800 (347) | 24 400 (410) | σ_{P^+} | $r^2 = 0.599$ | $r^2 = 0.829$ |
| 3e | 30 300 (330) | 23 300 (430) | Δ_{π} | $r^2 = 0.490$ | $r^2 = 0.859$ |

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 [22]. The strong absorption bands in the region between 320 and 347 nm presumably arise from $\pi-\pi^*$ as well as from ligand-to-metal (LM) and ILCT transitions. Surprisingly, there is only a good correlation between σ_{I} and the MLCT energies, presumably, due to a dominance of the electronic field effect transmitted through the σ -framework of the complexes.

It is very difficult to obtain reliable electrochemical data for the oxidation of **3** by cyclic voltammetry. Only for the ferrocenyl compound **3c** distinct oxidations can be detected in the anodic region up to 1.4 V. At $E_{\text{p}}^{\text{Ox}} = 740$ mV (shoulder) and 1180 mV two oxidation events are found together with the corresponding reduction waves at $E_{\text{p}}^{\text{Red}} = 880$ and 350 mV (both are shoulders). Although, it is difficult to extract any thermodynamic and more detailed electrochemical parameters it is very likely that the first oxidation occurs at the ferrocene center (ferrocene: $E_0^{0/+} = 450$ mV) [24], yet, considerably shifted anodically as a consequence of coinciding electron-withdrawing nature of the phenyl chromiumtricarbonyl and the butadiynyl fragment. Also, the second oxidation event is considerably shifted to more positive potentials compared to (benzene)Cr(CO)₃ ($E_0^{0/+} = 830$ mV) [24] as a consequence of the electron-withdrawing nature of the ferrocenium-type substituent. A similar electrochemical behavior has been observed for a heterobimetallic ethenylbridged (η^6 -phenyl)Cr(CO)₃-ferrocenyl dyad [25].

Furthermore, the butadiynyl substituted (η^6 -aryl) chromiumcarbonyl complexes **3** are highly unsaturated ligands for further complexation. Therefore, the doubly η^6 -complexed 1,4-diphenyl butadiyne **3e** was reacted with dicobaltoctacarbonyl to give the hexanuclear fully metallated butadiyne complex **5** in 68% yield as black micro crystals (Scheme 2).

The structure of **5** was unambiguously supported by spectroscopic and combustion analytical data, in particular, by the characteristic appearance of a single set of signals in the NMR spectra as a consequence of the highly symmetric solution structure. The ¹H-NMR spectrum of the hexanuclear complex **5** is not very well



Scheme 2. Synthesis of the fully metallated butadiyne complex **5**.

resolved and shows the expected shifts for the complexed arene protons as broad signals between δ 5.6 and 6.0. However, in the ¹³C-NMR spectrum the characteristic signals for the complexed phenyl carbon nuclei can be readily assigned by their relative intensity and their appearance in the DEPT spectra.

With the exception of the *ortho*-phenyl nuclei, presumably, as a consequence of the congested steric bulk of the adjacent dicobalthexacarbonyl cluster substituent, all other complexed phenyl and alkynyl carbon resonances are affected by the cobaltcarbonyl complexation of the butadiynyl substituent and appear shifted downfield (Table 4). Most characteristically, two resonances of the quaternary carbonyl nuclei can be detected at δ 197.9 for the 12 chemically and magnetically equivalent cobalt-bound carbonyl ligands and at δ 232.9 (**3e**: δ 232.8) for the two free rotating chromiumcarbonyl tripods.

Expectedly, the IR spectrum is dominated by the appearance of the strong CO stretching vibrations of the dicobalthexacarbonyl fragments at 2089, 2065, 2044, 2030 and 2010 cm⁻¹, and of the chromiumtricarbonyl moieties at 1964 and 1897 cm⁻¹. Although, the dominant absorption in the UV–vis spectrum of **5** stems from the $\pi-\pi^*$ transition within the hydrocarbon ligand the dark color of this compound can be easily explained by the long tail of the absorption band onto the NIR with significant shoulders at 410 and 560 nm, that arise from chromium to ligand and cobalt to ligand CT transitions, respectively.

Finally, we were interested in the thermal solid-state reactivity of butadiynyl substituted complexes **3** with their inherent dichotomy to react either as a diyne in the sense of a topochemical solid-state polymerization to poly(diacetylenes) or as coordinating σ -donor ligands in

Table 4

^{13}C -NMR data (recorded in $\text{Me}_2\text{SO}-d_6$, 75 MHz, 25 °C) of the hexanuclear (**5**) and the dinuclear complex (**3e**), and complexing chemical shifts ($\text{CCS} = \delta_{\text{complex}} - \delta_{\text{ligand}}$)

| | CrCO | CoCO | C_{para} | C_{meta} | C_{ortho} | C_{ipso} | C_{α} | C_{β} |
|-----------|-------|-------|--------------------------|--------------------------|---------------------------|--------------------------|---------------------|--------------------|
| 5 | 232.9 | 197.9 | 98.0 | 98.9 | 90.1 | 110.7 | 96.4 | 91.8 |
| 3e | 232.8 | | 95.2 | 93.3 | 98.4 | 86.7 | 79.0 | 72.1 |
| CCS | 0.1 | | 2.8 | 5.6 | -8.3 | 24.0 | 17.4 | 19.7 |

the sense of cross-linking polycluster formation initiated by a dissociation of carbon monoxide ligands.

The results of the thermal analyses of the complexes **3b**, **3c** and **3e** with differential scanning calorimetry (DSC; Figs. 4–6) and thermal gravimetric analysis (TGA) under an atmosphere of nitrogen reveal an interesting thermal behavior (Table 5). In all cases reactions with a strong exothermic heat flow take place at 165, 175 and 185 °C, respectively. For the phenyl substituted complex **3b** this peculiar reaction clearly occurs in the melt (**3b**: m.p. 131 °C) whereas the bimetallic compounds **3c** and **3e** undergo the thermolysis in the solid state. According to the weight loss in the TGA measurements this exothermic process can be interpreted as an extrusion of one molecule of carbon monoxide per formula unit for **3b** and **3c** with a concomitant cluster formation, whereas compound **3e** presumably loses four equivalents of carbon monoxide at a peak maximum of 180 °C and a further equivalent is expelled at 206 °C.

This weight loss of the butadiynyl complexes **3** upon thermolysis is a behavior that significantly deviates from ordinary butadiyne derivatives, which are known to polymerize in a topochemical reaction if the solid-state requirements are fulfilled [7].

In analogy to thermal analyses on chromiumcarbonyl complexed poly(phenylene ethynyls), where the

weight loss in the TGA was assigned to a cross-linking of the polymer chains after CO extrusion [12b], a similar behavior can be assumed for the complexes **3b** and **3c**, and thus, a cross-linking polymerization of **3b** and **3c** could furnish polymeric clusters with the proposed structures **6** and **7** (Fig. 7).

The comparison of the IR spectra of **3e** and its solid, black thermolysis product **8** (as obtained from a DSC experiment) clearly shows that the thermal reaction leads to a loss of the chromium complexed carbonyl ligands (Fig. 8). Simultaneously, a moderated and an intense unstructured absorption band at 1408 and 570 cm^{-1} , respectively, can be detected in the spectrum of **6**. In particular, the broad vibration band at 570 cm^{-1} can be tentatively assigned to bonds between unsaturated carbon centers and chromium atoms. On the other hand the two absorptions at 756 and 698 cm^{-1} can be assigned unequivocally to the presence of uncomplexed phenyl rings. Thus, from the vibration spectrum of **8** a cluster-like structure can be deduced. However, as the comparison of the powder diffraction spectra of **3e** and **8** clearly shows (Fig. 9), the black powder of **8** is highly amorphous and, it is yet not possible to propose a conclusive structure for the thermolysis product **8**.

Thus, the thermolyses of **3c** and **3e** were performed on a preparative scale at 200 °C (**3c**) and 215 °C (**3e**), respectively, to furnish in both cases black amorphous

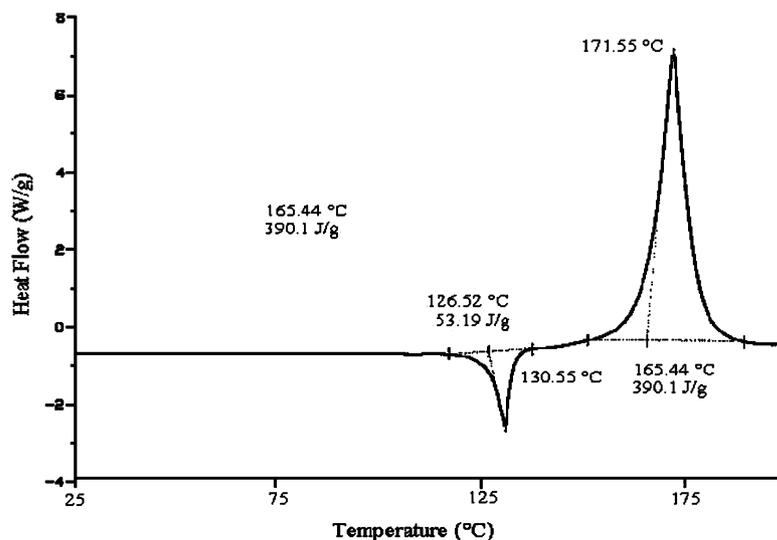


Fig. 4. DSC traces of complex **3b** (heating rate: 10 K min^{-1} under nitrogen).

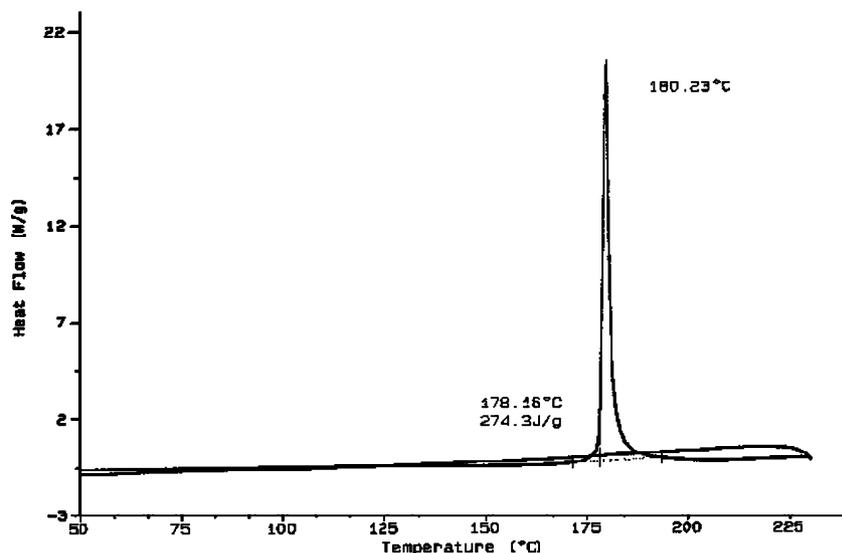


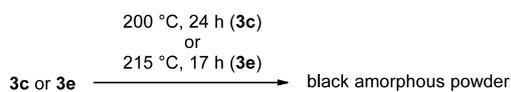
Fig. 5. DSC traces of complex **3c** (heating rate: 10 K min⁻¹ under nitrogen).

powders that were insoluble in common organic solvents (e.g. THF, toluene, dichloromethane, chloroform, acetone, DMSO, methanol) and water (Scheme 3).

In both cases, according to IR spectra of the reaction products (Fig. 10) residual traces of chromiumtricarbonyl complexes are enclosed as detected by the characteristic *A*₁ and *E* carbonyl vibration bands at 1969 and 1895 (**3c**) and 1971 and 1901 cm⁻¹ (**3e**), respectively. Presumably, in contrast to analytical measurements (DSC, TGA) longer reaction times are necessary for a complete conversion of bulk material. Yet, the combus-

tion analyses clearly indicate that a considerable amount of the hydrocarbon ligand is present in the novel amorphous material.

These results are corroborated by the ¹³C solid-state NMR investigation of **8**. No signal can be obtained with CP [18] or other high-power decoupling sequences. According to our experience [19] this is an indication that the proton relaxation is too fast for efficient magnetization transfer. So, there must be paramagnetic species present in the sample. Single pulse sequences with high-power decoupling also did not give a signal even after 6000 transients. This could either be due to an interference of the proton decoupling frequency with some motional process (see above) [19], or, more probable, simply be the result of too low intensity of a very broad signal. Indeed, applying 100 000 scans of a single-pulse sequence without proton decoupling and



Scheme 3. Preparative thermolysis of **3c** and **3e**.

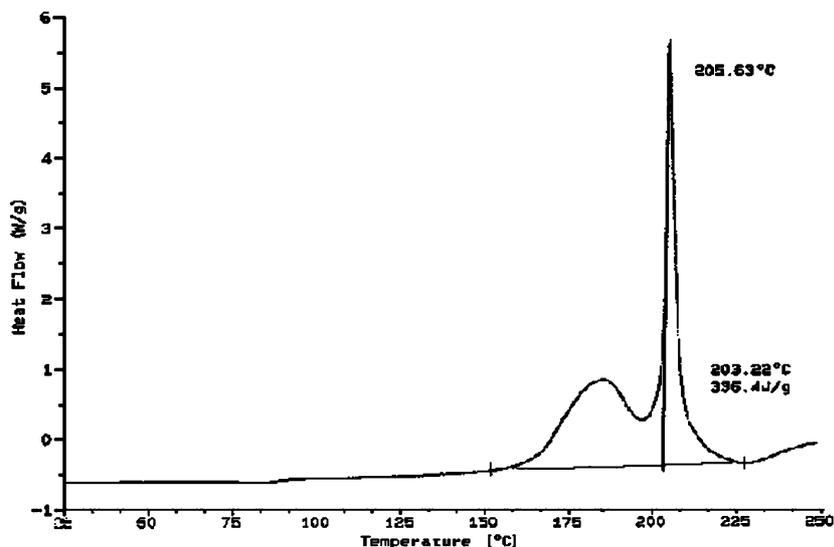
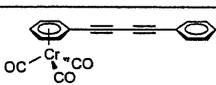
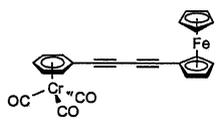
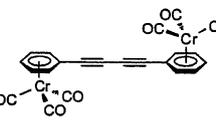


Fig. 6. DSC traces of complex **3e** (heating rate: 10 K min⁻¹ under nitrogen).

Table 5

DSC parameters ($T_{\text{transition}}$, heat flow: negative: exothermic; positive: endothermic) and TGA of the complexes **3b**, **3c** and **3e**

| | $T_{\text{transition}}$ | Heat flow [Jg ⁻¹] ([kJmol ⁻¹)] | Weight loss | Fragments lost |
|--|-------------------------|---|----------------|-------------------|
|  3b | 131 °C | +53.2 (+18.0) | | |
| | 172 °C | -390.1 (-131.9) | 8.3 % | -CO |
|  3c | 180 °C | -274.3 (-122.4) | 6.5 % | -CO |
| | | | | |
|  3e | 190 °C | -335.4 (-159.6) | 24 % | -4 CO |
| | 206 °C | | 6 % | -CO |

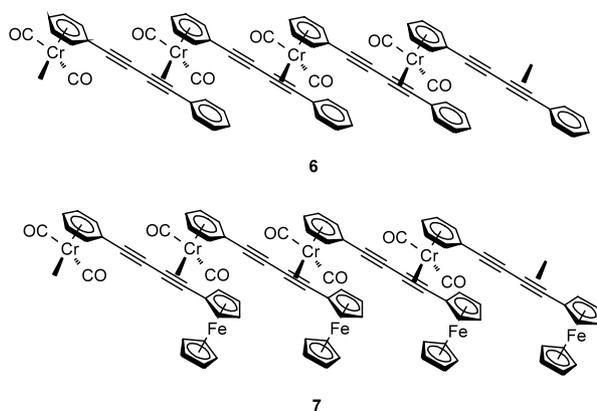


Fig. 7. Proposed structures of the thermolysis products **6** (from **3b**) and **7** (from **3c**).

with a short pulse delay of 200 ms gives a very broad symmetrical signal with a halfwidth of about 3 kHz at δ 129. Due to the presence of a large range of rotational sidebands spanning from about δ -200 to 600, one can exclude the assumption that it might be a background signal from the probehead. Furthermore, the signal from the KelF rotor cap would be of a different shape and of low intensity under the applied measurement conditions. Therefore, we assume that the signal stems from uncomplexed phenyl carbons, which also corroborates the IR results. The fast relaxation of the carbon nuclei again indicates that there must be paramagnetic centers in close proximity. However, no resonances outside the diamagnetic region could be detected, which rules out the possibility of paramagnetic benzenechromium-type species [19]. This finding is also corroborated by the fact that the chemical shift of the resonance at δ 129 does not change with the spinning speed and thus the sample temperature, as it is usually observed for

paramagnetic compounds [19]. Analogous results have been obtained with ¹H MAS measurements, done also with a short relaxation delay of 200 ms. No paramagnetic ¹H-NMR signals are visible in the spectrum, but the fast proton relaxation together with a chemical shift of the resonance of about $\Delta\delta$ 6, which does not change with the spinning speed and thus with the temperature, again indicates uncomplexed phenyl groups close to paramagnetic centers.

3. Conclusion

Chromiumtricarbonyl complexed phenyl acetylene and 1-bromo alkynes can be very efficiently coupled by applying the copper-catalyzed Cadiot–Chodkiewicz reaction to furnish butadiynyl substituted tricarbonyl- η^6 -benzene-chromium(0) complexes **3** in excellent yields. In these complexes the substituent effects at the remote end of the butadiynyl side chain are efficiently transmitted through the bridge even to chromiumcarbonyl tripod by resonance mechanisms as established by excellent correlations between Hammett's σ_p , σ_R and σ_{p+} parameters and selected ¹³C-NMR shifts. Interestingly, the transmission of substituent effects for the electronic excitation of the MLCT bands occurs through the σ -framework of the molecules as shown by the correlation with σ_I parameters. Therefore, butadiynyl substituted complexes are highly interesting new chromophores and electrophores, that additionally can act as cluster forming ligands upon reaction with unsaturated complex fragments. Most interesting, however, is their unusual thermal behavior that leads to intractable paramagnetic polymers of unknown structure. Future studies will address the structure elucidation and the magnetic and electric properties of these novel solids that can be obtained from well-defined molecular complexes.

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 [26]. Column chromatography: silica gel 60 (Merck, Darmstadt), mesh 70–230. TLC: silica gel plates (60 F₂₅₄ Merck, Darmstadt). Melting points (uncorrected values): Reichert-Jung Thermovar and Büchi Melting Point B-540. The η^6 -phenylacetylene complex **1** was prepared by a previously published procedure [4h]. The bromo alkynes **2a** [27] and **2b** [28] were prepared according to literature methods and the bromo alkynes **2c** and **2d** were synthesized by lithiation (^{*n*}BuLi) and subsequent reaction with NBS in THF at

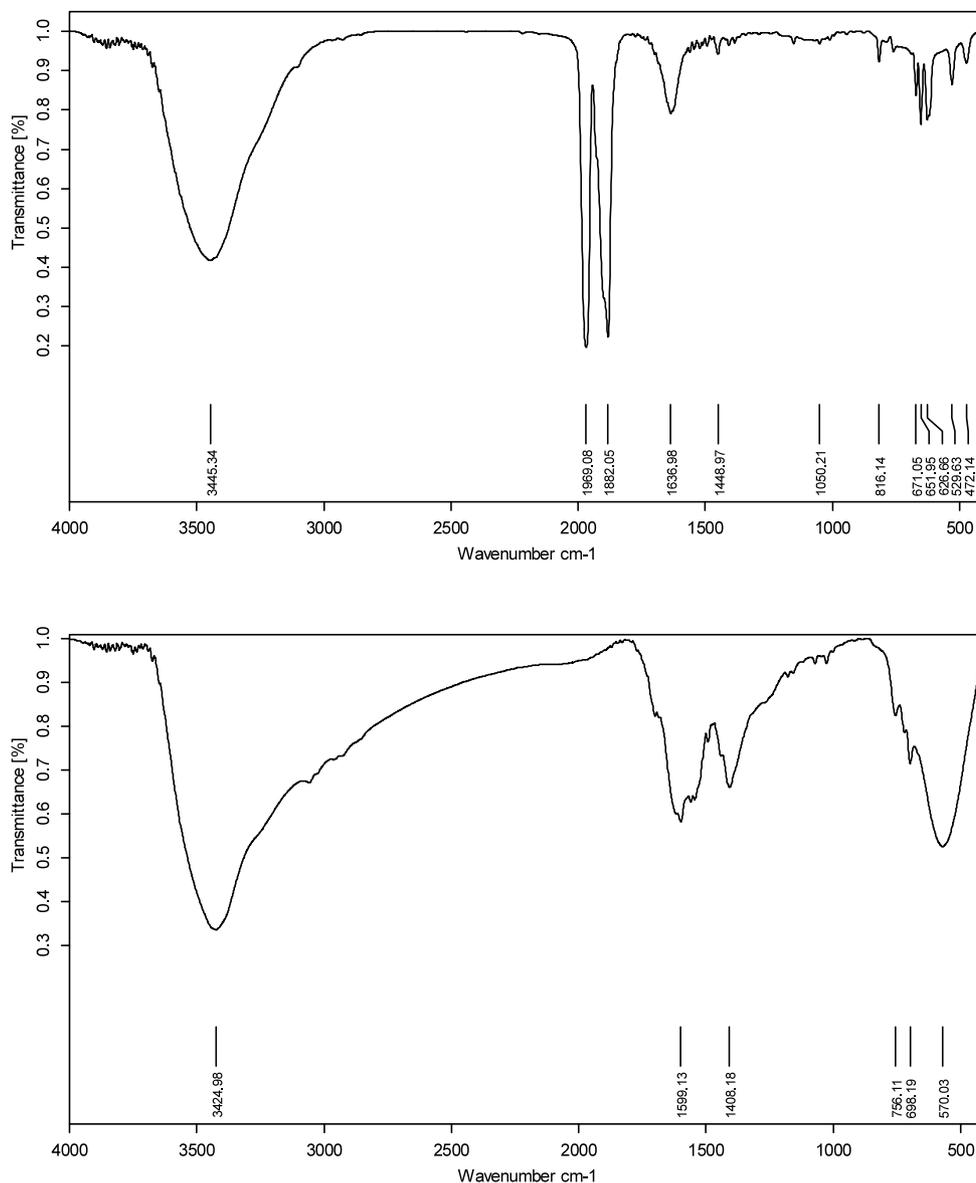


Fig. 8. IR spectra (recorded in KBr, 20 °C) of complex **3e** (top) and its thermolysis product **8** (bottom).

–78 °C of the corresponding terminal alkynes. Copper(I) chloride, hydroxylamine hydrochloride, and ethylamine were purchased from Merck and used without further purification. The ^1H - and ^{13}C -NMR spectra of liquids were measured with the instruments Bruker ARX 300 and Varian VXR 400S. If not stated otherwise, $\text{Me}_2\text{SO}-d_6$ was used as the solvent. The assignments of quaternary C, CH, CH_2 and CH_3 has been made by using DEPT spectra.

The solid-state NMR spectra were recorded on a fully digital Bruker Avance 400 NMR spectrometer equipped with a 4 mm MAS probehead. The recycle delay was 6 s for CP [18] and high-power decoupling pulse programs, and 200 ms for single-pulse sequences without proton decoupling. For CP a contact time of 5 ms was applied, and the spectra were referenced by setting the high-field

signal of the external standard adamantane to δ 29.47 [29]. Adamantane was also used to optimize the pulse powers for the Hartmann–Hahn condition. The polycrystalline **3e** and amorphous **8** were thoroughly grinded and densely packed into 4 mm ZrO_2 rotors equipped with Kelf caps. The rotational sidebands were distinguished from the isotropic lines by changing the spinning speeds (4–10 kHz). Further details of the measurements are given in the text.

IR: Perkin Elmer Models Lambda 16. MS: Finnigan MAT 90 and MAT 95 Q. Differential Scanning Calorimeter: DuPont 912 DS-DSC, LNCA-II probe. Thermal balances: Perkin Elmer TGA-2, heating rate: 10 K min^{-1} under nitrogen. Elemental analyses were carried out in the Microanalytical Laboratories of the Institut für Organische Chemie, Technische Hochschule

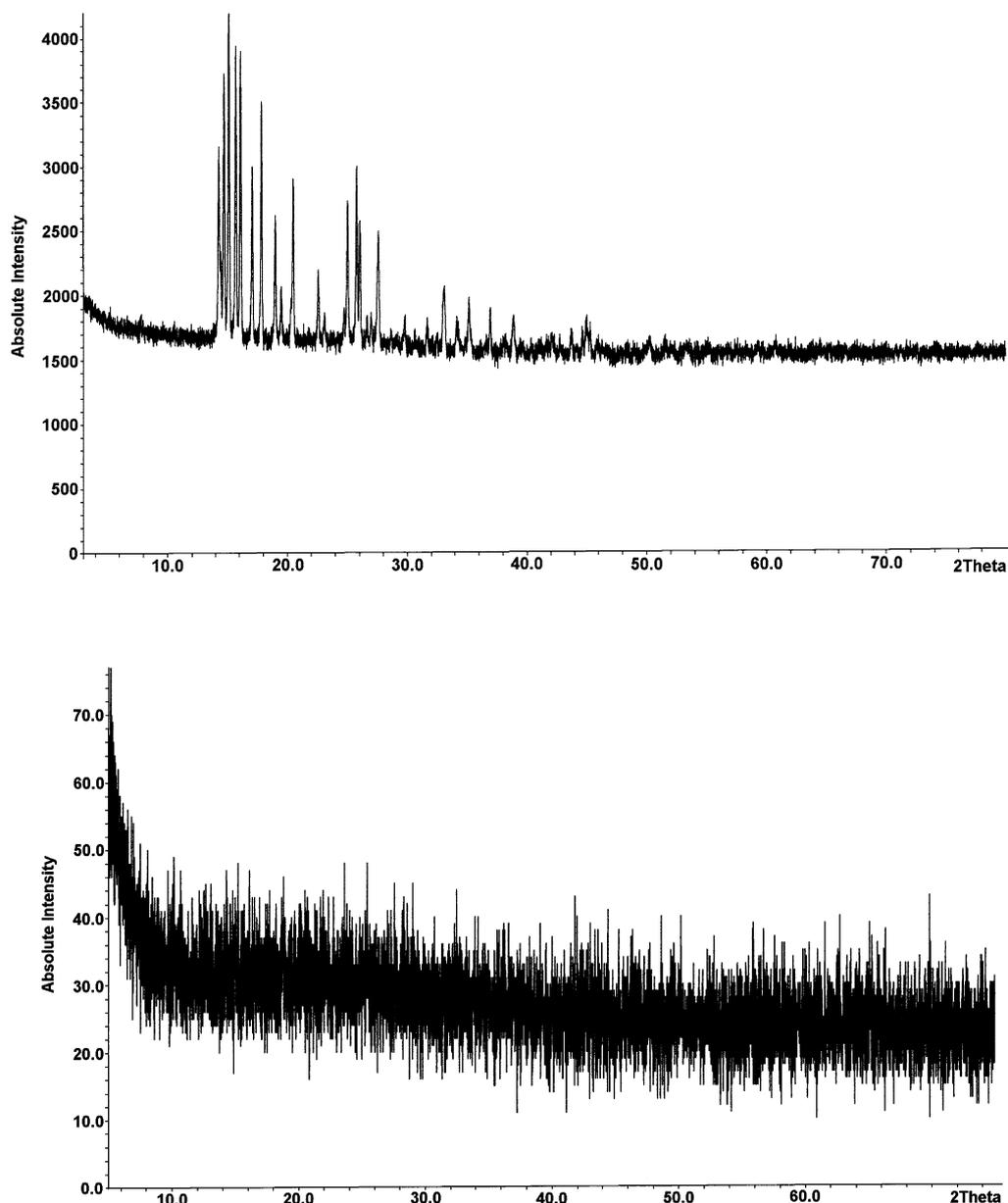


Fig. 9. Powder diffraction spectra ($\lambda(\text{Cu}-K\alpha) = 1.54060 \text{ \AA}$, Debye–Scherrer scanning mode) of complex **3e** (top) and its thermolysis product **8** (bottom).

Darmstadt, and the Department Chemie, Ludwig-Maximilians-Universität München.

X-ray structure determination of compound **3e**: $\text{C}_{22}\text{H}_{10}\text{Cr}_2\text{O}_6$, $M = 474.32$, monoclinic, space group $P2_1/c$, $a = 1118.2(4)$, $b = 719.8(4)$, $c = 1251.4(2)$ pm, $\alpha = 90$, $\beta = 101.09(2)$, $\gamma = 90^\circ$, $V = 0.9884(7) \text{ nm}^3$, $Z = 2$, $\lambda(\text{Mo}-K\alpha) = 0.71093 \text{ \AA}$, $\mu = 1.11 \text{ mm}^{-1}$, $D_x = 1.594 \text{ mg m}^{-3}$, $F(000) = 476$, $T = 297(2) \text{ K}$. An orange platelet with the dimensions $0.65 \times 0.175 \times 0.025 \text{ mm}$ was mounted on a capillary and transferred to an Enraf-Nonius CAD4 diffractometer. A total of 1670 intensities ($-6 \leq h \leq 2$, $0 \leq k \leq 14$, $-20 \leq l \leq 20$; $\omega/2\theta$ scan, 1361 unique, $R_{\text{int}} = 0.0643$) were measured in a θ range from

1.86 to 22.98° . 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 0.1341, with conventional $R(F)$ [$I > 2\sigma(I)$] of 0.0582 for 156 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC 100553, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +1223-336-033, e-mail: teched@chemcrs.cam.ac.uk).

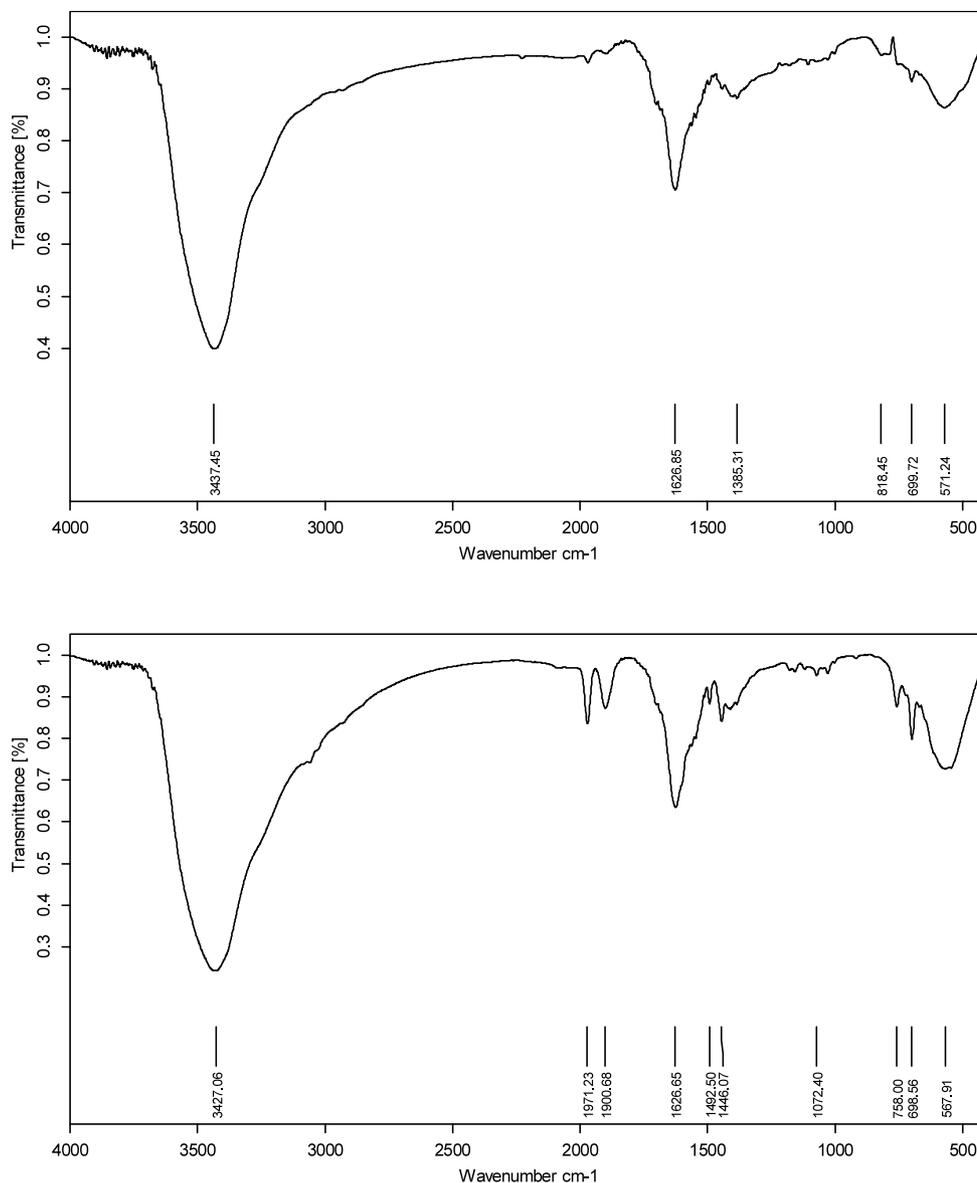


Fig. 10. IR spectra (recorded in KBr, 20 °C) of the amorphous polymers from **3c** (top) and from **3e** (bottom).

*General procedure (GP) for the Cadiot–Chodkiewicz coupling of tricarbonyl(η^6 -ethynylbenzene)chromium(0) (**1**) or phenyl acetylene with bromo alkynes **2**:* one equivalent of **1** or one equivalent of phenyl acetylene and 5 mg (0.1 equivalents) of hydroxylamine hydrochloride were suspended in 20 ml of degassed methanol. To this mixture a solution of 4 mg (0.05 equivalents) of copper(I) chloride in 3 ml of ethylamine (70% in water) was added under nitrogen at room temperature (r.t.). To this mixture a solution of one equivalent of the corresponding bromo alkyne **2** dissolved in 2 ml of *N,N*-dimethylformamide was added dropwise over a period of 2 min. Then the reaction mixture was stirred at r.t. under nitrogen overnight. To this suspension was then added 20 ml of diethylether and 15 ml of water.

The aqueous layer was extracted twice with portions of 20 ml of diethylether. The combined organic phases were washed twice with 20 ml of brine and then dried with magnesium sulfate. The solvents were evaporated in vacuo to give the crystalline butadiynes **3** (TLC). Further purification was achieved by recrystallization.

4.1. Tricarbonyl(η^6 -[(4-nitrophenylbutadiynyl)-benzene])chromium(0) (**3a**)

According to the GP the reaction was carried out with 0.150 g (0.63 mmol) of **1** and 0.142 g (0.60 mmol) of 1-(4-nitrophenyl)-2-bromo acetylene [27] (**2a**) to give 0.204 g (90%) of pure **3a** as orange red crystals, m.p. 140 °C (dec.) (diethylether/pentane). —¹H-NMR (Me₂SO-*d*₆, 300 MHz): δ 5.77 (dd, J = 6.1 Hz, 2H), 5.86 (t, J = 6.0

Hz, 1H), 6.14 (d, $J = 6.1$ Hz, 2H), 7.92 (d, $J = 8.3$ Hz, 2H), 8.28 (d, $J = 8.3$ Hz, 2H). $^{13}\text{C-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 75 MHz): δ 72.1 ($\text{C}_{\text{quat.}}$), 77.1 ($\text{C}_{\text{quat.}}$), 80.2 ($\text{C}_{\text{quat.}}$), 81.0 ($\text{C}_{\text{quat.}}$), 86.5 ($\text{C}_{\text{quat.}}$), 93.3 (CH), 95.3 (CH), 98.5 (CH), 124.2 (CH), 126.9 ($\text{C}_{\text{quat.}}$), 134.2 (CH), 147.9 ($\text{C}_{\text{quat.}}$), 232.8 ($\text{C}_{\text{quat.}}$, CO). EIMS (70 eV), m/z (%): 383 [M^+ , 8], 327 [$\text{M}^+ - 2\text{CO}$, 5], 299 [$\text{M}^+ - 3\text{CO}$, 13], 247 [$\text{M}^+ - \text{Cr}(\text{CO})_3$, 60], 200 [$\text{M}^+ - \text{Cr}(\text{CO})_3 - \text{HNO}_2$, 29], 52 (Cr^+ , 100). IR (KBr): $\tilde{\nu}$ 2214 cm^{-1} , 1976, 1898, 1592, 1522, 1343, 852, 748, 667, 649, 614, 531. UV-vis (Me_2SO): λ_{max} (ϵ) 320 nm (27 700), 434 (6700). $\text{C}_{19}\text{H}_9\text{CrNO}_5$ (383.3) Calc. C 59.54, H 2.37, N 3.65; Found: C 59.08, H 2.47, N 4.09%.

4.2. Tricarbonyl(η^6 -[(phenylbutadiynyl)benzene])chromium(0) (**3b**)

According to the GP the reaction was carried out with 0.150 g (0.63 mmol) of **1** and 0.114 g (0.63 mmol) of bromo phenylacetylene [**28**] (**2b**) to give 0.203 g (95%) of pure **3b** as yellow platelets, m.p. 125–126 °C (dichloromethane/pentane). $^1\text{H-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 300 MHz): δ 5.78 (m, 3H), 6.10 (d, $J = 6.1$ Hz, 2H), 7.48 (m, 3H), 7.64 (d, $J = 6.9$ Hz, 2H). $^{13}\text{C-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 75 MHz): δ 72.8 ($\text{C}_{\text{quat.}}$), 73.0 ($\text{C}_{\text{quat.}}$), 78.6 ($\text{C}_{\text{quat.}}$), 82.6 ($\text{C}_{\text{quat.}}$), 87.7 ($\text{C}_{\text{quat.}}$), 93.5 (CH), 95.0 (CH), 98.3 (CH), 120.0 ($\text{C}_{\text{quat.}}$), 129.2 (CH), 130.6 (CH), 132.8 (CH), 233.0 ($\text{C}_{\text{quat.}}$, CO). EIMS (70 eV), m/z (%): 338 [M^+ , 25], 282 [$\text{M}^+ - 2\text{CO}$, 32], 254 [$\text{M}^+ - 3\text{CO}$, 100], 202 [$\text{M}^+ - \text{Cr}(\text{CO})_3$, 34], 80 ($\text{Cr}(\text{CO})^+$, 9), 52 (Cr^+ , 21). IR (KBr): $\tilde{\nu}$ 2216 cm^{-1} , 1977, 1914, 1891, 1455, 1442, 813, 755, 687, 670, 652, 618. UV-vis (Me_2SO): λ_{max} (ϵ) 280 nm (16 700), 299 (19 000), 320 (19 100), 415 (5300). $\text{C}_{19}\text{H}_{10}\text{CrO}_3$ (338.3) Calc. C 67.46, H 2.98; Found: C 67.47, H 2.85%.

4.3. Tricarbonyl(η^6 -[(ferrocenylbutadiynyl)benzene])chromium(0) (**3c**)

According to the GP the reaction was carried out with 0.150 g (0.63 mmol) of **1** and 0.182 g (0.63 mmol) of 1-ferrocenyl-2-bromo acetylene (**2c**) to give 0.272 g (97%) of pure **3c** as orange platelets, m.p. 171 °C (dec.) (dichloromethane/pentane). $^1\text{H-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 300 MHz): δ 4.28 (s, 5H), 4.41 (m, 2H), 4.66 (m, 2H), 5.75 (m, 3H), 6.03 (m, 2H). $^{13}\text{C-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 75 MHz): δ 61.2 ($\text{C}_{\text{quat.}}$), 70.2 ($\text{C}_{\text{quat.}}$), 70.3 (CH), 72.3 (CH), 72.5 (CH), 74.0 ($\text{C}_{\text{quat.}}$), 75.6 ($\text{C}_{\text{quat.}}$), 84.0 ($\text{C}_{\text{quat.}}$), 88.8 ($\text{C}_{\text{quat.}}$), 93.7 (CH), 94.7 (CH), 98.0 (CH), 233.1 ($\text{C}_{\text{quat.}}$, CO). EIMS (70 eV), m/z (%): 446 [M^+ , 25], 362 [$\text{M}^+ - 3$, 100], 310 [$\text{M}^+ - \text{Cr}(\text{CO})_3$, 16], 306 [$\text{M}^+ - 3\text{CO} - \text{Fe}$, 5], 189 [$\text{M}^+ - \text{Cr}(\text{CO})_3 - \text{FeCp}$, 6], 121 (FeCp^+ , 13), 52 (Cr^+ , 69). IR (KBr): $\tilde{\nu}$ 2220 cm^{-1} , 1963, 1880, 1106, 1001, 823, 671, 654, 619, 532. UV-vis (Me_2SO): λ_{max} (ϵ) 305 nm (15 200sh), 322 (16 900), 411

(6800). $\text{C}_{23}\text{H}_{14}\text{CrFeO}_3$ (446.2) Calc. C 61.91, H 3.16; Found: C 61.50, H 3.02%.

4.4. Tricarbonyl(η^6 -[(4-*N,N*-dimethylaminophenyl)butadiynyl]benzene)chromium(0) (**3d**)

According to the GP the reaction was carried out with 0.150 g (0.63 mmol) of **1** and 0.146 g (0.65 mmol) of 1-(4-*N,N*-dimethylaminophenyl)-2-bromo acetylene (**2d**) to give 0.238 g (96%) of pure **3d** as yellow platelets, m.p. 160 °C (dec.) (diethylether/pentane). $^1\text{H-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 300 MHz): δ 2.99 (s, 6H), 5.77 (m, 3H), 6.04 (m, 2H), 6.72 (m, 2H), 7.44 (m, 2H). $^{13}\text{C-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 75 MHz): δ 39.7 (CH_3), 71.6 ($\text{C}_{\text{quat.}}$), 74.2 ($\text{C}_{\text{quat.}}$), 77.8 ($\text{C}_{\text{quat.}}$), 85.1 ($\text{C}_{\text{quat.}}$), 89.2 ($\text{C}_{\text{quat.}}$), 93.8 (CH), 94.6 (CH), 98.0 (CH), 105.1 ($\text{C}_{\text{quat.}}$), 112.0 (CH), 134.1 (CH), 151.2 ($\text{C}_{\text{quat.}}$), 233.3 ($\text{C}_{\text{quat.}}$, CO). EIMS (70 eV), m/z (%): 381 [M^+ , 21], 325 [$\text{M}^+ - 2\text{CO}$, 17], 297 [$\text{M}^+ - 3\text{CO}$, 100], 245 [$\text{M}^+ - \text{Cr}(\text{CO})_3$, 19], 80 ($\text{Cr}(\text{CO})^+$, 5), 52 (Cr^+ , 21). IR (KBr): $\tilde{\nu}$ 2205 cm^{-1} , 1963, 1896, 1878, 1602, 1518, 1447, 1367, 1182, 1151, 813, 671, 654, 627, 614, 533. UV-vis (Me_2SO): λ_{max} (ϵ) 278 nm (12 600), 333 (28 800sh), 347 (33 400), 410 (13 600sh). $\text{C}_{21}\text{H}_{15}\text{CrNO}_3$ (381.3) Calc. C 66.14, H 3.96, N 3.67; Found: C 66.01, H 4.28, N 3.54%.

4.5. 4-Nitrophenylbutadiynylbenzene (**4a**)

According to the GP the reaction was carried out with 0.102 g (1.00 mmol) of phenyl acetylene and 0.225 g (1.00 mmol) of 1-(4-nitrophenyl)-2-bromo acetylene (**2a**) to give 0.164 g (66%) of pure **4a** as yellow crystals, m.p. 209 °C (dec.) (diethylether/pentane). $^1\text{H-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 300 MHz): δ 7.48 (m, 3H), 7.64 (m, 1H), 7.89 (m, 2H), 8.26 (m, 2H). $^{13}\text{C-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 75 MHz): δ 73.1 ($\text{C}_{\text{quat.}}$), 77.9 ($\text{C}_{\text{quat.}}$), 79.9 ($\text{C}_{\text{quat.}}$), 84.4 ($\text{C}_{\text{quat.}}$), 120.0 ($\text{C}_{\text{quat.}}$), 124.1 (CH), 127.4 ($\text{C}_{\text{quat.}}$), 129.2 (CH), 130.7 (CH), 132.8 (CH), 133.9 (CH), 147.7 ($\text{C}_{\text{quat.}}$). UV-vis (Me_2SO): λ_{max} (ϵ) 282 nm (14 300), 303 (14 300sh), 338 (23 500).

4.6. Ferrocenylbutadiynylbenzene (**4c**)

According to the GP the reaction was carried out with 0.102 g (1.00 mmol) of phenyl acetylene and 0.289 g (1.00 mmol) of 1-ferrocenyl-2-bromo acetylene (**2c**) to give 0.124 g (38%) of pure **4c** as orange crystals, m.p. 112 °C (dec.) (diethylether/pentane). $^1\text{H-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 300 MHz): δ 4.29 (s, 5H), 4.39 (dd, $J = 1.8, 1.75$ Hz, 2H), 4.65 (dd, $J = 1.8, 1.75$ Hz, 2H), 7.43 (m, 3H), 7.56 (m, 2H). $^{13}\text{C-NMR}$ ($\text{Me}_2\text{SO}-d_6$, 75 MHz): δ 61.8 ($\text{C}_{\text{quat.}}$), 69.9 (CH), 70.1 (CH), 72.0 ($\text{C}_{\text{quat.}}$), 72.1 (CH), 74.6 ($\text{C}_{\text{quat.}}$), 79.0 ($\text{C}_{\text{quat.}}$), 83.0 ($\text{C}_{\text{quat.}}$), 121.0 ($\text{C}_{\text{quat.}}$), 128.9 (CH), 129.6 (CH), 132.2 (CH). UV-vis (Me_2SO): λ_{max} (qual.) 266sh nm, 277, 296, 311, 330sh, 358sh, 451.

4.7. 4-*N,N*-Dimethylaminophenylbutadiynylbenzene (**4d**)

According to the GP the reaction was carried out with 0.102 g (1.00 mmol) of phenyl acetylene and 0.225 g (1.00 mmol) of 1-(4-*N,N*-dimethylaminophenyl)-2-bromo acetylene (**2d**) to give 0.044 g (18%) of pure **4d** as pale yellow crystals, m.p. 113 °C (diethylether/pentane). —¹H-NMR (Me₂SO-*d*₆, 300 MHz): δ 2.95 (s, 6H), 6.69 (d, *J* = 9.0 Hz, 2H), 7.41 (br, 5H), 7.55 (m, 2H). ¹³C-NMR (Me₂SO-*d*₆, 75 MHz): δ 40.2 (CH₃), 72.1 (C_{quat.}), 74.7 (C_{quat.}), 81.2 (C_{quat.}), 84.3 (C_{quat.}), 105.9 (C_{quat.}), 112.0 (CH), 121.3 (CH), 129.0 (CH), 129.7 (CH), 132.3 (CH), 133.8 (CH), 151.0 (C_{quat.}). UV-vis (Me₂SO): λ_{max} (ε) 284 nm (11 400), 305 (13 300sh), 334 (35 000), 370 (30 200).

4.8. μ- $\{\eta^6\text{:}\eta^6\text{:}\eta^4\text{:}\eta^4\text{-}[1,4\text{-Butadiynediylbis}(\text{benzene})]\}$ bis[tricarbonylchromium(0)] (**3e**)

To a solution of 0.147 g (0.62 mmol) of **1** in 10 ml of methanol was added dropwise a solution of 0.247 g (1.24 mmol) of copper(II) acetate monohydrate in 10 ml of methanol and 10 ml of pyridine. Then the reaction mixture was heated to reflux temperature for 15 min. After cooling to r.t. 50 ml of 2 N aqueous HCl was added and extracted with diethylether (3 × 30 ml). The combined organic phases were washed twice with portions of 30 ml of water and then dried with magnesium sulfate. The solvents were removed in vacuo and the residue was recrystallized from trichloromethane to give 0.140 g (95%) of pure **3e** as orange platelets, m.p. 180 °C (dec.). —¹H-NMR (Me₂SO-*d*₆, 300 MHz): δ 5.73 (dd, *J* = 6.2, 6.3 Hz, 4H), 5.81 (dd, *J* = 6.0, 6.1 Hz, 2H), 6.10 (d, *J* = 6.1 Hz, 4H). ¹³C-NMR (Me₂SO-*d*₆, 75 MHz): δ 72.1 (C_{quat.}), 79.0 (C_{quat.}), 86.7 (C_{quat.}), 93.3 (CH), 95.2 (CH), 98.4 (CH), 232.8 (C_{quat.}, CO). EIMS (70 eV), *m/z* (%): 474 [M⁺, 5], 390 [M⁺ - 3CO, 7], 338 [M⁺ - Cr(CO)₃, 8], 306 [M⁺ - 6 CO, 25], 282 [M⁺ - Cr(CO)₅, 11], 277 (10), 254 [M⁺ - Cr(CO)₆, 47], 202 [M⁺ - 2 Cr(CO)₃, 11], 52 (Cr⁺, 100). IR (KBr): ν̄ 1950 cm⁻¹, 1867, 1438, 812, 667, 646. UV-vis (Me₂SO): λ_{max} (ε) 288 nm (15 100), 313 (17 100sh), 325 (18 700sh), 330 (18 900), 430 (8700). C₂₂H₁₀Cr₂O₆ (474.3) Calc. C 55.71, H 2.13; Found: C 55.55, H 2.09%.

4.9. 1,4-Diphenylbutadiyne (**4b**)

To a solution of 0.408 g (4.00 mmol) of phenyl acetylene in 10 ml of methanol was added dropwise a solution of 1.20 g (6.00 mmol) of copper(II) acetate monohydrate in 10 ml of methanol and 10 ml of pyridine. Then the reaction mixture was heated to reflux temperature for 15 min. After cooling to r.t. 50 ml of 2 N aqueous HCl was added and extracted with diethylether (3 × 30 ml). The combined organic phases were

washed twice with portions of 30 ml of water and then dried with magnesium sulfate. The solvents were removed in vacuo and the residue was recrystallized from pentane/diethylether to give 0.376 g (93%) of pure **4b** as colorless needles, m.p. 87 °C (diethylether/pentane). —¹H-NMR (Me₂SO-*d*₆, 300 MHz): δ 7.45 (m, 6H), 7.59 (m, 4H). ¹³C-NMR (Me₂SO-*d*₆, 75 MHz): δ 73.7 (C_{quat.}), 82.0 (C_{quat.}), 120.6 (C_{quat.}), 129.1 (CH), 130.2 (CH), 132.6 (CH). UV-vis (Me₂SO): λ_{max} (ε) 274 nm (14 900), 291 (22 500), 310 (33 600), 320 (13 500sh), 331 (30 600).

4.10. μ- $\{\eta^6\text{:}\eta^6\text{:}\eta^4\text{:}\eta^4\text{-}[1,4\text{-Butadiynediylbis}(\text{benzene})]\}$ bis[tricarbonylchromium(0)]-bis[hexacarbonyldicobalt(0)] (**5**)

To a degassed solution of 0.100 g (0.21 mmol) of **3e** in 20 ml of dichloromethane was added a solution of 0.180 g (0.53 mmol) of dicobaltoctacarbonyl in 5 ml of dichloromethane. Then the reaction mixture was stirred at room temperature for 2 d. The solvent was removed in vacuo and the residue was chromatographed on silica gel (pentane to diethylether/pentane 1:1) to give 0.150 g (68%) of pure **5** as black platelets, m.p. > 280 °C (dec.). —¹H-NMR (Me₂SO-*d*₆, 300 MHz): δ 5.6 (br, 4H), 5.8 (br, 2H), 6.0 (br, 4H). ¹³C-NMR (Me₂SO-*d*₆, 75 MHz): δ 90.1 (CH), 91.8 (C_{quat.}), 96.4 (C_{quat.}), 98.0 (CH), 98.9 (CH), 110.7 (C_{quat.}), 197.9 (C_{quat.}, CoCO), 232.9 (C_{quat.}, CrCO). FDMS (70 eV), *m/z* (%): 1046 [M⁺, 22], 990 [M⁺ - 2CO, 18], 910 [M⁺ - Cr(CO)₃, 25], 854 [M⁺ - Cr(CO)₅, 11], 760 [M⁺ - Co₂(CO)₆, 6], 642 (Co₄Cr₂(CO)₁₅, 25), 624 (Co₂Cr(CO)₉, 7), 80 (CrCO⁺, 100). IR (KBr): ν̄ 2089 cm⁻¹, 2065, 2044, 2030, 2010, 1964, 1897, 1150, 660, 645, 618, 594, 563, 5114, 491. UV-vis (Me₂SO): λ_{max} (ε) 324 nm (29 200), 410 (6900sh), 560 (2300sh). C₃₄H₁₀Co₄Cr₂O₁₈ (1046.2) Calc. C 39.03, H 0.96; Found: C 38.50, H 0.99%.

4.11. Thermolysis of compound **3c**

In a 10 ml Schlenk flask 89 mg (0.20 mmol) of **3c** were heated under argon at 200 °C (oil bath) for 24 h to give 65 mg of a black amorphous powder.

Combustion analysis: C 53.02, H 3.36 (**3c**: C 61.97, H 3.36).

4.12. Thermolysis of compound **3e**

In a 10 ml Schlenk flask 112 mg (0.24 mmol) of **3e** were heated under argon to 210–215 °C (oil bath) for 17 h to give 79 mg of a black amorphous powder.

Combustion analysis: C 50.52, H 3.51 (**3e**: C 55.71, H 2.13).

Acknowledgements

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References

- [1] For reviews, see e.g. (a) F. Diederich, *Chem. Comm.* (2001) 219; (b) U.H.F. Bunz, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 1073; (c) F. Diederich, *Nature* 369 (1994) 199; (d) F. Diederich, Y. Rubin, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1101.
- [2] For recent reviews, see e.g. (a) U.H.F. Bunz, *NATO ASI Ser., Ser. C* 499 (1997) 473; (b) Bunz, U.H.F. *Top. Curr. Chem.* 201 (Carbon Rich Compounds II) (1999) 131; (c) U.H.F. Bunz, Y. Rubin, Y. Tobe, *Chem. Soc. Rev.* 28 (1999) 107; (d) U.H.F. Bunz, *Angew. Chem., Int. Ed. Engl.* 33 (1994) 1073.
- [3] M. Altmann, U.H.F. Bunz, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 569.
- [4] See e.g. (a) T.J.J. Müller, *Eur. J. Org. Chem.* (2001) 2021; (b) A. Netz, K. Polborn, T.J.J. Müller, *J. Am. Chem. Soc.* 123 (2001) 3441; (c) A. Netz, T.J.J. Müller, *Tetrahedron* 56 (2000) 4149; (d) T.J.J. Müller, A. Netz, M. Ansorge, E. Schmälzlin, C. Bräuchle, K. Meerholz, *Organometallics* 18 (1999) 5066; (e) T.J.J. Müller, M. Ansorge, K. Polborn, *J. Organomet. Chem.* 578 (1999) 252; (f) T.J.J. Müller, M. Ansorge, *Tetrahedron* 54 (1998) 1457; (g) T.J.J. Müller, *Tetrahedron Lett.* 38 (1997) 1025; (h) T.J.J. Müller, H.J. Lindner, *Chem. Ber.* 129 (1996) 607.
- [5] For a comprehensive study of the oxidation potentials of arene Cr(CO)₃ complexes, see e.g. A.D. Hunter, V. Mozol, S.D. Tsai, *Organometallics* 11 (1992) 2251.
- [6] For reduction potentials of arene Cr(CO)₃ complexes, see e.g. (a) S.N. Milligan, R.D. Rieke, *Organometallics* 2 (1983) 171; (b) R.D. Rieke, S.N. Milligan, L.D. Schulte, *Organometallics* 6 (1987) 699; (c) L.D. Schulte, R.D. Rieke, *J. Org. Chem.* 52 (1987) 4829.
- [7] (a) G. Wegner, *Pure Appl. Chem.* 49 (1977) 443; (b) D. Bloor, in: G. Allen, J.C. Bevington (Eds.), *Comprehensive Polymer Science*, vol. 5, Pergamon Press, Oxford, New York, Beijing, Frankfurt, São Paulo, Sydney, Tokyo, Toronto, 1990, p. 233.
- [8] For representative butadiynyl bridged transition metal fragments, see e.g. (a) M. Brady, W. Weng, Y. Zhou, J. W. Seyler, A.J. Amoroso, A.M. Arif, M. Böhme, G. Frenking, J.A. Gladysz, J. Am. Chem. Soc. 119 (1997) 775; (b) J.-G. Rodriguez, A. Oñate, R.M. Martin-Villamil, I. Fonseca, *J. Organomet. Chem.* 153 (1996) 71; (c) U.H.F. Bunz, *Pure Appl. Chem.* 38 (1996) 309 and references cited therein; (d) H. Lang, *Angew. Chem. Int. Ed. Engl.* 35 (1994) 969.
- [9] M.J. Morris, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), *Comprehensive Organometallic Chemistry II*, vol. 5 (Chapter 8), Pergamon Press, Oxford, New York, Beijing, Frankfurt, São Paulo, Sydney, Tokyo, Toronto, 1995, p. 506 (Chapter 8).
- [10] L.K. Yeung, J.E. Kim, Y.K. Chung, P.H. Rieger, D.A. Sweigart, *Organometallics* 15 (1996) 3891.
- [11] For an (areneCrCO)cluster, see e.g. P. Klüfers, L. Knoll, C. Reiners, K. Reiß, *Chem. Ber.* 118 (1985) 1825.
- [12] (a) W. Strohmeier, H. Hellmann, *Chem. Ber.* 98 (1965) 1598; (b) M.E. Wright, *Macromolecules* 22 (1989) 3256; (c) H.G. Alt, H.E. Engelhardt, A.C. Filippou, *J. Organomet. Chem.* 355 (1988) 139; (d) R.D. Rogers, H.G. Alt, H.E. Engelhardt, *J. Organomet. Chem.* 366 (1989) 305; (e) H.G. Alt, H.E. Engelhardt, R.D. Rogers, S.T. Abu-Orabi, *J. Organomet. Chem.* 378 (1989) 33.
- [13] (a) P. Cadiot, W. Chodkiewicz, in: H.G. Viehe (Ed.), *Chemistry of Acetylenes*, Marcel Dekker, New York, 1969, p. 597f; (b) L.T. Scott, M.J. Cooney, in: P.J. Stang, F. Diederich (Eds.), *Modern Acetylene Chemistry*, VCH, Weinheim, 1995, p. 321f.
- [14] T.J.J. Müller, M. Ansorge, H.J. Lindner, *Chem. Ber.* 129 (1996) 1433.
- [15] G.M. Bodner, L.J. Todd, *Inorg. Chem.* 13 (1974) 360.
- [16] X. He, A.Y.H. Lo, M. Trudeau, R.W. Schurko, D. Antonelli, *Inorg. Chem.* 42 (2003) 335.
- [17] W.M. Shirley, S.P. Scoville, *Inorg. Chem.* 42 (2003) 358.
- [18] S. Reinhard, J. Blümel, *Magn. Reson. Chem.* 41 (2003) 406 (and literature cited therein).
- [19] (a) J. Blümel, M. Herker, W. Hiller, F.H. Köhler, *Organometallics* 15 (1996) 3474; (b) M. Schnellbach, F.H. Köhler, J. Blümel, *J. Organomet. Chem.* 520 (1998) 227.
- [20] T.M. Duncan, *A Compilation of Chemical Shift Anisotropies (and literature cited therein)*, Farragut Press, Chicago, 1990 (and literature cited therein).
- [21] (a) J. Blümel, *J. Am. Chem. Soc.* 117 (1995) 2112; (b) Ch. Merckle, J. Blümel, *Chem. Mater.* 13 (2001) 3617.
- [22] D.R. Kanis, M.A. Ratner, T.J. Marks, *J. Am. Chem. Soc.* 114 (1992) 10338.
- [23] (a) R.T. Lundquist, M. Cais, *J. Org. Chem.* 27 (1962) 1167; (b) D.G. Carroll, S.P. McGlynn, *Inorg. Chem.* 7 (1968) 1285.
- [24] P. Zanello, in: A. Togni, T. Hayashi (Eds.), *Ferrocenes*, VCH, Weinheim, New York, Basel, Cambridge, Tokyo, 1995, p. 317.
- [25] T.J.J. Müller, *J. Organomet. Chem.* 578 (1999) 95.
- [26] Various editors, *Organikum*, 14th ed., VEB Deutscher Verlag der Wissenschaften, Berlin (1993).
- [27] H.J. Bestmann, H. Frey, *Liebig. Ann. Chem.* 1 (1980) 2061.
- [28] S.I. Miller, G.R. Ziegler, R. Wielseck, *Org. Synth. Coll. V* (1973) 921.
- [29] S. Hayashi, K. Hayamizu, *Bull. Chem. Soc. Jpn* 64 (1991) 685.