Synthesis and Structure of Allenyl-Substituted η^6-Benzene(tricarbonyl)chromium Complexes☆

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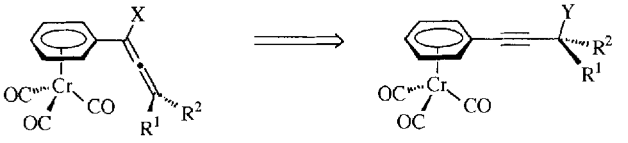
The $Cr(CO)_3$-complexed η^6-phenylpropargylic alcohols **3** react in a displacement rearrangement with thionyl chloride or chlorodiphenylphosphane to give the chloro- or phosphorylallenyl substituted η^6-phenyl complexes **4** and **6**, respectively. In the X-ray crystal structure of the novel organometallic allenic derivatives **4b** and **6b** the vicinal chloro or phosphoryl substituent and the benzene(tricarbonyl)chromium fragment are arranged coplanarily. Palladium/copper-catalyzed couplings of the chloroallene **4b** with terminal alkynes disclose a facile access to ynallene derivatives **8**, novel carbon-rich organometallic π-systems.

Allenes represent a venerable class of unsaturated compounds in the field of preparative chemistry[1] and have recently attracted a considerable theoretical and synthetical interest. Especially, since enyne allenes are known to form highly reactive DNA cleaving diradicals via the Myers or Myers-Saito cyclization, respectively, the research activities in the field of allene chemistry have rapidly expanded[2]. In addition, allenes are known to react readily with a number of nucleophiles[3] and thus synthetic studies have been initiated to develop potential anti-tumor agents based upon allenic substructures[4].

Among the numerous substituted transition metal π-complexes there are very few examples of allenyl derivatives bearing organometallic moieties. So far, there are only a couple of allenes bearing ferrocenyl[5] and (butadienyl)-$Fe(CO)_3$[6] substituents and their chemistry still is in its infancy. As part of our program to synthesize arene $Cr(CO)_3$ complexes bearing π-substituents[7] (alkynes, alkenes etc.) and to investigate their synthetic and opto-electronic potential we were looking for a straight forward preparation of arene $Cr(CO)_3$ substituted allenes taking into account that the direct complexation of phenyl-substituted alkynes, alkenes, and allenes with $Cr(CO)_6$ or $Cr(CO)_3$ transferring reagents proceeds if at all only in low yields and with poor regioselectivity. Furthermore, the $Cr(CO)_3$ complexation can be expected to exert unique steric and electronic effects on the reactivity of aryl allenes such as the stabilization of benzylic charges which can be exploited for efficient side-chain activations[8]. Here we communicate the synthesis and structure of (allenylbenzene)chromium complexes and palladium/copper-catalyzed couplings of a chloroallenyl-substituted complex to give first representatives of organometallic yne allenes.

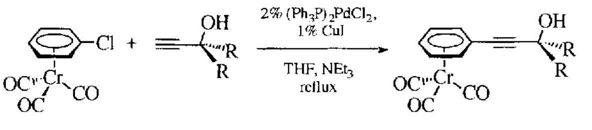
Retrosynthetically, the displacement rearrangement of complexed aryl-substituted propargylic alcohols to allenyl-substituted (arene)$Cr(CO)_3$ complexes lies at hand (see Scheme 1). In many examples the propargylic-type rearrangement for the preparation of allenes has proved to be highly stereoselective and synthetically advantageous[9].

Scheme 1



Recently, we found a facile access to complexed phenylacetylenes[7a,b] using palladium/copper-catalyzed coupling reactions with chlorobenzenechromium complexes[10]. Analogously, the chlorobenzene complex **1** is coupled with propargylic alcohols **2** to give the complexed phenylpropargylic alcohols **3** in good to excellent yields as yellow to brown crystalline solids (see Scheme 2). In the NMR spectra the η^6-complexation of the phenylpropargylic alcohols **3** is supported by the considerable upfield shift of the arene proton and carbon resonances.

Scheme 2



1 **2** **3**

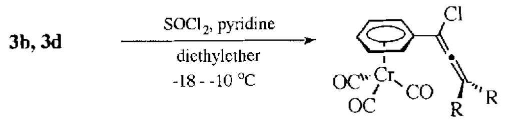
	3a	**3b**	**3c**	**3d**
R,R	H, H	Me, Me	$(CH_2)_5$	Ph, Ph

The propargylic alcohol complexes **3b** and **3d** react with equimolar amounts of thionyl chloride (**4**) and 2 equivalents of pyridine between −18°C and room temperature[9] to give the chloroallenyl-substituted complexes **4** in moderate to good yields as yellow to orange crystalline solids (see Scheme 3)[11].

In a similar manner, diphenylchlorophosphane (**5**) transforms the propargylic alcohols **3b** and **3c** in the presence of triethylamine between −78°C and room temperature[9] to furnish the (arene)$Cr(CO)_3$-substituted phosphorylallenes **6** as yellow crystalline solids (see Scheme 4). In general, the phosphorylallenyl-substituted complexes **6** are formed in higher yields compared to the corresponding chloroallene derivatives **4**.

The chloroallene-substituted complex **4b** can be successfully coupled with terminal alkynes **7** under palladium/copper catalysis to give rise to ynallenyl arene complexes **8** as orange to red crystalline solids in good yields (see Scheme 5). Despite the highly unsaturated nature of these ynallene[12] derivatives representing a novel class of carbon-rich organometallic π-systems the complexes **8** display remarkably high decomposition points and can be expected to behave thermally in analogy to ene ynallenes. The strongly electron-withdrawing (phenyl)$Cr(CO)_3$ fragment diminishes the electron density in the ynallene moiety as reflected in the downfield shifts of the β-allene carbon resonances (see Table 1).

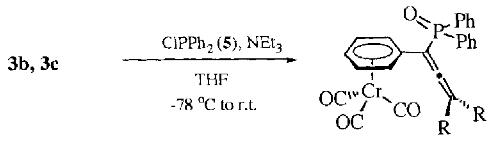
Scheme 3



4

	4a	**4b**
R,R	Me, Me	Ph, Ph

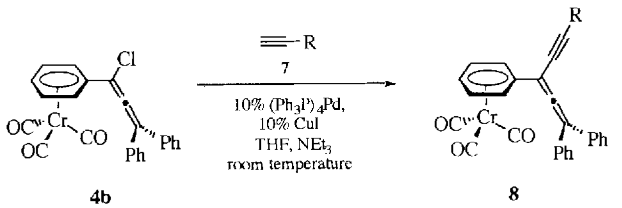
Scheme 4



6

	6a	**6b**
R,R	Me, Me	$(CH_2)_5$

Scheme 5



4b **8**

	8a	**8b**
R	$Si(CH_3)_3$	$(CO)_3CrPh$

The characteristic shift of the central allenic carbon atom in the carbon-NMR spectra of the complexes **4**, **6**, and **8** strongly supports their allenic substructure. Especially, the substitution pattern on the sp^2-hybridized termini strongly influences the carbon resonances of the allene nuclei (see Table 1). The α-allenic carbon signals appear between δ = 93.1 and 102.7 depending on the vicinal and the γ-substituents. A similar influence of the allenic substituents on the γ-carbon resonances is observed (see Table 1). The central allenic carbon resonances in the spectra of **4**, **6**, and **8** vary in a wide range between δ = 197.3 and 212.4 reflecting the electron withdrawing character of the vicinal substituent of the benzene(tricarbonyl)chromium moiety, i.e. the stronger electron-withdrawing the substituent the stronger the downfield shift of the central allenic signal. Furthermore, the α-allenic carbon signals in the spectra of the complexes **6** display strong ^{13}C-^{31}P coupling constants ($J^1_{C\text{-}P}$ = 105 Hz). The resonances of the phosphorus nuclei in the ^{31}P-NMR spectra of **6** appear quite in accordance with organic allene derivatives[9] between δ = 27.9 and 28.2. Interestingly, the carbonyl carbon signals appearing in the region between δ = 233.2 and 233.7 only experience a small influence of the allenic substituents (see Table 1).

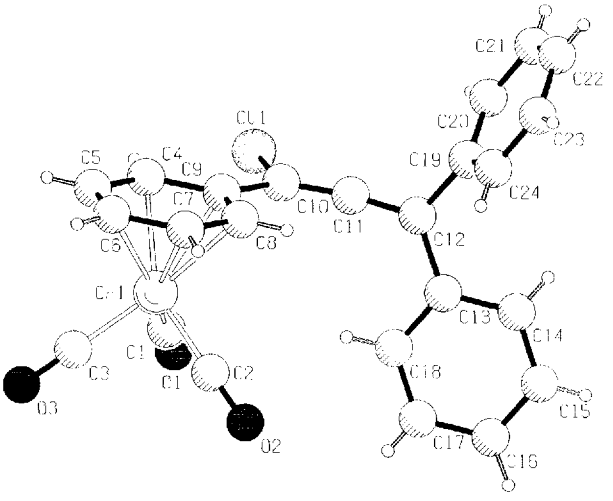
Table 1. Selected ^{13}C-NMR data of the allene derivatives **4**, **6**, and **8** recorded in $[D_6]DMSO$

	C_α	C_β	C_γ	CO
4a	98.64	197.29	111.73	233.65
4b	102.72	202.04	121.11	233.24
6a	95.52 (J^1 = 105.5 Hz)	209.37 (J^2 = 5.6 Hz)	102.80 (J^3 = 12.5 Hz)	233.74
6b	95.51 (J^1 = 105.0 Hz)	205.79 (J^2 = 5.3 Hz)	108.11 (J^3 = 12.2 Hz)	233.74
8a	93.82	211.80	116.60	233.51
8b	93.18	212.37	117.10	233.30 233.46

The X-ray crystal analyses should provide further insight into the structural features of allenyl-substituted arene complexes. The crystal structure determination[13] of the chloroallene-substituted complex **4b** (see Figure 1) reveals that the allenic substructure deviates by 8.7° [C(10)−C(11)−C(12): 171.3(2)] from an ideal linear arrangement. Compared to organic allenes the allenic bond lengths [C(10)−C(11): 129.4, C(11)−C(12): 131.2 pm] lie within the expected margin[14]. Interestingly, the torsional angles [C(8)−C(9)−C(10)−Cl(1): 178.4; C(8)−C(9)−C(10)−C(11): −1.5°] confirm the coplanarity of the chloro substituent, the complexed phenyl ring, and the allene framework. In comparison, the X-ray structure analysis of the diphenylphosphorylallene-substituted complex **6b** (see Figure 2) clearly shows that the allene carbon atoms are collinear [C(24)−C(23)−C(10); 178.5(6)°]. Selected torsion angles [C(8)−C(9)−C(10)−C(23): −174.2(4); C(8)−C(9)−C(10)−P(2): 1.6(5)°] reveal that the allene framework, the complexed phenyl ring and the phosphorus atom are arranged coplanarily. The tetrahedral geometry at the phosphorus atom is reflected by the bond angles [O(4)−

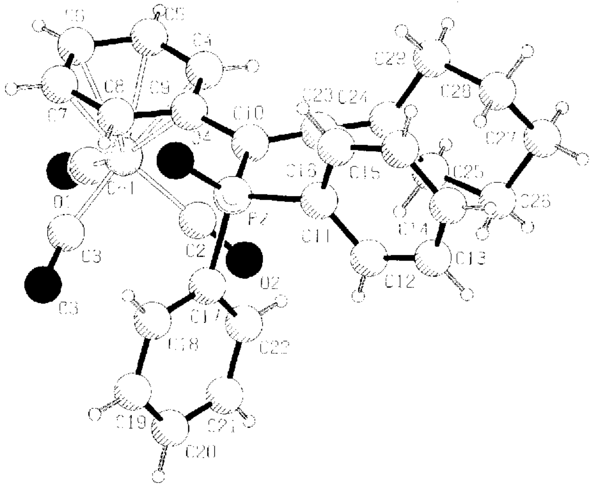
P(2)–C(10): 112.6(2); O(4)–P(2)–C(11): 112.0(2); O(4)–P(2)–C(17). 112.1(2)°]. Interestingly, the P–O bond points at the *ortho* hydrogen atoms of the complexed phenyl rings presumably as a consequence of the steric interactions of the bulky phenyl substituents at the phosphorus atom with the (arene)$Cr(CO)_3$ and the cyclohexylidene moiety, respectively. Since arene $Cr(CO)_3$ complexes are known to possess considerably acidic ring protons an *ortho*-directing effect of the preoriented phosphoryl substituent in ring lithiation experiments forming a six-membered chelate with the lithium cation can be conceived.

Figure 1. Crystal structure of **4b**[a]



[a] Selected bond lengths [pm], angles [°], and torsional angles [°]: Cr(1)–C(centroid) 169.9, C(10)–C(11) 129.4(3), C(11)–C(12) 131.2(3), C(10)–Cl(1) 175.8(2), C(9)–C(10) 147.2(3); C(10)–C(11)–C(12) 171.3(2), C(9)–C(10)–Cl(1) 116.5(2), C(13)–C(12)–C(19) 120.3(2); C(8)–C(9)–C(10)–C(11) –1.5(3), C(4)–C(9)–C(10)–Cl(1) –0.8(3), C(11)–C(12)–C(13)–C(18) –10.7(3), C(11)–C(12)–C(19)–C(20) –60.8(3).

Figure 2. Crystal structure of **6b**[a]



[a] Selected bond lengths [pm], angles [°], and torsional angles [°]: Cr(1)–C(centroid) 167.9, C(10)–C(23) 132.4(6), C(23)–C(24) 130.1(7), C(10)–P(2) 181.0(5), C(9)–C(10) 147.9(7); C(24)–C(23)–C(10) 178.5(6), C(9)–C(10)–P(2) 120.7(3), C(25)–C(24)–C(29) 115.0(5); C(8)–C(9)–C(10)–C(23) –174.2(4), C(8)–C(9)–C(10)–P(2) 1.6(5), C(9)–C(10)–P(2)–O(4) –42.4(4), C(9)–C(10)–P(2)–C(17) 81.4(3).

In conclusion we have shown that allenyl-substituted arene(carbonyl)chromium complexes can be efficiently synthesized by application of displacement rearrangements to η^6-complexed arene propargylic alhohols. The structural features of these novel allene derivatives are largely in agreement with their organic analogs but sterical and electronical influences of α-substituents can exert steering features in the activation of arene side chains. Studies addressing the directed *ortho* lithiation and the nucleophilic reactivity of phosphorylallene-substituted complexes are currently underway. Further investigations on the thermal properties of ynallenyl-substituted complexes and the synthetic potential of allenyl substituted arene complexes will soon be reported.

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Experimental Section

General: 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[15]. – Column chromatography: silica gel 60 (Macherey-Nagel, Düren), mesh 64–200. TLC: silica gel plates (60 F_{254} Merck, Darmstadt). – Melting points (uncorrected values): Büchi SMP-20. – The chlorobenzene complex **1**[16] was prepared by literature methods. Bis(triphenylphosphane)palladium(II) dichloride, copper(I) iodide, the propargylic alcohols **2**, phenylacetylene (**7a**), and (trimethylsilyl)acetylene (**7c**) were purchased from Merck or Aldrich, and used without furhter purification. Chlorodiphenylphosphane (**5**) (Aldrich) was destilled prior to use. The complexed phenylacetylene (**7b**) was prepared according to literature. – ^{1}H- and ^{13}C-NMR spectra: Bruker WM 300 or Bruker AC 300, $[D_6]$DMSO. – 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 **4b**: $C_{24}H_{15}ClCrO_3$, $M = 438.84$, triclinic, space group $P\bar{}-1$, $a = 893.2(2)$, $b = 968.1(2)$, $c = 1252.8(3)$ pm, $\alpha = 99.80(2)$, $\beta = 104.48(3)$, $\gamma = 93.82(3)°$, $V = 1.0268(4)$ nm^3, $Z = 2$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, $\mu = 0.69$ mm^{-1}, $D_x = 1.419$ Mgm^{-3}, $F(000) = 448$, $T = 298(2)$ K. A orange rhombic crystal with the dimensions $0.575 \times 0.4 \times 0.325$ mm was mounted on a capillary and transferred to an Enraf-Nonius CAD4 diffractometer. A total of 3588 intensities ($-9 \leq h \leq 2$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$; $\omega/2\Theta$ scan, 2846 unique, $R_{int} = 0.0147$) were measured in a Θ range from 1.71 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 $wR(F^2)$ for all reflections was 0.0791, with a conventional $R(F)$ $[I > 2\sigma(I)]$ of 0.0284 for 322 parameters.

X-ray Structure Determination of Compound **6b**: $C_{29}H_{25}CrO_4P$, $M = 520.51$, monoclinic, space group $P2_1/c$, $a = 1039.3(1)$, $b = 1949.6(3)$, $c = 1257.6(2)$ pm, $\alpha = 90$, $\beta = 97.12(1)$, $\gamma = 90°$, $V =$

2.5285(6) nm^3, $Z = 4$, $\lambda(\text{Mo-}K_\alpha) = 0.71093$ Å, $\mu = 0.54$ mm^{-1}, $D_x = 1.367$ Mgm^{-3}, $F(000) = 1080$, $T = 298(2)$ K. A bright yellow rhombic crystal with the dimensions 1.0 × 0.325 × 0.25 mm was mounted on a capillary and transferred to an Enraf-Nonius CAD4 diffractometer. A total of 7984 intensities ($-11 \leq h \leq 2$, $0 \leq k \leq 21$, $-13 \leq l \leq 13$; $\omega/2\Theta$ scan, 3516 unique, $R_{\text{int}} = 0.2686$) were measured in a Θ range from 1.94 to 23.00°. 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 0.1744, with a conventional $R(F)$ [$I > 2\sigma(I)$] of 0.0624 for 325 parameters.

General Procedure (GP) for the Palladium/Copper-Catalyzed Coupling of Tricarbonyl(η⁶-chlorobenzene)chromium(0) (1) with Propargylic Alcohols: 1.24 g (4.99 mmol) of **1**, 70 mg (0.10 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. 6 mmol of the corresponding propargylic alcohol **2** dissolved in 15 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 and the suspension was filtered. The solvents of the filtrate were removed in a rotary evaporator. The residue was chromatographed on silica gel and the intense yellow band was collected. Further purification was achieved by recrystallization from dichloromethane/pentane.

Tricarbonyl{η⁶-[(3-hydroxyprop-1-yn-1-yl)benzene]}chromium(0) (**3a**): 1.00 g (75%), yellow needles, m.p. 91–92°C. – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 4.28 (d, J = 5.7 Hz, 2H), 5.44 (t, J = 5.9 Hz, 1H, OH), 5.69–5.77 (m, J = 6.4 Hz, 3H), 5.87 (d, J = 6.0 Hz, 2H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 49.36 (CH$_2$), 79.84 (C$_{\text{quat.}}$), 90.18 (C$_{\text{quat.}}$), 91.60 (C$_{\text{quat.}}$), 94.17 (CH), 94.29 (CH), 97.31 (CH), 233.46 (C$_{\text{quat.}}$, CO). – MS (FD), *m/z*: 268 [M$^+$]. – IR (KBr): $\tilde{\nu}$ = 1955 cm^{-1}, 1903, 1871. – UV/VIS (DMSO): $\lambda_{\max}$ (ε) = 322 nm (9160), 382 (2640). – $C_{12}H_8CrO_4$ (268.2) calcd. C 53.74, H 3.01; found C 53.52, H 2.88.

Tricarbonyl{η⁶-[(3-hydroxy-3-methylbut-1-yn-1-yl)benzene]}chromium(0) (**3b**): 1.33 g (90%), yellow crystals, m.p. 70–72°C. – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.41 (s, 6H), 5.52 (s, 1H, OH), 5.61–5.73 (m, 5H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 31.55 (CH$_3$), 55.04 (C$_{\text{quat.}}$), 63.67 (C$_{\text{quat.}}$), 76.67 (C$_{\text{quat.}}$), 92.53 (C$_{\text{quat.}}$), 93.25 (CH), 94.85 (CH), 96.54 (CH), 233.50 (C$_{\text{quat.}}$, CO). – MS (FD), *m/z*: 296 [M$^+$]. – IR (KBr): $\tilde{\nu}$ = 1962 cm^{-1}, 1899, 1872. – UV/VIS (DMSO): $\lambda_{\max}$ = 321 nm, 380. – $C_{14}H_{12}CrO_4$ (296.2): calcd. C 56.76, H 4.08; found C 57.58, H 4.58.

Tricarbonyl{η⁶-[2-(1-hydroxycyclohex-1-yl)ethyn-1-yl]benzene}chromium(0) (**3c**): 1.45 g (86%), yellow crystals, m.p. 112–114°C. – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.20–1.83 (m, 10H), 5.53 (s, 1H, OH), 5.65–5.78 (m, 5H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 22.94 (CH$_2$, 2 signals), 25.01 (CH$_2$), 67.21 (C$_{\text{quat.}}$), 79.29 (C$_{\text{quat.}}$), 92.52 (C$_{\text{quat.}}$), 93.45 (CH), 94.85 (CH), 95.31 (C$_{\text{quat.}}$), 96.83 (CH), 233.57 (C$_{\text{quat.}}$, CO). – MS (FD), *m/z*: 336 [M$^+$]. – IR (KBr): $\tilde{\nu}$ = 1964 cm^{-1}, 1909. – UV/VIS (DMSO): $\lambda_{\max}$ (ε) = 321 nm (9280), 385 (2290). – $C_{17}H_{16}CrO_4$ (336.3) calcd. C 60.71, H 4.80; found C 61.58, H 5.00.

Tricarbonyl{η⁶-[(3-hydroxy-3,3-diphenylprop-1-yn-1-yl)benzene]}chromium(0) (**3d**): 1.55 g (92%), yellow-orange crystals, m.p. 130–133°C. – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.79–5.98 (m, 5H), 7.05 (s, 1H, OH), 7.27–7.61 (m, 10H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 73.29 (C$_{\text{quat.}}$), 81.87 (C$_{\text{quat.}}$), 91.24 (C$_{\text{quat.}}$), 93.40 (C$_{\text{quat.}}$), 94.14 (CH), 94.45 (CH), 97.29 (CH), 125.79 (CH), 127.52 (CH), 128.31 (CH), 146.00 (C$_{\text{quat.}}$), 233.50 (C$_{\text{quat.}}$, CO). – MS (FD), *m/z*: 420 [M$^+$]. – IR (KBr): $\tilde{\nu}$ = 1967 cm^{-1}, 1890. – UV/VIS (DMSO): $\lambda_{\max}$ = 324 nm, 384. – $C_{24}H_{16}CrO_4$ (420.4) calcd. C 68.57, H 3.84; found C 67.73, H 3.82.

Tricarbonyl[η⁶-(1-chloro-3-methylbuta-1,2-dien-1-yl)benzene]chromium(0) (**4a**): A solution of 48 μl (0.67 mmol) of thionyl chloride in 4 ml of diethyl ether was added dropwise over 10 min to a cooled mixture (−18°C) of 0.20 g (0.67 mmol) of **3b** and 108 μl (1.35 mmol) of pyridine dissolved in 20 ml of degassed diethyl ether. The reaction mixture was stirred at −18 to −10°C for 1.5 h, then at room temp. for 4 h. The suspension was filtered through a short pad (3–5 cm) of silica gel using a 1:4 mixture of ether/pentane as eluent. The solvents were evaporated in vacuo (water bath not more than 30°C) to give 120 mg (57%) of **4a** as a yellow oil (contaminated with small amounts, i.e. 5–10%, of the corresponding enynylbenzene complex). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.91 (s, 6H), 5.72–5.83 (m, 5H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 20.68 (CH$_3$), 92.62 (CH), 94.18 (CH), 94.57 (CH), 98.64 (C$_{\text{quat.}}$), 105.14 (C$_{\text{quat.}}$), 111.73 (C$_{\text{quat.}}$), 197.29 (C$_{\text{quat.}}$), 233.65 (C$_{\text{quat.}}$, CO). – MS (FD), *m/z*: 314 [M$^+$, chloroallene], 278 [M$^+$, enyne].

Tricarbonyl[η⁶-(1-chloro-3,3-diphenylpropa-1,2-dien-1-yl)benzene]chromium(0) (**4b**): In analogy to **4a** the reaction with 1.00 g (2.38 mmol) of the complexed phenylpropargylic alcohol **3d**, 0.39 ml (4.76 mmol) of pyridine and 172 μl (0.67 mmol) of thionyl chloride in 80 ml of diethyl ether gave rise to 0.80 (77%) of pure **4b** as rhombic orange crystals, m.p. 94°C (dec.). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.81–6.00 (m, 5H), 7.41–7.47 (m, 10H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 92.67 (CH), 94.29 (CH), 94.81 (CH), 102.72 (C$_{\text{quat.}}$), 104.54 (C$_{\text{quat.}}$), 121.11 (C$_{\text{quat.}}$), 128.82 (CH), 129.20 (CH), 129.60 (CH), 133.68 (C$_{\text{quat.}}$), 202.04 (C$_{\text{quat.}}$), 233.24 (C$_{\text{quat.}}$, CO). – MS (FD), *m/z*: 438 [M$^+$]. – IR (KBr): $\tilde{\nu}$ = 1959 cm^{-1}, 1889 – UV/VIS (DMSO): $\lambda_{\max}$ (ε) = 320 nm (10100), 390 (3070). – $C_{24}H_{15}ClCrO_3$ (438.8) calcd. C 65.69, H 3.45; found C 65.74, H 3.49.

Tricarbonyl{η⁶-[1-(diphenylphosphoryl)-3-methylbuta-1,2-dien-1-yl]benzene}chromium(0) (**6a**): A solution of 0.22 g (1.00 mmol) of chlorodiphenylphoshpane (**5**) in 5 ml of THF was added dropwise over 10 min to a cooled mixture (−78°C) of 0.30 g (1.01 mmol) of **3b** and 153 μl (1.10 mmol) of triethylamine dissolved in 10 ml of degassed THF. The reaction mixture was allowed to come to room temp. and was then stirred for 4 h. After aqueous work up and extraction with ether the combined organic phases were dried over magnesium sulfate. The solvents were evaporated in vacuo and the residue was chromatographed on silica gel (ether/pentane) to give 360 mg (75%) of **6a** as yellow crystals, m.p. 152–154°C (diethyl ether). – ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.49 (d, J = 5.4 Hz, 6H), 5.62 (m, 1H), 5.72 (pt, J = 6.1 Hz, 2H), 5.91 (d, J = 6.2 Hz, 2H), 7.57–7.72 (m, 10H). – ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 18.92 (CH$_3$, d, J = 4.8 Hz), 94.01 (CH), 94.28 (CH), 94.78 (CH, d, J = 3.1 Hz), 95.52 (C$_{\text{quat.}}$, d, J = 105.5 Hz), 102.80 (C$_{\text{quat.}}$, d, J = 12.5 Hz), 104.84 (C$_{\text{quat.}}$, d, J = 11.1 Hz), 128.80 (CH, d, J = 12.2 Hz), 131.21 (CH, d, J = 10.7 Hz), 132.13 (C$_{\text{quat.}}$, d, J = 105.3 Hz), 132.35 (CH), 209.37 (C$_{\text{quat.}}$, d, J = 5.6 Hz), 233.74 (C$_{\text{quat.}}$, CO). – ^{31}P NMR ([D$_6$]DMSO, 121 MHz): δ = 28.18. – MS (FD), *m/z*: 480 [M$^+$]. – IR (KBr): $\tilde{\nu}$ = 1960 cm^{-1}, 1904, 1887, 1880. – UV/VIS (DMSO): $\lambda_{\max}$ (ε) = 326 nm (8500), 390 (2240). – $C_{26}H_{21}CrO_4P$ (480.4) calcd. C 65.00, H 4.40; found C 65.08, H 4.34.

Tricarbonyl{η⁶-[1-(diphenylphosphoryl)-2-cyclohexylideneethen-1-yl]benzene}chromium(0) (**6b**): 258 mg (50%), yellow crystals, m.p. 174−178°C (dichloromethane/pentane). − ^{1}H NMR ($[D_6]$DMSO, 300 MHz): δ = 0.93−1.00 (m, 2H), 1.29 (m, 2H), 1.46−1.49 (m, 2H), 1.84−1.91 (m, 2H), 2.07−2.14 (m, 2H), 5.61 (t, J = 6.2 Hz, 1H), 5.71 (pt, J = 6.4 Hz, 2H), 5.90 (d, J = 6.4 Hz, 2H), 7.54−7.72 (m, 10H). − ^{13}C NMR ($[D_6]$DMSO, 75 MHz): δ = 24.81 (CH_2), 25.84 (CH_2), 29.48 (CH_2, d, J = 4.1 Hz), 94.14 (CH), 94.83 (CH), 94.88 (CH), 95.51 ($C_{quat.}$, d, J = 105.0 Hz), 105.08 ($C_{quat.}$, d, J = 11.6 Hz), 108.11 ($C_{quat.}$, d, J = 12.2 Hz), 128.87 (CH, d, J = 12.2 Hz), 131.35 (CH, d, J = 10.7 Hz), 132.20 ($C_{quat.}$, d, J = 105.3 Hz), 132.34 (CH, J = 3.1 Hz), 205.79 ($C_{quat.}$, d, J = 5.3 Hz), 233.74 ($C_{quat.}$, CO). − ^{31}P NMR ($[D_6]$DMSO, 121 MHz): δ = 27.95. − MS (FD), *m/z*: 526 [M^+]. − IR (KBr): $\tilde{\nu}$ = 1957 cm^{-1}, 1871. − UV/VIS (DMSO): λ_{max} (ε) = 327 nm (8370), 388 (2360). − $C_{29}H_{25}CrO_4P$ (520.5): calcd. C 66.92, H 4.84; found C 66.41, H 4.65.

Tricarbonyl[η^6-(5,5-diphenyl-1-trimethylsilylpenta-3,4-dien-1-yn-3-yl)benzene]chromium(0) (**8a**): A solution of 34 mg (0.35 mmol) of trimethylsilyl)acetylene (**7a**) in 2 ml of THF was added dropwise over 10 min to a mixture of 150 mg (0.34 mmol) of **4b**, 39 mg (34 µmol) of tetrakis(triphenylphosphane)palladium(0) and 6.4 mg (34 µmol) of copper(I) iodide dissolved in a degassed mixture of 5 ml of THF and 5 ml of triethylamine. The reaction mixture was stirred at room temp. for 20 h. 30 ml of diethyl ether was added and the resulting suspension was filtered. The filtrate was concentrated in vacuo and chromatography of the residue on silica gel with ether/pentane furnished 140 mg (82%) of **8a** as a reddish brown crystalline solid, m.p. >300°C (dichloromethane/pentane). − ^{1}H NMR ($[D_6]$DMSO, 300 MHz): δ = 0.23 (s, 9H), 5.78−5.94 (m, 5H), 7.32−7.44 (m, 10H). − ^{13}C NMR ($[D_6]$DMSO, 75 MHz): δ = −0.53 (CH_3), 92.87 (CH), 93.82 ($C_{quat.}$), 94.25 (CH), 94.83 ($C_{quat.}$), 95.11 (CH), 101.13 ($C_{quat.}$), 102.89 ($C_{quat.}$), 116.60 ($C_{quat.}$), 128.56 (CH), 129.10 (CH), 129.24 (CH), 133.75 ($C_{quat.}$), 211.80 ($C_{quat.}$), 233.51 ($C_{quat.}$, CO). − MS (FD), *m/z*: 500 [M^+]. − IR (KBr): $\tilde{\nu}$ = 1967 cm^{-1}, 1894. − UV/VIS (DMSO): λ_{max} (ε) = 324 nm (9660), 365 (9520), 464 (3130). − $C_{29}H_{24}CrO_3Si$ (500.6) calcd. C 69.58, H 4.83; found C 69.32, H 4.94.

µ-{η^6:η^6-[(5,5-Diphenylpenta-3,4-dien-1-yne)-1,3-diyl]bis(benzene)}bis[tricarbonylchromium(0)] (**8b**): 150 mg (69%), reddish brown crystalline solid, m.p. >300°C (dichloromethane/pentane). − ^{1}H NMR ($[D_6]$DMSO, 300 MHz): δ = 5.74−6.21 (br, m, 10H), 6.98−7.62 (m, 10H). − ^{13}C NMR ($[D_6]$DMSO, 75 MHz): δ = 79.44 ($C_{quat.}$), 90.23 ($C_{quat.}$), 90.73 ($C_{quat.}$), 92.59 (CH), 93.18 ($C_{quat.}$), 93.95 (CH), 94.39 (CH), 94.54 (CH), 94.82, (CH), 97.03 (CH), 102.86 ($C_{quat.}$), 117.10 ($C_{quat.}$), 128.68 ($C_{quat.}$), 129.24 (CH), 133.64 ($C_{quat.}$), 212.37 ($C_{quat.}$), 233.30 ($C_{quat.}$, CO), 233.46 ($C_{quat.}$, CO). − MS (FD), *m/z*: 640 [M^+]. − IR (KBr): $\tilde{\nu}$ = 1968 cm^{-1}, 1897. − UV/VIS (DMSO): λ_{max} (ε) = 321 nm (19100), 403 (5980). − $C_{35}H_{20}Cr_2O_6$ (640.5): calcd. C 65.63, H 3.14; found C 63.00, H 3.11.

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[*] Dedicated to Prof. Dr. *Wolfgang Beck* on the occasion of his 65th birthday.

[1] For comprehensive reviews of allene chemistry see, e.g. D. R. Taylor, *Chem. Rev.* **1967**, *67*, 317−359; T. F. Rutledge, *Acetylenes and Allenes*, Reinhold Book Corporation, New York, Amsterdam, London, **1969**, parts 1−3; W. T. Brady in *The Chemistry of Ketenes, Allenes and Related Compounds*, part 1, (Ed.: S. Patai), J. Wiley & Sons, Chichester, New York, Brisbane, Toronto, **1980**, 298−308; H. Hopf in *The Chemistry of Ketenes, Allenes and Related Compounds*, part 2, (Ed.: S. Patai), J. Wiley & Sons, Chichester, New York, Brisbane, Toronto, **1980**, 779−902; W. Smadja, *Chem. Rev.* **1983**, *83*, 263−320; D. J. Pasto, *Tetrahedron* **1984**, *40*, 2805−2827; H. F. Schuster, G. M. Coppola, *Allenes in Organic Synthesis*, J. Wiley & Sons, Chichester, New York, Brisbane, Toronto, **1984**.

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[3] See, e.g. H.-J. Altenbach, R. Korff, *Tetrahedron Lett.* **1984**, *22*, 5175−5178; F. Palacios, D. Aparicio, J. Garcia, *Tetrahedron*, **1996**, *52*, 9609−9628.

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[8] For excellent reviews for nucleophilic additions see, e.g. M. F. Semmelhack in *Comprehensive Organometallic Chemistry II*, E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds., Pergamon **1995**, Vol. 12, pp. 979−1015; for ring lithiations see, e.g. M. F. Semmelhack, *ibid.*, Vol. 12, pp. 1017−1038; for side chain activation see, e.g. S. G. Davies, T. D. McCarthy, *ibid.*, Vol. 12, pp. 1039−1070; for stabilization of positive charge in the benzylic positions see, e.g. S. G. Davies, T. J. Donohoe, *Synlett* **1993**, 323−332.

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[11] Surprisingly, the propargylic alcohols **3a**, **c** do not furnish the expected chloro allenes but the corresponding propargylic chloride derivatives. Basically, the fragmentation of the initially formed chloro sulfenyl ester gives rise to two possible products: the propargylic chloride and the "rearranged" allenyl chloride. Obviously, the stability of the propargylic carbenium ion has a crucial influence on the product distribution chloro allene/allenyl chloride, i.e. the higher the stabilization of the carbenium ion the more chloro allene is formed. Besides, another competing reaction is the β-elimination to give the enyne product (together with **4a**).

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