ELSEVIER

Journal of Organometallic Chemistry 630 (2001) 198–204

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

# Synthesis and structure of the chromiumcarbonyl complexed phenyl allene

Markus Ansorge, Kurt Polborn, Thomas J.J. Müller *

*Department Chemie der Ludwig-Maximilians-Universität München, Butenandtstraße 5-13 (Haus F), D-81377 München, Germany*

Received 6 March 2001; accepted 24 April 2001

**Abstract**

The chromiumtricarbonyl complexed phenyl allene **4** can be readily synthesized by palladium catalyzed hydride reduction or dimethyl cuprate mediated reduction of suitable propargyl ester derivatives **3** and **5**. This parent compound of chromiumcarbonyl complexed aryl allenes is fairly stable and is unambiguously characterized by an X-ray structure analysis. Thiolate adds to **4** to give a 3.5:1 distribution between the nonconjugated and the conjugated addition products **7** and **8** in good yield. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Addition; Allenes; Arene complexes; Chromium; Structure

## 1. Introduction

In the last two decades, chromiumcarbonyl complexed arenes have found remarkable applications in the synthesis of complex natural and non-natural structural motifs [1]. Besides highly stereoselective transformations as a consequence of planar chirality and neighboring group assisted conformational fixation, additionally, the chromiumcarbonyl complexation significantly alters the reactivity of the arene ligands [2]. Thus, new reaction pathways readily open from the taming of otherwise highly reactive intermediates. In particular, the activation of the benzylic position has received the most attention and has been intensively studied [2c,3]. Basically, the stabilization of complexed benzylic anions can be attributed to the strong electron withdrawing nature of the (arene)$Cr(CO)_3$ fragment [4]. Two different ways have been successfully applied to the generation of complexed benzylic anions: (a) by deprotonation of toluene complexes [5]; or (b) by addition of a nucleophile to the β-position of styrene or dihydronaphthalene complexes [6]. Especially, the addition of nucleophiles to an alkenyl side chain of an arene complex represents an extremely useful reaction allowing a consecutive trapping of the complexed benzylic anion by a suitable electrophile [6a,b]. In order to overcome the poor nucleophilic susceptibility of the β-carbon atom in styrene complexes, we have investigated the syntheses, structure and reactivity of allenyl phosphonic ester substituted arene complexes [7] which upon nucleophilic addition to the β-carbon atom of the allenyl side chain give rise to (arene)$Cr(CO)_3$ stabilized allyl anions that led us to a straightforward consecutive heterocycle synthesis on a metal template [7b]. Here, we wish to report two synthetic accesses, the structure and a representative addition reaction of the parent compound of this class of organometallic allenes, i.e. the chromiumcarbonyl complexed phenyl allene.

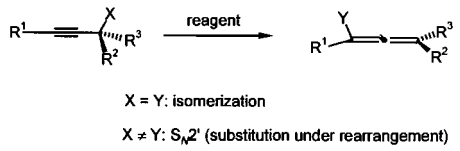
## 2. Results and discussion

Allenes are constitutional isomers of propargyl compounds. They represent a venerable class of unsaturated compounds in the field of preparative chemistry [8] and have recently attracted a considerable theoretical and synthetic 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

* Corresponding author. Tel.: +49-89-2180-7714; fax: +49-89-2180-7717.

*E-mail address:* tom@cup.uni-muenchen.de (T.J.J. Müller).


PII: S0022-328X(01)00867-1



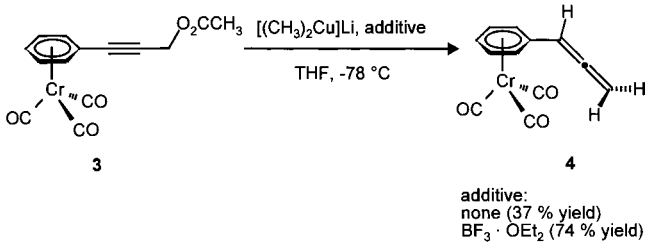

Scheme 1. Schematic proargyl-allene transformations.

have rapidly expanded [9]. A natural access can be accomplished by isomerizations or rearrangements of alkynes or also very elegantly by $S_N2'$-substitutions on propargyl compounds (Scheme 1). In many cases, propargyl rearrangements have been advantageous for efficient and highly stereoselective preparations of allenes [10].

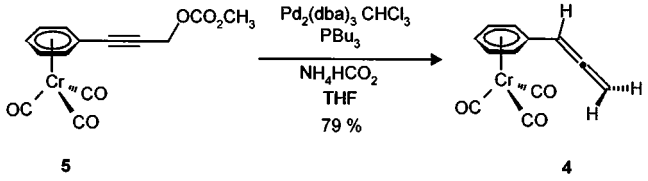
Recently, we have demonstrated that (arene)-chromiumcarbonyl complex substituted chloro and phosphonate allenes can be readily synthesized via esterification of aryl complexed propargyl alcohols **1** with thionyl chloride, diphenyl chloro phosphane or diethoxy chloro phosphane and subsequent thermal rearrangement to the corresponding allenyl derivatives **2** in good yields (Scheme 2) [7].

During our studies of α,α-disubstituted allenyl arene complexes [11] using nucleophilic substitutions with cuprates, we found that the reaction of the propargyl acetate complex **3** with dimethyl cuprate after aqueous work up preferentially led to the formation of the phenyl complex substituted allene **4** in 37% yield. Upon addition of boron trifluoride etherate as an activating Lewis acid, the yield of **4** was improved to 74% (Scheme 3).

The reaction with a (arene)chromiumcarbonyl substituted propargyl acetate is per se fairly interesting since the normal reaction course with purely organic propargyl derivatives furnishes an α-methyl allene as substitution product [12]. Here, however, the initially formed α-allenyl cuprate by a formal oxidative addition of the propargyl acetate to the dimethyl cuprate is a fairly stable species reluctant in transferring the methyl group



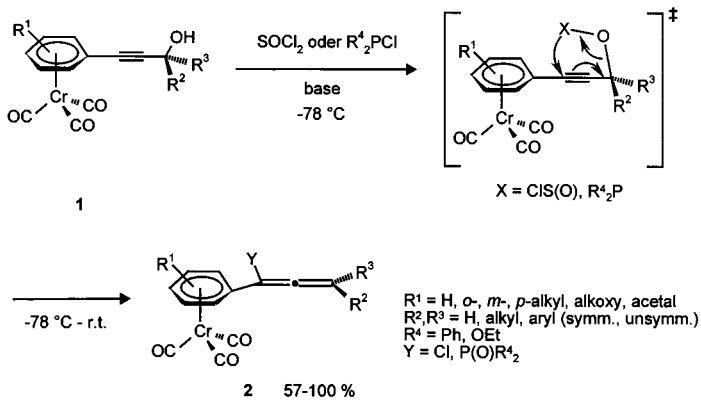

Scheme 3.




Scheme 4.

via reductive elimination. At this point it is still unclear if the influence of the phenyl chromiumcarbonyl substituent is only steric or also electronic. Thus, hydrolysis of the organometallic intermediate led to the formation of the organometallic allene **4**. To circumvent the rather uneconomical use of dimethyl cuprate as a reducing agent, we now sought a hydride reduction under sufficiently mild reaction conditions.

Applying the same principle of a substitution under propargyl rearrangement, however, using an established protocol of a palladium-catalyzed hydrogenolysis [13] of the corresponding propargyl carbonate **5** with ammonium formiate as hydride donor, the $Cr(CO)_3$ complexed phenyl allene **4** can be prepared in good yield as a yellow crystalline material (Scheme 4). Due to their electron deficiency, acceptor substituted allenes are more stable towards electrophilic oligo- and polymerization. In contrary to the corresponding ferrocenyl substituted allene [14], compound **4** can be handled in air without any problems.




Scheme 2.

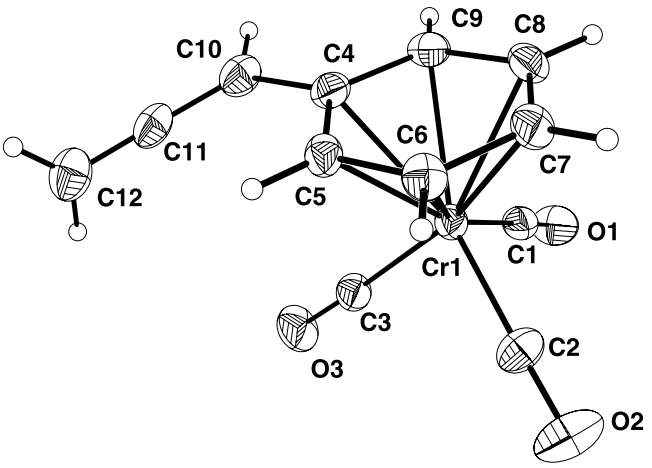



Fig. 1. ORTEP plot of **4**. Selected bond lengths (Å), angles (°) and dihedral angles (°): C(4)–C(10): 1.482(8), C(10)–C(11): 1.318(10), C(11)–C(12): 1.250(11), C(11)–C(10)–C(4): 125.4(6), C(12)–C(11)–C(10): 178.9(8), C(5)–C(4)–C(10)–C(11): −12.5(9), C(9)–C(4)–C(10)–C(11): 165.6(6).

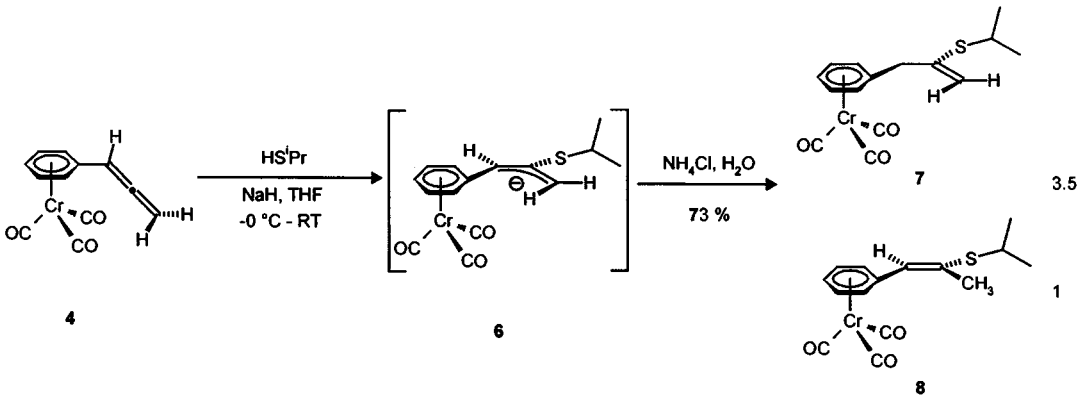
Table 1
Crystal data and structure refinements for **4**

| | |
|---|---|
| Empirical formula | $C_{12}H_8CrO_3$ |
| Formula weight | 252.18 |
| Temperature (K) | 293(2) |
| Radiation (Å) | 0.71073 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | |
| $a$ (Å) | 6.968(3) |
| $b$ (Å) | 8.038(4) |
| $c$ (Å) | 9.963(6) |
| $\alpha$ (°) | 93.83(4) |
| $\beta$ (°) | 92.10(4) |
| $\gamma$ (°) | 103.37(4) |
| Volume (Å$^3$) | 540.9(5) |
| $Z$ | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 1.548 |
| Absorption correction | $\varphi$-scans |
| Absorption coefficient (mm$^{-1}$) | 1.043 |
| $F(000)$ | 256 |
| Crystal size (mm) | $0.27 \times 0.40 \times 0.53$ |
| Index ranges | $-7 \le h \le 7$, $-8 \le k \le 8$, $-10 \le l \le 0$ |
| $\theta$ range (min/max) | 2.61–23.00° |
| Reflections collected | 1606 |
| Reflections observed [$I > 2\sigma(I)$] | 1504 |
| Independent reflections | 1504 [$R_{int} = 0.0319$] |
| Max/min transmission | – |
| Refinement method | SHELXL-93 on $F^2$ |
| Data/restraints/parameters | 1504/2/151 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0623$, $wR_2 = 0.1828$ |
| $R$ indices (all data) | $R_1 = 0.0623$, $wR_2 = 0.1828$ |
| Goodness of fit on $F^2$ | 1.172 |
| Largest difference peak and hole (e Å$^{-3}$) | 1.270 and −0.347 |

In the $^1$H-NMR spectrum of **4**, the well-resolved coupling pattern of the *ortho* ($\delta = 5.69$), *meta* ($\delta = 5.84$) and *para* proton resonances ($\delta = 5.58$) of the complexed arene ring can be observed. The resonance of the α-allenyl proton appears as a triplet at $\delta = 6.11$ ($J = 6.6$ Hz) and the two terminal γ-allenyl protons as a doublet at $\delta = 5.43$ ($J = 6.6$ Hz). Most characteristically, the central β-allenyl carbon resonance in the $^{13}$C-NMR spectrum is detected at $\delta = 208.6$ and the α-allenyl ($\delta = 90.7$) and γ-allenyl carbon signals ($\delta = 81.1$) appear in the expected region [15]. Compared to the free hydrocarbon ligand [16], the α-nucleus of the allenyl fragment is significantly ($\Delta\delta = -3.3$) and β-nucleus slightly ($\Delta\delta = -1.0$) shielded and can be found at higher field. However, the π-electron density at the γ-terminus of the complex substituted allene is reduced and, thus, this nucleus is shifted to downfield in comparison to the free ligand ($\Delta\delta = +2.3$). According to the X-ray structure analysis of **4** (Fig. 1, Table 1), the complex substituted allene can be considered as an 'organic' allene since the bond lengths of cumulated double bonds and the perfectly linear orientation within the allenyl fragment are in good agreement with the expected data [8c]. Interestingly, the allenyl side chain points towards the chromiumcarbonyl tripod with a relatively small torsional angle (−12.5°). Summarizing the structural features this organometallic allene should display a reactivity comparable to organic allenes with weak electron acceptors.

With the prototype of (arene) chromiumcarbonyl substituted allenes in hand we now intended to scrutinize two reactivity features: (a) the nucleophilic addition of soft nucleophiles to give complex stabilized allyl anions and (b) the regioselectivity of the electrophilic attack at this allyl anion. The nucleophilic addition of sodium isopropyl thiolate to the allene **4** between 0 °C and room temperature furnished an orange solution indicating the formation of the resonance stabilized allyl anionic species **6** (Scheme 5). After work up with aqueous ammonium chloride solution, a 3.5:1 mixture of the isomeric alkenyl derivatives **7** and **8** were obtained as a result of α- (**7**) and γ-protonation (**8**) of the intermediate allyl anion **6**.

Most remarkably, the major isomer is the nonconjugated one (**7**). It has been known for quite some time that the isomerization of chromiumtricarbonyl complexed allyl benzene under equilibrium conditions furnishes a 2.7:1 distribution of $Cr(CO)_3$-complexed allyl benzene/$Cr(CO)_3$-complexed 1-propenyl benzene [17]. However, the free ligand furnishes under these conditions exclusively the conjugated isomer, i.e. 1-propenyl benzene. Thus, the complexed phenyl ring can be considered as strongly electron withdrawing reorganizing the charge distribution in the allyl anion. According to the principle of allopolarization [18], the electrophilic attack at α-acceptor substituted allyl anions preferentially occurs at the α-position, thus, furnishing the nonconjugated isomer **7** [19].

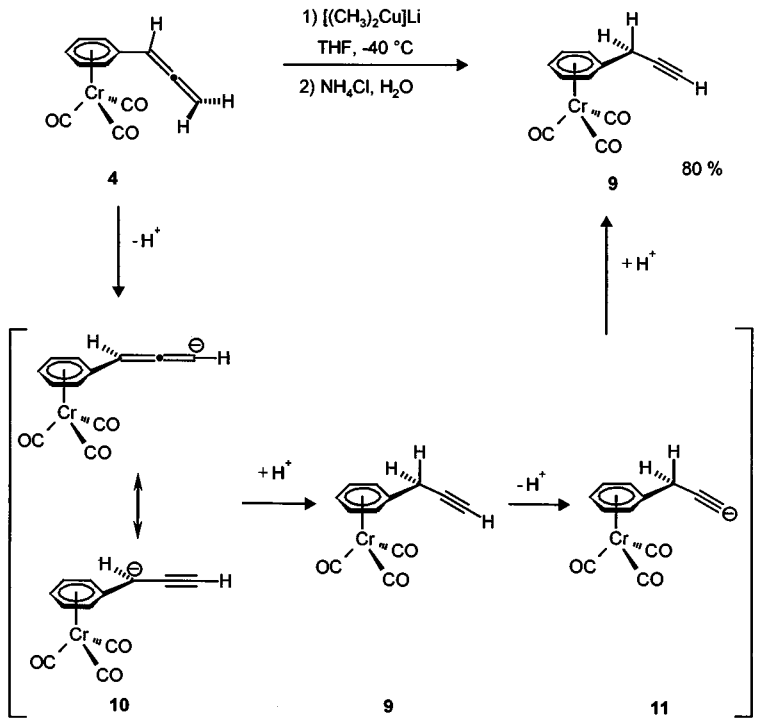



Scheme 5.

Another class of soft nucleophiles are cuprates. However, the reaction of the dimethyl Gilman cuprate with the complex substituted allene **4** exclusively leads to isomeric nonconjugated complexed phenyl propyne **9** (Scheme 6). Obviously, the γ-proton on the allenyl side chain is sufficiently acidified that the cuprate rather acts as a base than a nucleophile. Therefore, this isomerization can be rationalized as follows. Deprotonation of the allene **4** gives the resonance stabilized propargyl allenyl anion **10**. This anion is reprotonated according to the allopolarization principle [18] at the α-position. Under these basic conditions, the most acidic proton now is the terminal alkyne proton ($pK_a \sim 25$) now leading to a thermodynamic sink and giving rise to the acetylide **11**. Protic workup finally furnishes the isomeric nonconjugated complexed phenyl propyne **9**.

## 3. Conclusions

In conclusion, we have disclosed two straightforward accesses to the most simple (arene)chromiumcarbonyl substituted allene using reductive cupration and palladium-catalyzed hydride reduction. Compared to its ferrocenyl analogue this crystalline complex is remarkably stable and can be handled without special precautions. Structurally and electronically, the (phenyl)Cr(CO)$_3$-substituted allene behaves like an organic allene, i.e. the




Scheme 6.

central allenyl carbon atom displays a high nucleophilic susceptibility. Thus, the reaction with a thiolate leads to a rapid formation of a complex substituted allyl anion. Protonation of this allyl anion preferentially occurs at the α-carbon atom adjacent to the chromiumcarbonyl arene substituent in accordance with the electron withdrawing nature of the organometallic fragment. Further studies with this organometallic allenes will be directed towards their reactivity in cycloaddition reactions leading to heterocycle syntheses on a metal template.

## 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 [20]. Column chromatography: silica gel 60 (0.063–0.2 mm/70–230 mesh, Firma Merck, Darmstadt). TLC: silica gel plates (60 $F_{254}$ Merck, Darmstadt). Melting points (uncorrected values): Reichert–Jung Thermovar. The complexed propargyl alcohol **1** was synthesized according to our published procedure [7a]. All reagents used were purchased from Merck, Aldrich or Fluka and used without further purification, palladium bis(dibenzylidene acetone) chloroform was synthesized according to a literature procedure [21]. $^1$H- and $^{13}$C-NMR spectra: Bruker WM 300, Bruker AC 300, Bruker ARX 300 or Varian VXR 400S DMSO-$d_6$. IR: Perkin–Elmer FTIR spectrometer 1000 or Perkin–Elmer FTIR Paragon 1000 PC. The samples were pressed into KBr pellets and recorded on NaCl plates. UV–vis: Beckman DK-2-a or Beckman UV 5240. UV–vis: Perkin–Elmer Models Lambda 16. MS: Finnigan MAT 311-A/100MS, Finnigan MAT 90 and MAT 95 Q. Elemental analysis were carried out in the Microanalytical Laboratories of the Department Chemie, Ludwig-Maximilians-Universität München.

### 4.1. [$\eta^6$-$C_6H_5C{\equiv}CCH_2O(CO)CH_3$]$Cr(CO)_3$ (3)

To a solution of 1.01 g (3.73 mM) of the propargyl alcohol **1** ($R^1 = R^2 = R^3 = H$) in 50 ml of $CH_2Cl_2$ and 1.03 ml (7.64 mM) of $Et_3N$ cooled (0 °C) under nitrogen a solution of 2.40 ml (33.5 mM) of $CH_3COCl$ in 2.5 ml of $CH_2Cl_2$ was added dropwise. The reaction mixture was allowed to warm to room temperature (r.t.) within 2 h. The solvents were removed in vacuo and the residue chromatographed on silica gel ($Et_2O$–pentane, 1:1) to furnish 1.10 g (95%) of the acetate **3**. Further purification was achieved by recrystallization from $Et_2O$–pentane to give yellow plates, m.p. 65 °C. $^1$H-NMR (DMSO-$d_6$, 300 MHz): $\delta$ 2.07 (s, 3H), 4.91 (s, 2H), 5.73–5.75 (m, 3H), 5.89–5.91 (m, 2H). $^{13}$C-NMR (DMSO-$d_6$, 75 MHz): $\delta$ 20.63 ($CH_3$), 51.97 ($CH_2$), 82.05 ($C_{quat.}$), 84.34 ($C_{quat.}$), 89.96 ($C_{quat.}$), 94.16 (CH), 94.31 (CH), 97.36 (CH), 169.81 ($C_{quat.}$), 233.22 ($C_{quat.}$, CO). MS (70 eV, EI), $m/z$ (%): 310 ($M^+$, 34), 254 ($M^+ - 2CO$, 2), 226 ($M^+ - 3CO$, 94), 167 $C_6H_5C{\equiv}CCH_2Cr^+$, 19), 111 ($Cr(OAc)^+$, 100), 52 ($Cr^+$, 84). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ 1952, 1882, 1743, 1452, 1431, 1371, 1269, 1220, 1021, 953, 823, 674, 651, 629, 526, 469. UV–vis: $\lambda_{max}$ (nm) ($\varepsilon$, $M^{-1}\,cm^{-1}$) (DMSO): 322 (9300). Anal. Found: C, 52.82; H, 3.31. Calc. for $C_{14}H_{10}CrO_6$ (326.22): C, 54.20; H, 3.25%.

### 4.2. [$\eta^6$-$C_6H_5C{\equiv}CCH_2O(CO)OCH_3$]$Cr(CO)_3$ (5)

To a solution of 0.20 g (0.74 mM) of the propargyl alcohol **1** ($R^1 = R^2 = R^3 = H$) in 10 ml of $CH_2Cl_2$ and 0.16 ml (2.00 mM) of pyridine cooled (0 °C) under nitrogen a solution of 116 μl (1.50 mM) of methyl chloroformiate in 2 ml of $CH_2Cl_2$ was added dropwise. The reaction mixture was allowed to warm to r.t. and was stirred for 3 h before adding 10 ml of distilled water. After extraction of the aqueous phase with several portions of $CH_2Cl_2$ the combined organic layers were dried with $MgSO_4$. After filtration, the solvents were removed in vacuo and the residue was dried under high vacuum ($10^{-2}$ mbar) to remove traces of pyridine. The residual oil was crystallized from $Et_2O$–pentane to furnish 200 mg (83%) of the propargyl carbonate **5** as yellow needles, m.p. 72 °C. $^1$H-NMR (DMSO-$d_6$, 300 MHz): $\delta$ 3.73 (s, 3H), 4.98 (s, 2H), 5.71–5.73 (m, 3H), 5.87–5.89 (m, 2H). $^{13}$C-NMR (DMSO-$d_6$, 75 MHz): $\delta$ 55.3 ($CH_3$), 55.5 ($CH_2$), 82.8 ($C_{quat.}$), 83.6 ($C_{quat.}$), 89.5 ($C_{quat.}$), 94.0 (CH), 94.3 (CH), 97.3 (CH), 154.6 ($C_{quat.}$), 233.1 ($C_{quat.}$, CO). MS (70 eV, EI), $m/z$ (%): 326 ($M^+$, 41), 270 ($M^+ - 2CO$, 2), 242 ($M^+ - 3CO$, 20), 168 ($C_6H_5CH{=}C{=}CH_2Cr^+$, 100), 52 ($Cr^+$, 49). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ 1969, 1894, 1756, 1636, 1447, 1374, 1278, 973, 940, 790, 674, 654, 629, 531, 475. UV–vis: $\lambda_{max}$ (nm) ($\varepsilon$, $M^{-1}\,cm^{-1}$) (DMSO): 322 (9600). Anal. Found: C, 51.94; H, 3.22. Calc. for $C_{14}H_{10}CrO_6$ (326.22): C, 51.54; H, 3.09%.

### 4.3. ($\eta^6$-$C_6H_5CH{=}C{=}CH_2$)$Cr(CO)_3$ (4)

#### 4.3.1. Reductive cupration without additive

A suspension of 0.61 g (3.22 mM) of CuI in 20 ml of THF was cooled to 0 °C under nitrogen. To this suspension 4.02 ml (6.44 mM) of a 1.6 M methyllithium solution in ether was added dropwise over 3 min. After stirring at 0 °C for 30 min, the clear yellow solution was cooled to −30 °C and a solution of 1.0 g (3.22 mM) of the acetate complex **3** in 10 ml of THF was added dropwise over 5 min. The reaction mixture was allowed to warm to 5 °C over 2.5 h and after adding 1 ml of water the solution was filtered, extracted several times with $Et_2O$ and the organic phases were removed in vacuo. The residue was chromatographed on silica

gel ($Et_2O$–pentane, 1:1 to $Et_2O$) to give 0.30 g (37%) of the complex substituted allene **4** as an orange oil that solidifies upon triturating with pentane and is recrystallized from $Et_2O$–pentane.

*4.3.2. Reductive cupration with boron trifluoride as an additive*

To a cooled (0 °C) suspension of 511 mg (2.68 mM) of CuI in 20 ml of THF, 3.35 ml (5.36 mM) of a 1.6 M methyllithium solution in ether was added dropwise under nitrogen over 3 min. After stirring at 0 °C for 30 min, the mixture was cooled to −78 °C and 110 μl (0.92 mM) of boron trifluoride etherate was added dropwise. After 5 min, a solution of 300 mg (0.96 mM) of the acetate **3** in 5 ml of THF was added and the mixture was stirred for 15 min at −78 °C before adding 52 μl (0.42 mM) of boron trifluoride etherate. The reaction mixture was then stirred for 1 h at −78 °C before it was allowed to warm to r.t. After adding 10 ml of a saturated aqueous $NH_4Cl$ solution, the aqueous layer was extracted several times with $Et_2O$. The combined organic phases were dried with $MgSO_4$ and the solvents were removed in vacuo. The residue was chromatographed on silica gel ($Et_2O$–pentane, 1:3) to furnish 180 mg (74%) of the complexed phenyl allene **4** as yellow crystals, m.p. 60–63 °C.

*4.3.3. Palladium-catalyzed hydride reduction*

To a solution of 26 mg (0.05 mM) of $Pd_2(dba)_3{\cdot}CHCl_3$ and 63 mg (1.0 mM) of ammonium formiate in 5 ml of THF under nitrogen 50 μl (0.20 mM) of tributylphosphane was added dropwise and stirred continuously for 5 min at r.t. To this yellow solution was added dropwise a solution of 165 mg (0.50 mM) of the propargyl carbonate **5** in 5 ml of THF and the reaction mixture was stirred for 28 h at r.t. Then the solvent was evaporated in vacuo and the residue was chromatographed on silica gel ($Et_2O$–pentane, 1:4). The residual oil was dissolved in pentane and filtered. After evaporation of the pentane and recrystallization from a small amount of pentane 100 mg (79%) of **4** were obtained as yellow orange crystals, m.p. 60–63 °C. $^1$H-NMR (DMSO-$d_6$, 300 MHz): $\delta$ 5.43 (d, 2H, $J = 6.6$ Hz), 5.58 (d, 1H, $J = 6.3$ Hz), 5.69 (d, 2H, $J = 6.4$ Hz), 5.84 (t, 2H, $J = 6.6$ Hz), 6.11 (t, 2H, $J = 6.6$ Hz). $^{13}$C-NMR (DMSO-$d_6$, 75 MHz): $\delta$ 81.12 ($CH_2$), 90.71 (CH), 92.45 (CH), 92.94 (CH), 95.98 (CH), 106.71 ($C_{quat.}$), 208.60 ($C_{quat.}$), 234.26 ($C_{quat.}$, CO). MS (70 eV, EI), $m/z$ (%): 252 ($M^+$, 25), 224 ($M^+ - CO$, 3), 196 ($M^+ - 2CO$, 12), 168 ($M^+ - 3CO$, 63), 116 ($M^+ - Cr(CO)_3$, 13), 52 ($Cr^+$, 100). IR (KBr, $cm^{-1}$): $\tilde{\nu}$ 1964, 1881, 1636, 1529, 1461, 1433, 1409, 1283, 1153, 994, 860, 820, 694, 660, 631, 531, 475, 416. UV–vis: $\lambda_{max}$ (nm) ($\varepsilon$, $M^{-1}\,cm^{-1}$) (DMSO): 323 (9800). Anal. Found: C, 57.36; H, 3.20. Calc. for $C_{12}H_8CrO_3$ (252.18): C, 57.15; H, 3.19%.

*4.4. Thiolate addition products **7** and **8***

A suspension of 21 mg (0.87 mM) of NaH in 15 ml of THF was cooled to 0 °C under nitrogen. To this suspension, 85 μl (0.90 mM) of 2-propanethiol was added dropwise and the mixture was stirred for 15 min until the evolution of hydrogen had ceased. Then 200 mg (0.79 mM) of the allene **4** were added and the reaction mixture was stirred for 2 h at 0 °C and for 5 h at r.t. before 10 ml of water were added. The aqueous layer was extracted several times with $Et_2O$. After drying with $MgSO_4$ and evaporation of the solvents in vacuo, the residue was chromatographed on silica gel ($Et_2O$–pentane, 1:4) to give 190 mg (73%) of regioisomers **7** and **8** (3.5:1) as a pure yellow oil. $^1$H-NMR (DMSO-$d_6$, 300 MHz), **7**:**8** = 3.5:1, major isomer **7**:$\delta$ 1.20 (d, 6H, $J = 6.5$ Hz), 2.08 (m, 1H), 3.19 (s, 2H), 4.94 (s, 1H), 5.30 (s, 1H), 5.55 (t, 1H, $J = 6.4$ Hz), 5.61 (d, 2H, $J = 6.1$ Hz), 5.76 (t, 2H, $J = 6.6$ Hz); additional signals for the minor isomer **8**: $\delta$ 1.26 (d, 6H, $J = 6.6$ Hz), 2.08 (s, 3H), 3.42 (sept., 1H, $J = 6.6$ Hz), 5.54 (t, 1H, $J = 6.3$ Hz), 5.73 (d, 2H, $J = 6.5$ Hz), 5.81 (t, 2H, $J = 6.8$ Hz), 5.95 (s, 1H). $^{13}$C-NMR (DMSO-$d_6$, 75 MHz), major isomer **7**: $\delta$ 22.48 ($CH_3$), 34.68 (CH), 42.23 ($CH_2$), 93.06 (CH), 95.07 (CH), 96.03 (CH), 111.48 ($CH_2$), 112.15 ($C_{quat.}$), 142.41 ($C_{quat.}$), 234.18 ($C_{quat.}$); additional signals for the minor isomer **8**: $\delta$ 20.00 ($CH_3$), 22.43 ($CH_3$), 34.56 (CH), 92.80 (CH), 94.40 (CH), 95.99 (CH), 109.78 ($C_{quat.}$), 119.53 ($C_{quat.}$), 119.65 (CH), 234.37 ($C_{quat.}$). MS (70 eV, EI), $m/z$ (%): 328 ($M^+$, 9), 300 ($M^+ - CO$, 8), 272 ($M^+ - 2CO$, 8), 244 ($M^+ - 3CO$, 34), 192 ($M^+ - Cr(CO)_3$, 2), 52 ($Cr^+$, 32). IR (KBr, $cm^{-1}$): $\tilde{\nu} = 3091$, 2966, 2927, 2867, 1963, 1866, 1602, 1527, 1458, 1418, 1384, 1367, 1312, 1242, 1214, 1153, 1104, 1052, 1015, 997, 858, 835, 800, 661, 630, 534, 476. UV–vis: $\lambda_{max}$ (nm) ($\varepsilon$, $M^{-1}\,cm^{-1}$) (DMSO): 315 (10700). Anal. Found: C, 55.31; H, 4.97; S, 9.59. Calc. for $C_{15}H_{16}CrO_3S$ (328.35): C, 54.86; H, 4.91; S, 9.76%.

*4.5. Attempted cuprate addition to 4; ($\eta^6$-$C_6H_5CH_2C{\equiv}CH)Cr(CO)_3$, (**9**)*

A suspension of 95 mg (0.50 mM) of CuI in 10 ml of THF was cooled to 0 °C under nitrogen. To this suspension 0.62 ml (1.00 mM) of a 1.6 *M* methyllithium solution in ether was added dropwise and stirred for 30 min. After cooling to −40 °C and a solution of 100 mg (0.39 mM) of the allene **4** in 5 ml of THF was added dropwise over 5 min. The reaction mixture was stirred at −40 °C for 60 min before it was allowed to warm to 0 °C and stirring at that temperature was continued for 5 h. After adding 10 ml of a saturated aqueous $NH_4Cl$ solution the aqueous layer was extracted several times with $Et_2O$. The ether layer was washed with water, dried with $MgSO_4$ and the organic

phases were removed in vacuo. The residue was chromatographed on silica gel ($Et_2O$–pentane, 1:3 to $Et_2O$) to give 80 mg (80%) of the alkyne **9** as a yellow oil. $^1$H-NMR (DMSO-$d_6$, 300 MHz): $\delta$ 3.19 (t, 1H, $J = 2.5$ Hz), 3.47 (d, 2H, $J = 2.4$ Hz), 5.56 (t, 1H, $J = 6.2$ Hz), 5.68 (d, 2H, $J = 6.1$ Hz), 5.79 (t, 2H, $J = 6.4$ Hz). $^{13}$C-NMR (DMSO-$d_6$, 75 MHz): $\delta$ 23.36 ($CH_2$), 74.78 ($C_{quat.}$), 79.92 (CH), 93.07 (CH), 93.87 (CH), 95.90 (CH), 110.35 ($C_{quat.}$), 233.93 ($C_{quat.}$).

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 159172 for compound ($\eta^6$-$C_6H_5CH{=}C{=}CH_2)Cr(CO)_3$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

The financial support of the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We wish to express our appreciation to Professor H. Mayr for his generous support.

## References

[1] For a very recent overview on chromiumcarbonyl arene chemistry see, e.g. H.G. Schmalz, S. Siegel, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 1, Wiley–VCH, Weinheim, 1998, p. 550.

[2] (a) For excellent reviews for nucleophilic additions see, e.g. M.F. Semmelhack, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, Oxford, 1995, p. 979;
(b) For ring lithiations see, e.g. M.F. Semmelhack, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, Oxford, 1995, p. 1017;
(c) For side chain activation see, e.g. S.G. Davies, T.D. McCarthy, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, Oxford, 1995, p. 1039;
(d) For stabilization of positive charge in the benzylic positions see, e.g. S.G. Davies, T.J. Donohoe, Synlett (1993) 323.

[3] For neighboring group participation by chromium in substitutions at β- and γ-positions in the side chain see C.A. Merlic, M.M. Miller, Organometallics 20 (2001) 373.

[4] A. Ceccon, A. Gambaro, A. Venzo, J. Organomet. Chem. 275 (1985) 209.

[5] S.G. Davies, S.J. Coote, C.L. Goodfellow, in: L.S. Liebeskind (Ed.), Advances in Metal-Organic Chemistry, vol. 2, JAI Press, London, 1991, p. 1.

[6] (a) M.F. Semmelhack, W. Seufert, L. Keller, J. Am. Chem. Soc. 102 (1980) 6584.
(b) M. Uemura, T. Minami, Y. Hayashi, J. Chem. Soc., Chem. Commun. (1984) 1193. An interesting novel approach utilizes samarium iodide induced SET processes for radical additions to styrene complexes followed by the reduction of the benzylic radical to the benzylic anion, see, e.g.
(c) H.-G. Schmalz, S. Siegel, D. Bernicke, Tetrahedron Lett. 39 (1998) 6683.
(d) H.-G. Schmalz, S. Siegel, J.W. Bats, Angew. Chem., 107 (1995) 2597.
(e) H.-G. Schmalz, S. Siegel, J.W. Bats, Angew. Chem. Int. Ed. Engl. 34 (1995) 2383.

[7] (a) T.J.J. Müller, M. Ansorge, Chem. Ber./Recueil 130 (1997) 1135;
(b) T.J.J. Müller, M. Ansorge, Tetrahedron 54 (1998) 1457.

[8] For comprehensive reviews of allene chemistry see, e.g. (a) D.R. Taylor, Chem. Rev. 67 (1967) 317;
(b) T.F. Rutledge, Acetylenes and Allenes, Reinhold, New York, 1969, (parts 1–3);
(c) W.T. Brady,in: S. Patai, (Ed.), The Chemistry of Ketenes, Allenes and Related Compounds, Wiley, Chichester, UK, 1980, p. 298 (part 1);
(d) H. Hopf, in: S. Patai (Ed.), The Chemistry of Ketenes, Allenes and Related Compounds, Wiley, Chichester, UK, 1980, p. 779 (part 2);
(e) W. Smadja, Chem. Rev. 83 (1983) 263;
(f) D.J. Pasto, Tetrahedron, 40 (1984) 2805;
(g) H.F. Schuster, G.M. Coppola, in: Allenes in Organic Synthesis, Wiley, Chichester, UK, 1984.

[9] For excellent reviews on enyne and enallene cytostatics see, e.g. (a) K.C. Nicolaou, W.-M. Dai, Angew. Chem. 103 1991 1453 (Angew. Chem. Int. Ed. Engl. 30 (1991) 1387);
(b) K.C. Nicolaou, A.L. Smith, in: P.J. Stang, F. Diederich, Modern Acetylene Chemistry, VCH, Weinheim, 1995, p. 203.

[10] See, e.g. R.W. Saalfrank, A. Welch, M. Haubner, U. Bauer, Liebigs Ann. (1996) 171.

[11] M. Ansorge, K. Polborn, T.J.J. Müller, Eur. J. Inorg. Chem. (1999) 225.

[12] See, e.g. P. Vermeer, J. Meijer, L. Brandsma, Recl. Trav. Chim. Pays-Bas 94 (1975) 112.

[13] (a) J. Tsuji, T. Sugiura, I. Minami, Synthesis (1987) 603;
(b) J. Tsuji, T. Mandai, Angew. Chem. 107 (1995) 2830 (Angew. Chem. Int. Ed. Engl. 34 (1995) 2589).

[14] K. Schlögl, A. Mohar, Monatsh. Chem. 93 (1962) 861.

[15] H.-O. Kalinowski, S. Berger, S. Braun, $^{13}$C-NMR Spektroskopie, Georg Thieme, Stuttgart, 1984, p. 129.

[16] T. Schaefer, S. Kroeker, D.M. McKinnon, Can. J. Chem. 73 (1995) 1478.

[17] D. Gentric, J.-Y. Le Bihan, M.-C. Senechal-Tocquer, D. Senechal, B. Caro, Tetrahedron Lett. 27 (1986) 3849.

[18] (a) R. Gompper, H.-U. Wagner, Angew. Chem. 88 (1976) 389 (Angew. Chem. Int. Ed. Engl. 15 (1976) 321).

[19] The addition of ethyl thiolate to the cyano substituted allene gives rise to the allyl anion which, in turn, is exclusively protonated at the α-position, see e.g. F. Theron, R. Vessiere, Bull. Soc. Chim. Fr. (1968) 2994.

[20] Various editors, Organikum, 14th ed., VEB Deutscher Verlag der Wissenschaften, Berlin, 1993.

[21] T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnett, J.A. Ibers, J. Organomet. Chem. 65 (1974) 253.