The (η^6-benzene)Cr(CO)$_3$-Substituted Propargyl Cation: Spectroscopic Characterization and Reactions of an Ambident Electrophile†

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An (arene)Cr(CO)$_3$-stabilized propargyl cation can be easily generated upon ionization of the propargyl acetate Cr(CO)$_3$(η^6-C$_6$H$_5$)CH(OC(O)CH$_3$)C≡CPh with boron trifluoride. The structure investigation of this π-complex stabilized ambident electrophile by NMR spectroscopy and extended Hückel calculations reveals that the charge density in the propargylic position is higher than in the allenylic position. The rapid formation of the cation can be followed by measuring the UV/vis kinetics for the ionization of the acetate. The cationic species reacts with alcohols to give exclusively propargyl ethers Cr(CO)$_3$(η^6-C$_6$H$_5$)CH(OR)C≡CPh and with thiols to give regioselectively allenyl thioethers Cr(CO)$_3$(η^6-C$_6$H$_5$)CH=C=C(SR)-Ph.

Introduction

The stabilization of carbenium ions by the aid of transition metal π-complexes[1] has not only aroused considerable theoretical interest but has also had an increasing impact on the application in organic syntheses. Taking into account an ideal overlap of filled d-orbitals of the metal fragment, like (arene)Cr(CO)$_3$, (alkyne)Co$_2$(CO)$_6$, or ferrocene, and the vacant p-orbital of the carbenium ion in the α-position with the proper symmetry of the interacting wave functions, a rate-increasing anchimeric assistance of nucleophilic substitutions can be easily explained.[2] Thus, taking advantage of the α-activation, Cr(CO)$_3$-complexed benzyl derivatives can be ionized, spectroscopically studied,[2a,b,g,h] and even isolated.[2c] Therefore, a couple of syntheses have been based upon the stabilization of benzylic cations.[2c,3] In the extensive work of Nicholas the activation of the propargylic position was achieved by attaching a dicobalt hexacarbonyl cluster to a triple bond.[4] The generated propargylic cation stabilized by the adjacent cobalt(0) fragment under simultanous protection of the alkyne can be reacted with a number of nucleophiles giving rise to functionalized propargylic derivatives, interesting building blocks in complex natural product syntheses.[5] Surprisingly, no methodology taking advantage of the delocalization of benzylic charges by a conjugated chain has been investigated so far. In particular, upon ionization, propargylic systems form ambident propargylium−allenylium ions[6] that can be interesting intermediates for more sophisticated arene side chain functionalizations via aryl propargyl or aryl allenyl derivatives. As part of our program initiated to synthesize and to study (arene)Cr(CO)$_3$ complexes bearing π-substituents[7] and to probe their synthetic potential[8] we are particularly interested in conjugated cationic intermediates and their synthetic utility. Here we report on the spectroscopic characterization of a (benzene)Cr(CO)$_3$-stabilized propargylium ion and first nucleophilic trapping reactions.

Results and Discussion

Syntheses. The most efficient way to generate a propargylic cation starts from a propargylic derivative with an appropriate leaving group. Thus, nucleophilic addition of phenyl acetylide (**2**) to (η^6-benzaldehyde)Cr-

† This contribution is dedicated to Prof. Dr. Heinrich Nöth on the occasion of his 70th birthday.

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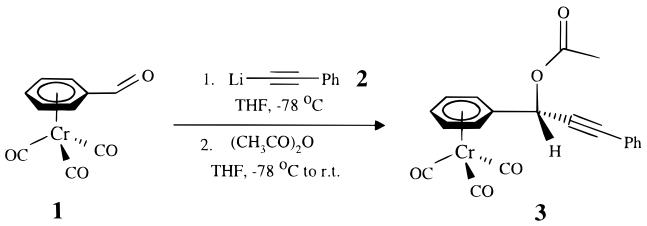
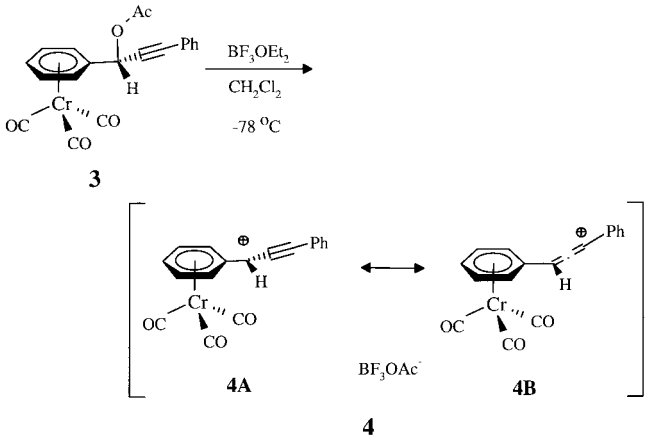
Scheme 1



Scheme 2

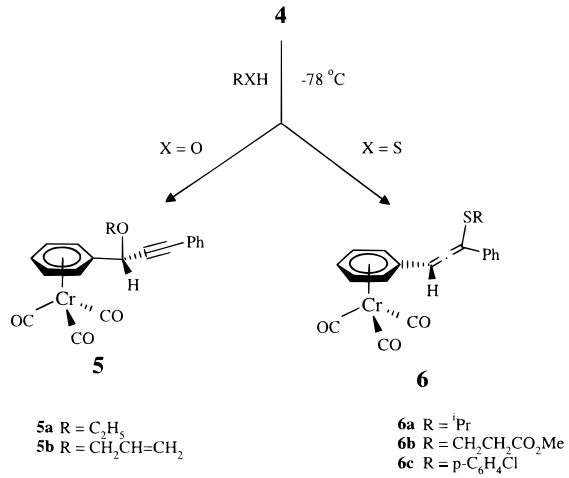


(CO)$_3$ (**1**)[9] at −78 °C in THF followed by the addition of acetic anhydride gives rise to the formation of a (benzene)Cr(CO)$_3$-substituted acetate **3** in excellent yields (Scheme 1).

First experiments showed that the ionization of **3** was smoothly carried out with boron trifluoride etherate in dichloromethane at −78 °C. Remarkably, the color of a solution of **3** changes immediately from light yellow to deep purple red upon the addition of the Lewis acid indicating the formation of a new species, a (benzene)-Cr(CO)$_3$-stabilized propargylium ion **4** (see Scheme 2). After a reaction time of 50 min the trapping alcohol or thiol was added, pure or dissolved in dichloromethane, to the solution of **4** resulting in a rapid color change from deep purple red to yellow. After workup the isolated products (Scheme 3) of the trapping alcohols were exclusively propargyl ethers **5** and those of the thiols were solely allenyl thioethers **6** as indicated by the characteristic appearance of the central allenyl carbon resonances in the ^{13}C NMR spectra between δ = 202 and 208.[10] Although allenes are the expected thermodynamic products,[6] no contamination of either allenes (in the case of **5**) or propargyl derivatives (in the case of **6**) can be detected. Thus, the nucleophilic attack of alcohols or thiols at low temperatures can be regarded as kinetically controlled trapping reactions. Interestingly, in the mass spectra of all propargylic and allenylic derivatives **3**, **5**, and **6** an intense fragment at m/z = 191 can be detected. This stable intermediate can be assigned to the 1,3-diphenylpropargyl cation, i.e., the hydrocarbon ligand of **4**.

^{13}C NMR Spectra of 3 and 4. The spectra (proton-decoupled and DEPT) of the propargylic acetate **3** and the propargylium ion **4** were both recorded at −70 °C

Scheme 3



(Figure 1). An unambiguous assignment of the quaternary resonances of the alkyne carbon atoms of the acetate **3** was based upon a thorough inspection of a selective proton-decoupled spectrum. The major differences in the spectra (Table 1) can be detected in the region of the CO-ligand resonance (Figure 2) and in the region of the complexed arene signals.

As expected, upon ionization, the rotation around the $C_{ipso}-C_\alpha$ bond is restricted due to the back-bonding of the chromium carbonyl tripod to the benzylic carbenium ion (Chart 1). According to molecular orbital calculations on a (η^6-phenyl)Cr(CO)$_3$-substituted propargyl cation at the extended Hückel level[11] the bending of the propargyl fragment by an angle of 10° (22° in the case of the Cr(CO)$_3$-complexed benzyl cation)[2h] toward the chromium carbonyl tripod results in a gain of ≈1.1 kcal/mol (Figure 3). In particular, the principal stabilizing interaction allowing the delocalization of the positive charge onto the Cr(CO)$_3$ fragment mainly stems from the in-phase combination of the vacant p_z orbital of the propargylic carbon atom with the filled $d_{x^2-y^2}$ orbital on the chromium atom (Figure 4). This orbital (HOMO-2) is gradually stabilized as the propargyl moiety bends down toward the tripod (Figure 5). The corresponding out-of-phase combination of the nonbonding propargylic π_z and the chromium $d_{x^2-y^2}$ orbitals is the LUMO (Figure 4), and expectedly, its energy gradually increases as shown in the Walsh diagram (Figure 5). The highest occupied molecular orbitals (HOMO and HOMO-1) display predominantly chromium 3d (d_{z^2} and d_{xy}) and carbonyl π* character and are only affected to a minor extent by the bending of the propargyl fragment. In turn, this back-bonding lowers the pseudo-C_{3v} symmetry of the carbonyl ligands now giving rise to a splitting to 3 CO resonances (Figure 2).

In comparison to the CO signal at δ = 229.4 the resonances at δ = 227.7 and 227.6 experience a considerably larger ionization shift. Therefore, they can be assigned to the CO ligands directly aligned with the *ortho*-carbon atoms in agreement with the charge distribution in arene complexes with electron-withdrawing substituents,[2h,12] i.e., the propargylium substituent.

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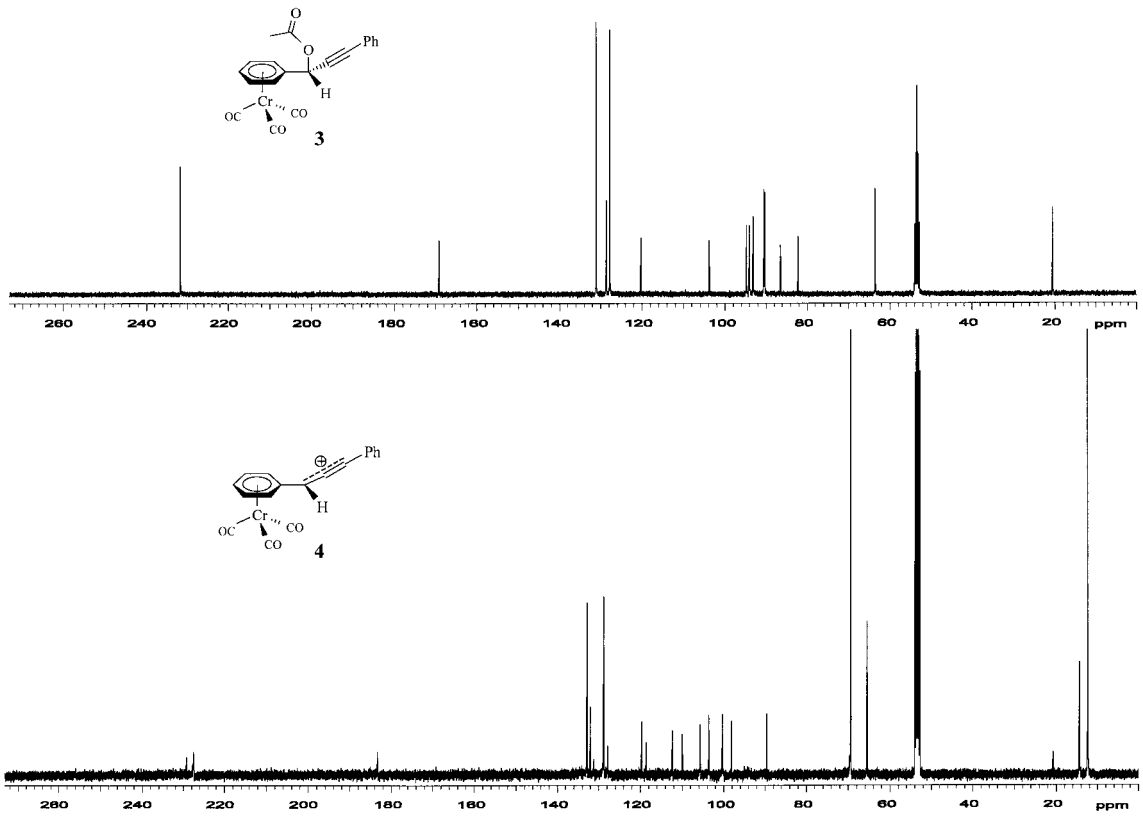

Figure 1. ^{13}C NMR spectra (−70 °C) of **3** (top) and of **4** (bottom).

Table 1. Assignment and Ionization Shifts of Selected ^{13}C NMR Signals (CD_2Cl_2, 100 MHz)

	acetate **3**	cation **4**	ionization shift
carbonyl	231.92	229.4	−2.5
		227.7	−4.2
		227.6	−4.3
ester carbonyl	169.27	183.5	14.2
ortho-phenyl	131.23	132.9	1.7
para-phenyl	128.79	132.2	3.4
meta-phenyl	127.96	128.9	1.0
ipso-phenyl	120.38	119.8	−0.6
ipso-η^6-phenyl	103.98	89.7	−14.3
ortho-η^6-phenyl	94.93	112.4	17.5
para-η^6-phenyl	94.14	103.7	9.56
ortho-η^6-phenyl	93.23	105.8	12.6
meta-η^6-phenyl	90.66	100.5	9.84
meta-η^6-phenyl	90.47	98.3	7.8
C_γ	86.55	118.7	32.1
C_β	82.27	110.1	27.8
C_α	63.69	128.0	64.3
CH_3	20.54	20.9	0.4

All complexed arene carbon signals experience a larger ionization shift than the uncomplexed phenyl carbon resonances at the γ-terminus (Table 1) indicating that the complexed aromatic ring system participates to a larger extent in the charge delocalization. The charge distribution as reflected by the ionization shifts also supports the view that in benzyl cations the *ipso*-carbon atom bears negative charge whereas the *ortho*-, *meta*-, and *para*-positions display less electron density. Additionally, the positive charge is also delocalized by the conjugating π-bridge. All three carbon resonances of the propargyl system are shifted to downfield: C_α appears at $\delta = 128.0$ ($\Delta\delta = 64.3$), C_β at $\delta = 110.1$ ($\Delta\delta = 27.8$), and C_γ at $\delta = 118.7$ ($\Delta\delta = 32.1$). Taking into account the resonance stabilization of a cation by several canonical structures, a major contribution of one resonance hybride can be estimated by applying a simple lever rule model.[13] The complexed benzylic cation **7** was considered as an equivalent for the C_α-localized carbenium ion **4A**, and the complexed styrene **8** serves as a model for an allenylium structure **4B** where the α-carbon does not bear the positive charge (Chart 2). The α-carbon resonances (**4**, $\delta = 128.0$; **7**,[14] $\delta = 126.6$; **8**,[15] $\delta = 133.6$) are substituted in eq 1 to give an 80%

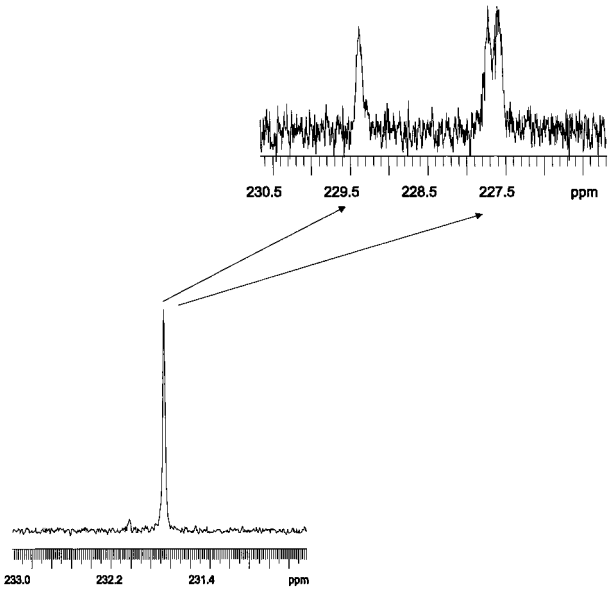

Figure 2. CO resonances of **3** (bottom) and **4** (top).

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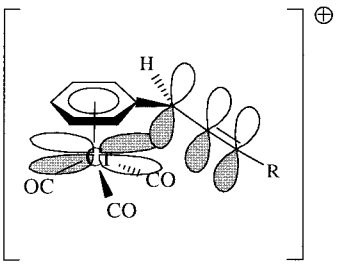
Chart 1



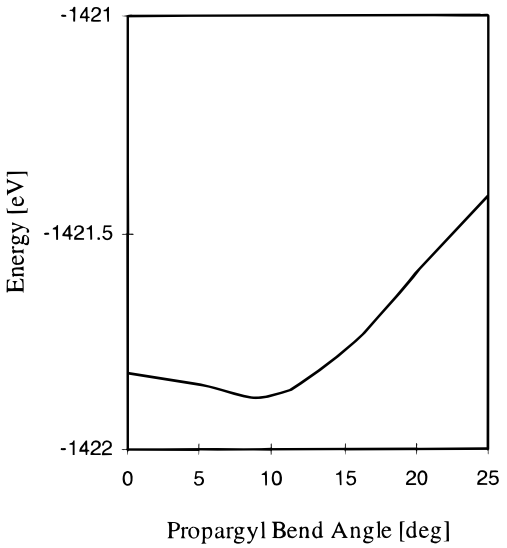


Figure 3.

contribution of the resonance structure **4A** to the stabilization of the cation **4**.

$$\text{relative contribution of } \mathbf{4A} = \frac{\delta(\mathbf{8},C\alpha) - \delta(\mathbf{4},C\alpha)}{\delta(\mathbf{8},C\alpha) - \delta(\mathbf{7},C\alpha)} \cdot 100\% = \frac{133.6 - 128.0}{133.6 - 126.6} \cdot 100\% = 80\% \quad (1)$$

The high positive charge density in the propargylic position is also reflected by the fact that the LUMO coefficient at the propargyl position (according to extended Hückel calculations[11]) is higher than in the allenyl position (Figure 3). Thus, considering the principle of hard and soft acids and bases[16] (HSAB), hard nucleophiles such as alcohols should react in a charge and orbital controlled fashion at the propargylic position whereas softer nucleophiles such as thiols tend to attack the less charged γ- or allenylic position. The product analyses of the nucleophilic trapping experiments with the ambident electrophile **4** just support this qualitative rationale.

UV/Vis Spectra and Ionization Kinetics. The successful NMR studies prompted us to investigate the electronic structure of the cationic intermediate **4**. Furthermore, the study of the ionization by UV/vis spectroscopy could also facilitate the following synthetic work. Upon addition of an excess (16-, 20-, or 40-fold) of a boron trifluoride etherate solution to a dichloromethane solution of **3** at −65 °C a color change from light yellow to deep purple red can be monitored by following the characteristic appearance of a long wavelength absorption band with a maximum at 485 nm (Figure 6). The ionization kinetics were determined by measuring the time-dependent increase of the long wavelength absorption at a wavelength of 485 nm (Table 2). After an induction period the formation of **4** can be described between 3.4 and 7.4 min (after addition of the Lewis acid) by a pseudo-first-order rate law. The evaluation gives for a conversion of 36% and an initial BF_3OEt_2 concentration of 3.2×10^{-3} mol L^{-1} a rate constant $\bar{k} = 2.95 \pm 0.33$ L mol^{-1} s^{-1} and half-life time $\tau_{1/2} = 73.5$ s. In the initial nonlinear phase rapid preequilibria forming Lewis acid adducts from BF_3 and **3** can be assumed which, in turn, decompose to give the title compound **4**. In an ionization interval between 9.4 and 12.3 min ($[\mathbf{3}]_0 = 1.6 \times 10^{-5}$ mol L^{-1}) the reaction converges toward complete formation of **4**.[17]

According to the UV/vis kinetical measurements the cationic species **4** is stable at −70 °C for several hours but readily decomposes on an increase of the temperature over −30 °C. The ambident cation **4** gains its stability to the largest extent by an intense backbonding of the chromium carbonyl tripod. In comparison, the free ligand **9**[18] (Chart 3) does not ionize under comparable circumstances, i.e., in particular, in the presence of the mild Lewis acid boron trifluoride.

Conclusion

NMR and UV/vis studies have shown that chromium carbonyl complexation can be applied to stabilize propargyl cations, an interesting class of ambident electrophiles. This represents an extension of a well-established feature of chromium arene complexes to conjugated side chains. (Arene)$Cr(CO)_3$-substituted propargyl cations such as **4** are stable intermediates that allow a facile access to (arene)$Cr(CO)_3$-substituted propargyl or allenyl derivatives such as **5** or **6**. This possibility implies the application to diastereoselective transformations with planar-chiral arene complexes with propargyl acetate substituents. Further studies directed to screen the scope, the regio- and the diastereoselectivity of the nucleophilic trapping reactions as a novel access to side chain functionalizations are currently underway.

Experimental Section

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.[19] Column chromatography: silica gel 60 (0.063−0.2 mm/70−230 mesh, Firma Merck). TLC: silica gel plates (60 F_{254} Merck, Darmstadt, Germany). Melting points (uncorrected values): Reichert-Jung Thermovar. The benzaldehyde complex **1** was prepared from the benzaldehyde dimethyl acetal complex according to the standard complexation procedure.[20] The trapping nucleophiles were purchased from Merck, Aldrich, or Fluka and used

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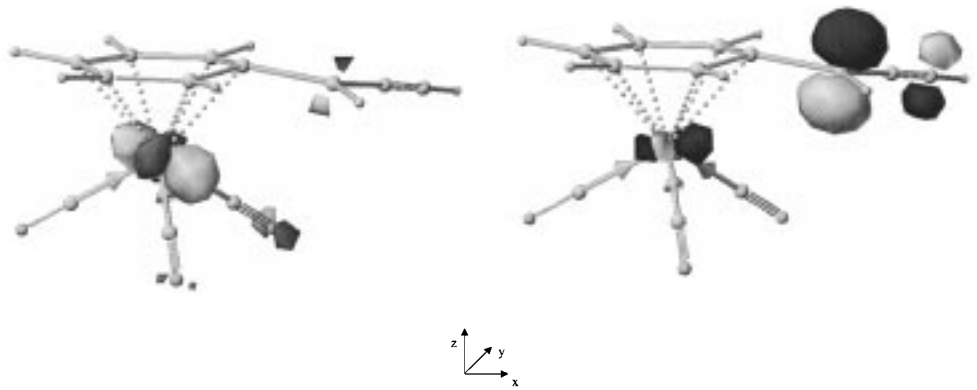


Figure 4. In-phase (HOMO-2, left) and out-of-phase (LUMO, right) combination of the chromium $d_{x^2-y^2}$ and the propargylic p_z/π_z orbitals.

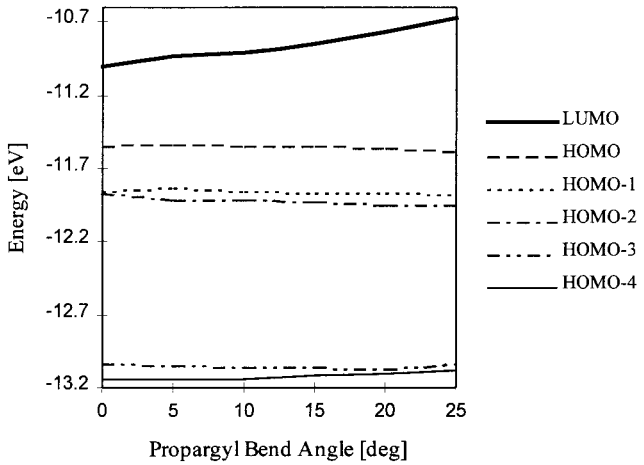


Figure 5.

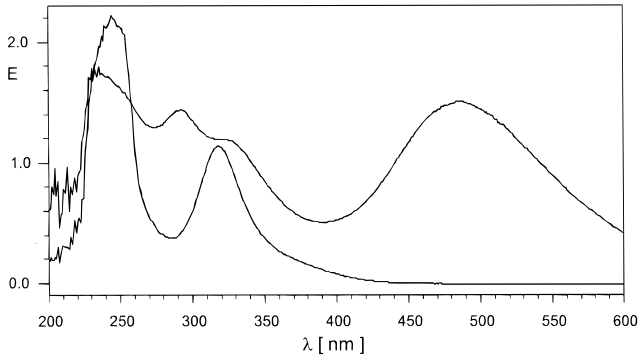
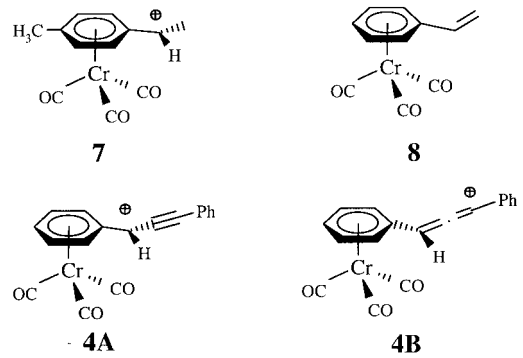


Figure 6. UV/vis spectra of **3** (λ_{max} at 325 nm) and **4** (λ_{max} at 485 nm).

Chart 2



without further purification. ^1H and ^{13}C spectra: Bruker ARX 300, Varian VXR 400S, [D_6]DMSO. IR: Perkin-Elmer FT-IR spectrometer 1000. The samples were pressed into KBr pellets. UV/vis: Perkin-Elmer Models Lambda 16, J&M TIDAS (transputer integrated diode array spectrometer) with a Hellma low-temperature quarz probe. MS: Finnigan MAT 90 and MAT 95 Q. Elemental analyses were carried out in the Microanalytical Laboratory of the Institut für Organische Chemie, Ludwig-Maximilians-Universität München.

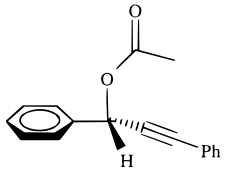
Synthesis of the Acetate 3. To a degassed solution of 0.91 mL (8.29 mmol) of phenylacetylene in 15 mL of THF, cooled to −78 °C, was added dropwise 5.68 mL (9.09 mmol) of a 1.6 M solution of *n*-butyllithium in hexanes. The turbid yellow suspension was stirred at −78 °C for 5 min and was then allowed to warm to room temperature. After being stirred for 80 min at room temperature, the clear yellow solution was cooled again to −78 °C. To the suspension a solution of 2.00 g (8.26 mmol) of benzaldehyde complex in 15 mL of THF was added dropwise. The reaction mixture turned to light orange

Table 2. Kinetics of the Ionization of Acetate 3 with Boron Trifluoride Etherate in Dichloromethane at −65 °C[a]

no.	$10^4[\mathbf{3}]_0$, mol L^{-1}	$10^3[BF_3OEt_2]_0$, mol L^{-1}	k, L mol^{-1} s^{-1}
1	1.60	2.61	3.13
2	1.60	2.61	2.58
3	1.59	3.16	2.66
4	1.58	3.15	3.36
5	1.59	6.25	3.00

[a] The kinetics of each measurement were evaluated according to a pseudo-first-order rate law to give the average rate constant $\bar{k} = 2.95 \pm 0.33$ L mol^{-1} s^{-1}; thus with $[BF_3OEt_2]_0 = 3.2 \times 10^{-3}$ mol L^{-1} the half-lifetime can be calculated to $\tau_{1/2} = \ln 2/(\bar{k}[BF_3OEt_2]_0) = 73.5$ s.

Chart 3



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and was stirred at that temperature for 2 h. Then a solution of 1.8 mL (19 mmol) of acetic anhydride in 3 mL of THF was added dropwise to the solution and the mixture was stirred for 100 min at −78 °C. The dry ice/acetone bath was removed, and 50 mL of water was added. The reaction mixture was allowed to come to room temperature. After several extractions with diethyl ether the combined organic phases were washed with a 5% sodium hydrogen carbonate solution and then dried over magnesium sulfate. After evaporation of the solvents in vacuo the residue crystallized at −20 °C in the refrigerator and recrystallized from diethyl ether/pentane to

give 2.75 g (86%) of pure acetate complex as yellow crystals. Mp: 95−97 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 2.12 (s, 3 H), 5.66−5.73 (m, J = 6.7 Hz, 2 H), 5.80 (m, 1 H), 6.02 (d, J = 6.4 Hz, 1 H), 6.08 (d, J = 6.4 Hz, 1 H), 6.40 (s, 1 H), 7.40−7.51 (m, 5 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 20.70 (CH_3), 63.97 (CH), 84.41 ($C_{quat.}$), 87.09 ($C_{quat.}$), 93.28 (CH), 94.91 (CH), 96.04 (CH), 107.31 ($C_{quat.}$), 121.05 ($C_{quat.}$), 128.95 (CH), 129.72 (CH), 131.91 (CH), 169.24 ($C_{quat.}$), 233.26 ($C_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 386 (M^+, 1), 330 (M^+ − 2CO, 11), 302 (M^+ − 3CO, 100), 243 ($C_{15}H_{11}Cr^+$, 14), 191 (C_6H_5-$CHCCC_6H_5^+$, 48). IR (KBr): $\bar{\nu}$ = 2236, 1981, 1906, 1744 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 317 nm (10 400). Anal. Calcd for $C_{20}H_{14}CrO_5$ (386.3): C, 62.18; H 3.65. Found: C, 61.98; H, 3.68.

Generation of the Cation and Nucleophilic Trapping Reactions (General Procedure, GP). To a solution of the acetate **3** in 18 mL of dichloromethane, cooled to −78 °C, was added dropwise 1.4 equiv of boron trifluoride etherate. The purple red solution was stirred at −78 °C for 50 min, and then the desired nucleophile was added dropwise in substance or dissolved in dichloromethane to the solution of the cation. The color of the solution turns from purple red to yellow, and the reaction mixture was stirred at the times indicated. Then 20 mL of diethyl ether and 20 mL of water were added successively to the reaction mixture which was subsequently allowed to come to room temperature. After several extractions with diethyl ether the combined organic phases were dried over magnesium sulfate. The solvents were evaporated in vacuo, and the residue was either recrystallized from diethyl ether/pentane or purified by flash chromatography to give pure allenyl or propargyl derivatives.

Cr(CO)$_3$(η^6-C$_6$H$_5$)CH(OC$_2$H$_5$)C≡CPh (5a). According to the GP 100 mg (0.26 mmol) of **3** was ionized and allowed to react for 15 min with 0.5 mL (8.6 mmol) of ethanol. After workup the crude product was purified by flash chromatography on silica gel (1:4 diethyl ether/pentane) to give 50 mg (52%) of pure **5a** as a yellow oil which crystallizes from pentane as a light yellow solid. Mp: 67 °C. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 1.19 (t, J = 6.8 Hz, 3 H), 3.62−3.66 (m, 1 H), 3.78−3.82 (m, 1 H), 5.25 (s, 1 H), 5.70−5.73 (m, 3 H), 5.93 (d, J = 6.1 Hz, 1 H), 5.97 (d, J = 5.8 Hz, 1 H), 7.41 (m, 3 H), 7.50 (m, 2 H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 15.09 (CH_3), 64.33 (CH_2), 69.59 (CH), 85.87 ($C_{quat.}$), 87.26 ($C_{quat.}$), 93.77 (CH), 93.82 (CH), 94.23 (CH), 95.34 (CH), 95.54 (CH), 110.06 ($C_{quat.}$), 121.58 ($C_{quat.}$), 128.83 (CH), 129.27 (CH), 131.72 (CH), 233.52 ($C_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 372 (M^+, 9), 316 (M^+ − 2CO, 7), 288 (M^+ − 3CO, 15), 244 ($C_{15}H_{12}Cr^+$, 100), 191 (C_6H_5-$CHCCC_6H_5^+$, 18), 52 (Cr^+, 20). IR (KBr): $\bar{\nu}$ = 1965, 1894, 1886 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 313 nm (10 800). Anal. Calcd for $C_{20}H_{16}CrO_4$ (372.3): C, 64.52; H, 4.33. Found: C, 64.74; H, 4.38.

Cr(CO)$_3$(η^6-C$_6$H$_5$)CH(OCH$_2$CH=CH$_2$)C≡CPh (5b). According to the GP 200 mg (0.52 mmol) of **3** was ionized and allowed to react for 60 min with 0.10 mL (1.46 mmol) of allyl alcohol. After workup the crude product was purified by flash chromatography on silica gel (1:3 diethyl ether/pentane) to give 122 mg (61%) of pure **5b** as a yellow orange oil.

^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 4.19 (s, 1 H), 4.30 (s, 1 H), 5.20−5.37 (m, 4 H), 5.72 (m, 3 H), 5.94−5.99 (m, 2 H), 7.41−7.52 (m, 5 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 69.3 (CH), 69.6 (CH_2), 85.4 ($C_{quat.}$), 87.6 ($C_{quat.}$), 93.6 (CH), 94.3 (CH), 95.4 (CH), 95.6 (CH), 109.5 ($C_{quat.}$), 117.5 (CH_2), 121.5 ($C_{quat.}$), 128.8 (CH), 129.3 (CH), 131.8 (CH), 134.4 (CH), 233.5 ($C_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 384 (M^+, 4), 328 (M^+ − 2CO, 5), 300 (M^+ − 3CO, 11), 244 ($C_{15}H_{12}Cr^+$, 100), 243 ($C_{15}H_{11}Cr^+$, 7), 191 ($C_6H_5CHCCC_6H_5^+$, 17), 52 (Cr^+, 29). IR (KBr): $\bar{\nu}$ = 1966, 1887, 1738 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 316 nm (9980). Anal. Calcd for $C_{21}H_{16}CrO_4$ (384.4): C, 65.62; H, 4.20. Found: C, 66.18; H, 4.32.

Cr(CO)$_3$(η^6-C$_6$H$_5$)CH=C=C[SCH(CH$_3$)$_2$]Ph (6a). According to the GP 150 mg (0.39 mmol) of **3** was ionized and allowed to react for 30 min with 0.08 mL (0.85 mmol) of 2-propanethiol. After workup the crude product was purified by flash chromatography on silica gel (1:2 diethyl ether/pentane) and recrystallization from pentane gave 112 mg (72%) of pure **6a** as a yellow powder. Mp: 97−98 °C. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 1.27 (d, J = 6.8 Hz, 3 H), 1.30 (d, J = 6.6 Hz, 3 H), 3.15 (m, 1 H), 5.72−5.79 (m, 3 H), 5.86 (d, J = 6.2 Hz, 1 H), 5.92 (d, J = 6.3 Hz, 1 H), 7.09 (s, 1 H), 7.30 (t, J = 6.9 Hz, 1 H), 7.36−7.43 (m, 4 H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 22.90 (CH_3), 23.12 (CH_3), 37.92 (CH), 93.21 (CH), 94.34 (CH), 94.42 (CH), 94.65 (CH), 101.17 (CH), 103.65 ($C_{quat.}$), 105.44 ($C_{quat.}$), 127.56 (CH), 128.50 (CH), 129.16 (CH), 132.37 ($C_{quat.}$), 204.61 ($C_{quat.}$), 233.66 ($C_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 402 (M^+, 4), 346 (M^+ − 2CO, 12), 318 (M^+ − 3CO, 44), 244 ($C_{15}H_{12}Cr^+$, 100), 243 ($C_{15}H_{11}Cr^+$, 6), 191 ($C_6H_5CHCCC_6H_5^+$, 50), 52 (Cr^+, 22). IR (KBr): $\bar{\nu}$ = 1964, 1901, 1875 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 319 nm (10 300). Anal. Calcd for $C_{21}H_{18}CrO_3S$ (402.4): C, 62.69; H, 4.51; S, 7.97. Found: C, 62.85; H, 4.76; S, 8.05.

Cr(CO)$_3$(η^6-C$_6$H$_5$)CH=C=C(SCH$_2$CH$_2$CO$_2$CH$_3$)Ph (6b). According to the GP 150 mg (0.39 mmol) of **3** was ionized and allowed to react for 50 min with 0.11 mL (0.85 mmol) of methyl 3-mercaptopropionate. After workup the crude product was purified by flash chromatography on silica gel (1:5−1:1 diethyl ether/pentane) to give 129 mg (74%) of pure **6b** as a yellow oil. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 2.64 (m, 2 H), 2.92 (m, 2 H), 3.52 (s, 3 H), 5.74−5.78 (m, 2 H), 5.81 (m, 1 H), 5.87 (m, 2 H), 7.15 (s, 1 H), 7.33−7.40 (m, 5 H). ^{13}C NMR ([D$_6$]-DMSO, 75 MHz): δ = 28.0 (CH_2), 33.6 (CH_2), 51.8 (CH_3), 93.1 (CH), 93.2 (CH), 94.5 (CH), 94.6 (CH), 94.7 (CH), 103.2 (CH), 104.7 ($C_{quat.}$), 105.0 ($C_{quat.}$), 127.6 (CH), 128.8 (CH), 129.3 (CH), 132.5 ($C_{quat.}$), 171.1 ($C_{quat.}$), 202.3 ($C_{quat.}$), 233.7 ($C_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 446 (M^+, 2), 362 (M^+ − 3CO, 51), 310 (M^+ − Cr(CO)$_3$, 1), 244 ($C_{15}H_{12}Cr^+$, 70), 243 ($C_{15}H_{11}Cr^+$, 12), 191 ($C_6H_5CHCCC_6H_5^+$, 100), 52 (Cr^+, 25). IR (KBr): $\bar{\nu}$ = 1965, 1887, 1732 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 318 nm (9400). Anal. Calcd for $C_{22}H_{18}CrO_5S$ (446.4): C, 59.19; H, 4.06; S, 7.18. Found: C, 59.45; H, 4.17; S, 7.01.

Cr(CO)$_3$(η^6-C$_6$H$_5$)CH=C=C(S-*p*-C$_6$H$_4$Cl)Ph (6c). According to the GP 100 mg (0.26 mmol) of **3** was ionized and allowed to react for 90 min with 85 mg (0.59 mmol) of *p*-chlorothiophenol. After workup the crude product was purified by crystallization from diethyl ether/pentane to give 98 mg (80%) of pure **6c** as yellow crystalls. Mp: 85 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.72−5.78 (m, 3 H), 5.92 (m, 2 H), 7.08 (s, 1 H), 7.34−7.39 (m, 7 H), 7.49 (d, J = 8.4 Hz, 2 H). ^{13}C NMR ([D$_6$]-DMSO, 75 MHz): δ = 93.3 (CH), 94.5 (CH), 94.6 (CH), 100.5 (CH), 102.6 ($C_{quat.}$), 104.2 ($C_{quat.}$), 127.7 (CH), 128.8 (CH), 129.2 (CH), 129.5 (CH), 131.4 ($C_{quat.}$), 132.1 (CH), 132.5 ($C_{quat.}$), 132.6 ($C_{quat.}$), 208.1 ($C_{quat.}$), 233.6 ($C_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 472, 470 (M^+, 4, 10), 388, 386 (M^+ − 3CO, 44, 100), 336, 334 (M^+ − Cr(CO)$_3$, 2, 5), 244 ($C_{15}H_{12}Cr^+$, 28), 243 ($C_{15}H_{11}$-Cr^+, 17), 191 ($C_6H_5CHCCC_6H_5^+$, 93), 52 (Cr^+, 43). IR (KBr): $\bar{\nu}$ = 1966, 1883 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 320 nm (11200). Anal. Calcd for $C_{24}H_{15}ClCrO_3S$ (470.9): C, 61.22; H, 3.21; S, 6.81; Cl, 7.53. Found: C, 61.45; H, 3.24; S, 6.86; Cl, 7.22.

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