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The deviating behavior of thiols in nucleophilic trapping reactions of chromiumcarbonyl phenyl complex substituted propargyl cation

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Abstract

The (phenyl)$Cr(CO)_3$-complex substituted propargyl cation **4** significantly deviates in the chemoselectivity of the nucleophilic attack of thiols from the previously reported planar chiral *ortho*-substituted arene complexes and furnishes allenyl thioethers **5**. This peculiar behavior can be rationalized assuming a subsequent base catalyzed propargyl–allenyl isomerization in acidic medium (!). An X-ray structure analysis of allenyl thioether **5c** recrystallized from acetonitrile over weeks reveals that the [2 + 2] cyclodimer **10** has been formed. Thiolate adds to **5c** to give a single diastereomer of the allyl compound **15** in good yield.

Keywords: Allenylation; Arene complexes; Chromium; Cycloaddition; Isomerization

1. Introduction

The advent of transition metal π-complex stabilized α-carbenium ions [1] has revolutionized the synthetic application of often elusive reactive carbocation intermediates, in particular, in stereoselective nucleophilic additions with retention of configuration. Among transition metal π-complex stabilized carbenium ions the most prominent representatives are ferrocenyl-, (alkyne)$Co_2(CO)_6$-, or (arene)$Cr(CO)_3$-substituted carbocations [1]. A pronounced neighboring group effect arising from an ideal overlap of occupied d-orbitals on the metal and the vacant p-orbital at the carbenium center in α-position also rationalizes the conservation of the stereochemical information at the previous sp^3-center as a consequence of an overall retention of configuration due to a double inversion mechanism [1c,1d,1f]. In particular, chromiumcarbonyl complexed benzylic cations [2] have found applications in asymmetric organic syntheses [1f] [3]. According to calculations at different levels of theory for chromium carbonyl complexed benzyl cations the carbenium center is significantly distorted from coplanarity with the phenyl ring upon bending towards the metal center [2d,2e] [4]. Since ionizations of propargyl precursors form ambident propargyl cations [5] that can be interesting intermediates for more sophisticated arene sidechain functionalizations via aryl propargyl or allenyl derivatives, we have initiated a program to investigate (arene)$Cr(CO)_3$-complexes bearing π-substituents, [6] particularly propargyl cations [7]. In kinetic studies we could determine the electrophilic reactivity of a (arene)$Cr(CO)_3$-complex substituted propargyl cation **1** ($R^1 = H$; $R^2 = Ph$) revealing that this system is by two orders of magnitude more reactive than the comparable Nicholas' cation **2** (R^1, $R^3 = H$; $R^2 = Ph$) [8] (Plate 1).

Recently, we have reported the regio- and diastereoselective addition of nucleophiles to planar chiral complex substituted α-propargyl cations furnishing propargyl derivatives [9]. Most interestingly, the chemoselectivity of the trapping reaction of thiols to the parent system **1** ($R^1 = H$, $R^2 = Ph$) deviates significantly from the *ortho*-substituted cases and leads to the formation of allenyl thioethers [10]. Now, in the light of nucleophilic addition-isomerization sequences [11], we wish to elucidate this peculiar allene formation and disclose a representative [2 + 2]-cycloaddition as well as a nucleophilic addition to these novel organometallic allenes.

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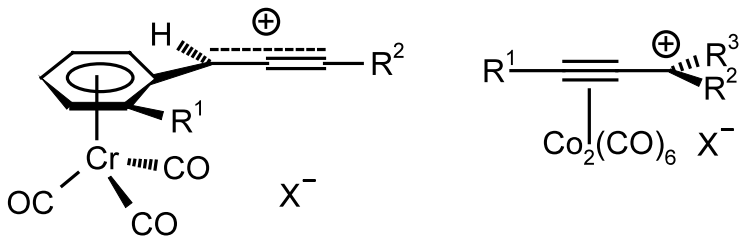


1 2

Plate 1.

2. Results and discussion

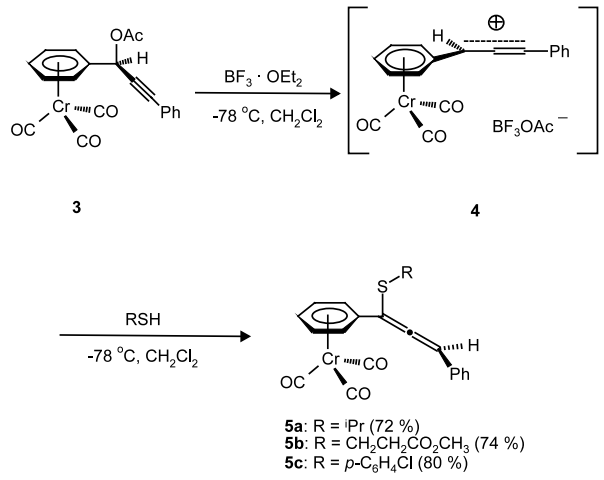
According to our general protocol the ionization of the racemic (phenyl)$Cr(CO)_3$-complex substituted propargyl acetate **3** furnishes quantitatively the propargyl cation **4** (i.e. **1** with $R^1 = H$, $R^2 = Ph$) at -78 °C in dichloromethane [7a]. The addition of a slight excess of the trapping thiols now gives rise to the formation of the allene derivatives **5** as racemic mixtures in good yields (Scheme 1).

Neither the ester functionality (**5b**) nor the aromatic substituent (**5c**) interfere with the chemoselectivity of this allenylation reaction. Characteristically, the central allenyl carbon resonances in the ^{13}C-NMR spectra of the allenes **5** appear between δ 202 and 208 [12]. Most interestingly, the nucleophilic attack of the thiols has obviously occurred at the α-position as shown by NOESY and selectively ^{1}H-decoupled ^{13}C-NMR spectra indicating a close spatial proximity of the allene proton and the *ortho*-protons on the terminal phenyl substituent (Scheme 2).

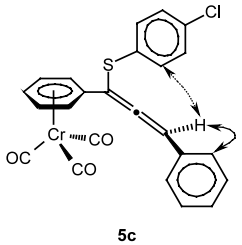
Interestingly, in all mass spectra of the allene derivatives **5** an intense fragment at $m/z = 191$ can be detected. This stable intermediate can be assigned to the 1,3-diphenyl propargyl cation, i.e. the hydrocarbon ligand of **4**.

Mechanistically, this process can be regarded as a nucleophilic addition-isomerization sequence and is related to our recent findings on the trapping reactions with triphenylphosphane [11]. Therefore, the following mechanistic scenario can be plausibly rationalized. The nucleophilic attack of the thiol occurs at the α-position to give the propargylated intermediate **6** (Scheme 3) in agreement with the findings from the diastereoselective propargylation studies with planar chiral complex substituted propargyl cations. Thioethers, however, are sufficiently Lewis basic so that a Lewis acid–base adduct **7** can be easily formed. As in the case of the phosphane adducts a subsequent isomerization can proceed through a propargyl anion [13] in the sense of a base catalyzed propargyl–allenyl isomerization if the chromiumcarbonyl complexed arene substituent can efficiently exert its amphoteric nature, i.e. in this case the stabilization of an adjacent anion. Thus, upon rotation of **7** an *anti*-periplanar alignment of the propargyl proton and the electron withdrawing chromiumcarbonyl tripod enhances the kinetic acidity of this propargyl proton now being stereoelectronically activated by two electron withdrawing substituents, the arene complex fragment and the sulfonium yield moiety. As a consequence, the deprotonation with any weakly basic molecule furnishes the reasonably stabilized propargyl anion **8** that is subsequently protonated to give after decoordination of the activating Lewis acid the thermodynamically more stable allene derivative **5**.

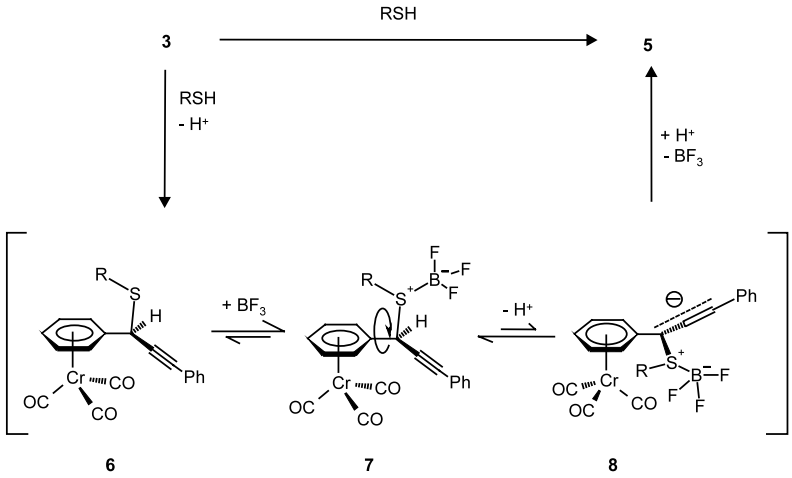
Hence, the question arises why this peculiar isomerization does not proceed in the case of *ortho*-substituted



Scheme 1.



Scheme 2. Selected nOe contacts (dotted line: weak contact) in the spectrum of **5c**



Scheme 3.

aryl complexed propargyl cations [9]. According to the postulated mechanistic rationale the crucial *anti*-periplanar conformation necessary for a kinetically controlled deprotonation can only be populated through an unhindered rotation of the Lewis acid–base adduct **7**. However, in the case of thiol adducts to *ortho*-substituted aryl complexed propargyl cations the rotation around the C_{ipso}–C_{α} bond in the resulting adduct **9** is massively hampered and, thus, the base-catalyzed subsequent isomerization is not feasible (Plate 2).

In crystallization attempts from various solvents and solvent mixtures in order to grow suitable crystals for an X-ray structure analysis of the organometallic allenes **5** we observed that compound **5c** only slowly forms red plates in acetonitrile as a solvent (recrystallization from diethylether or dichloromethane only gives yellow crystals of **5c** in poor quality) [14]. Most interestingly, the X-ray structure analysis of presumed compound **5c** (Fig. 1, Table 1) showed clearly that after several weeks a dimerization and crystallization at low temperatures (+4 °C refrigerator temperature) had taken place (Scheme 4).

A closer inspection of the bond distances and angles as well as the stereochemistry identifies compound **10** as a 1,2-bis(methylidene)cyclobutane derivative as a result of a [2 + 2]-cycloaddition of two molecules of **5c** with the same configuration. Most surprisingly, the bis(-methylidene)cyclobutane **10** is formed as a racemic mixture of a single diastereomer (out of eight possible racemic pairs of diastereomers) indicating a highly stereoselective cycloaddition. This reaction is additionally favored in a dipolar aprotic solvent and can be attributed to a more or less polar transition state. Assuming a concerted [2 + 2]-cycloaddition the transition state leading to the formation of **10** is best described by a mutually orthogonal arrangement of an internal allene double bond of the first molecule and a terminal allene double bond of its reaction partner (Scheme 5).

It is noteworthy to mention that out of eight racemic diastereomers only those four with a *s-anti* configuration of the non-complexed phenyl ring at the double bond can be realized assuming minimal steric interac-

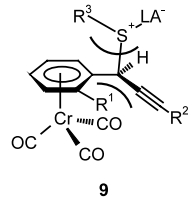


Plate 2.

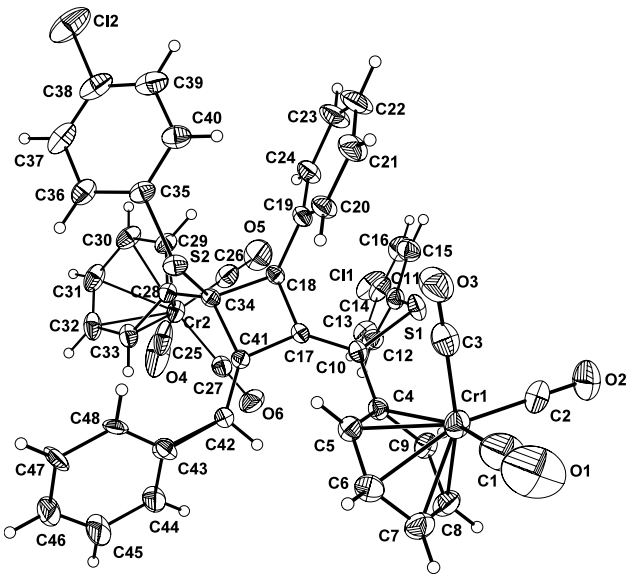
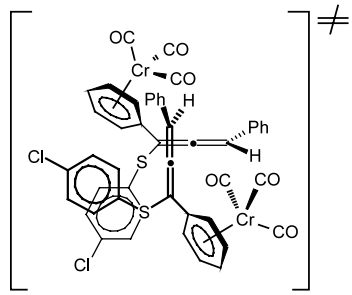


Fig. 1. ORTEP plot of **10**. Selected bond lengths [Å], angles [°] and dihedral angles [°]: C(34)-C(18): 1.589, C(18)–C(17): 1.507, C(17)–C(41): 1.454, C(34)–C(41): 1.542, C(17)–C(10): 1.341, C(41)–C(42): 1.336, C(17)–C(18)–C(34): 87.49, C(18)–C(34)–C(41): 87.00, C(18)–C(17)–C(41): 93.42, C(18)–C(34)–C(41)–C(42): 166.50, C(10)–C(17)–C(41)–C(42): 16.75.

Table 1
Crystal data and structure refinements for **10**

	10
Empirical formula	$C_{48}H_{30}Cl_2Cr_2O_6S_2$
Formula weight	941.74
Temperature (K)	293(2)
Radiation (Å)	0.71073
Crystal system	Anorthic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	12.154(3)
b (Å)	12.414(5)
c (Å)	15.635(7)
α (°)	84.37(3)
β (°)	72.79(3)
γ (°)	76.21(3)
Volume (Å^3)	2187.5(14)
Z	2
D_{calc} (g/cm^{-3})	1.430
Absorption correction	φ-scans
Absorption coefficient (mm^{-1})	0.763
Max/min transmission	–
F(000)	960
Crystal size (mm)	$0.40 \times 0.40 \times 0.27$
θ range (min/max) (°)	2.73–23.98
Index ranges	$-13 \leq h \leq 13$
	$-14 \leq k \leq 14$
	$-0 \leq l \leq 17$
Reflections collected	7116
Independent reflections	6829 [R(int) = 0.0145]
Reflections observed	6829 [$I > 2\sigma$(I)]
Refinement method	SHELXL-93 on F^2
Data/restraints/parameters	6829/2/561
Goodness of fit on F^2	1.086
Final R indices [$I > 2\sigma(I)$]	
R_1	0.0504
wR_2	0.1090
R indices (all data)	
R_1	0.0790
wR_2	0.1249
Largest difference peak and hole (e Å^{-3})	0.455 and −0.326

tions in the transition state and in the product (Scheme 6). Considering the relative heats of formation according to calculations on the diastereomeric structures **10** to **13** on the extended Hückel level of theory [15] and assuming a late polar transition state for the [2 + 2] cycloaddition only structure **10** can be formed under the observed conditions.

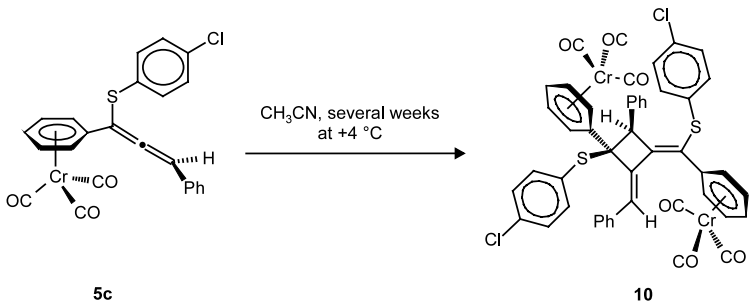


Scheme 5.

Since allenes are an interesting class of unsaturated compounds in the field of preparative chemistry [16] we are intrigued to study nucleophilic additions at organometallic allenes like **5** [17]. Upon addition of allene **5c** to a solution of sodium isopropyl thiolate a color change from yellow to orange indicates the formation of an intermediate with extended π-conjugation presumably the allyl anion **14** (Scheme 7). Aqueous workup of this solution furnishes the allyl derivative **15** as yellow needles in 78% yield as a single diastereomer.

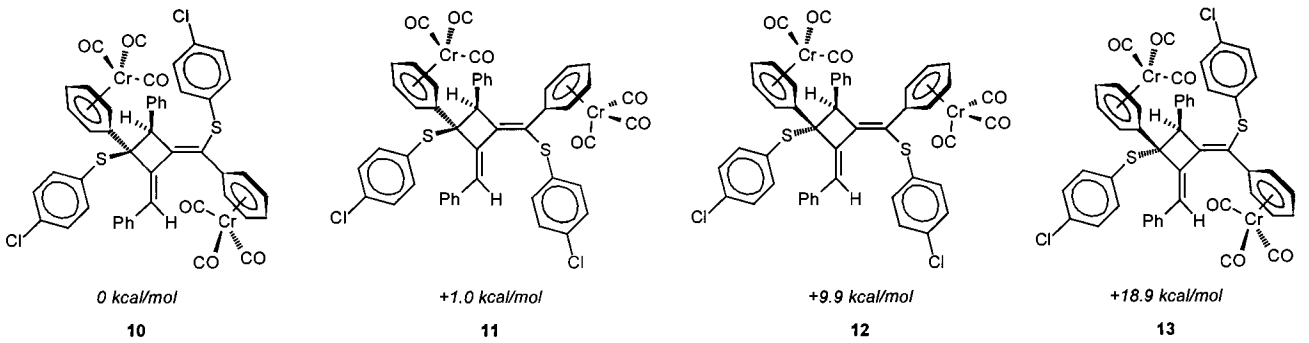
According to NOESY and HETCOR-NMR spectra of **15** the α-allyl proton adjacent to the phenyl chromiumcarbonyl and the aryl thioether unambiguously establishes the regiochemistry of the protonation of the allyl anion **14** and the Z-configuration of the double bond can be readily assigned by several diagnostic nOe (*n*uclear *O*verhauser *e*ffect) contacts (Scheme 8).

The terminating and highly regioselective protonation of the allyl anion is in agreement with the principle of allopolarization [18] where the electrophilic attack at α-acceptor substituted allyl anions preferentially occurs at the α-position, thus, furnishing a non-conjugated regioisomer. However, the highly stereoselective formation of the trisubstituted double bond with Z-configuration is accomplished in the nucleophilic addition step to **5c** in the sequence. According to calculations on the extended Hückel level of theory [15] the energy difference between the Z-configured isomer **15** and the E-configured diastereomer **19** is too small to explain the pronounced stereoselectivity (Scheme 9). Thus, each

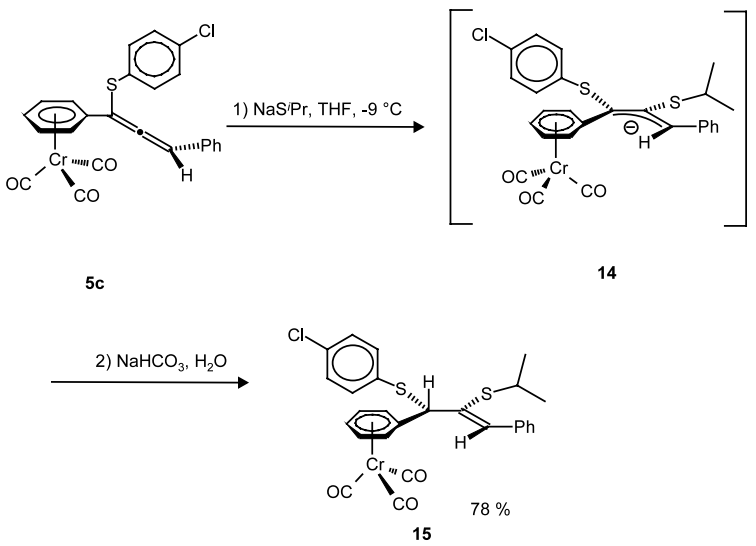


5c **10**

Scheme 4.



Scheme 6. Extended Hückel calculations on the four most probable cycloadduct diastereomers.

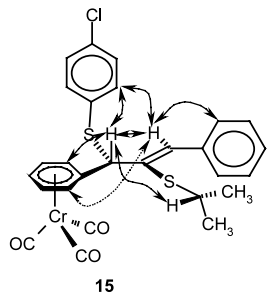


Scheme 7.

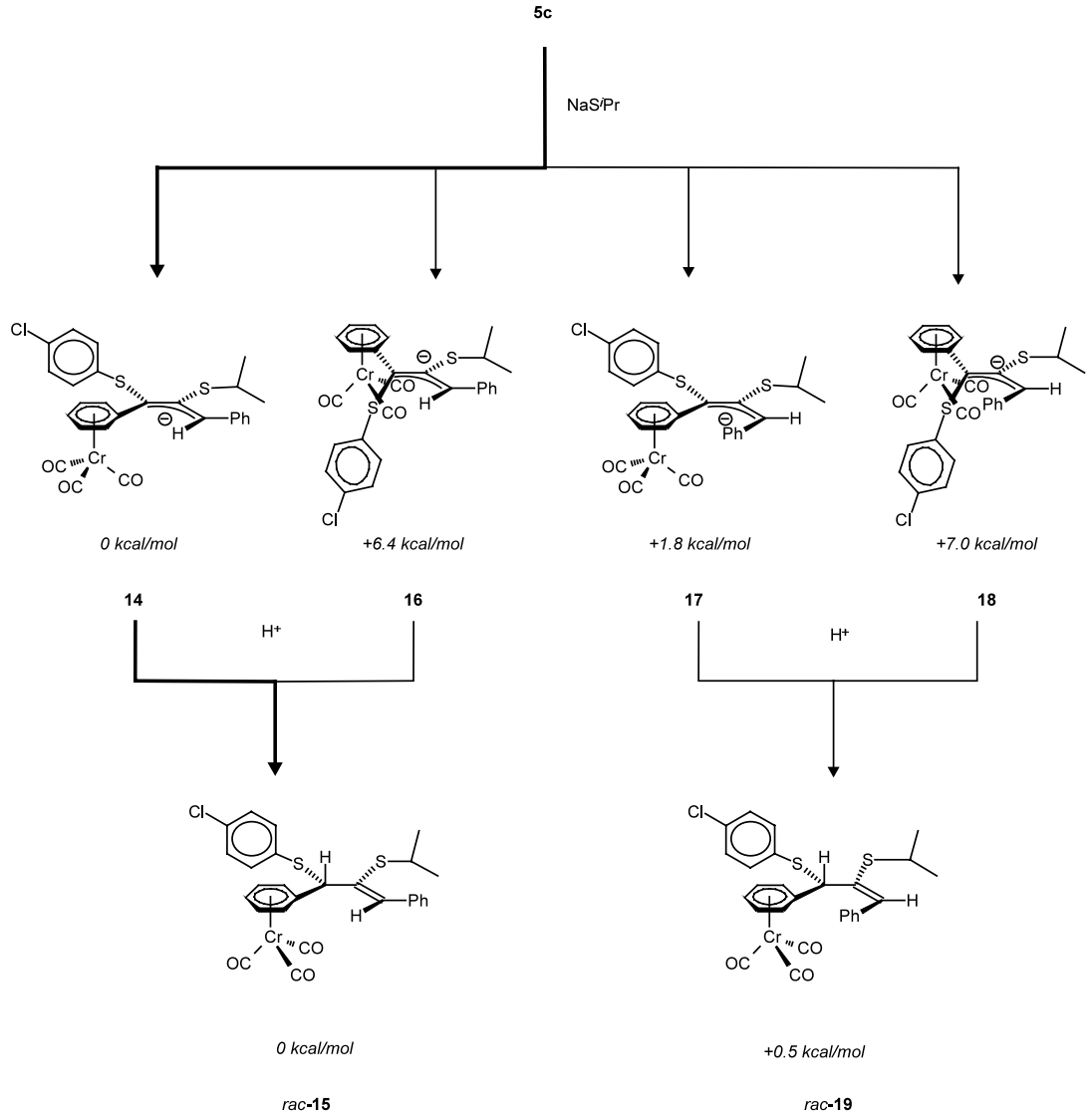
allyl product can be derived from two corresponding allyl anions. The inspection of the stereochemical correlation shows that the observed product **15** is formed by protonation of either allyl anion **14** or **16**. In turn, the hypothetical *E*-isomer is deduced from the protonation of the allyl anions **17** and **18**. The extended Hückel calculations [15] on the four diastereomeric allyl anions **14**, **16**, **17**, and **18** reveal that the most stable allyl anion in this series is **14**. Therefore, the stereochemical outcome of this addition-protonation sequence is determined by its stereochemistry in the initial nucleophilic addition of the thiolate to the allene giving rise to the highly stereoselective generation of the allyl anion **14**. Finally, the regioselective protonation at the α-position is achieved and concludes this sequence.

3. Conclusion

In conclusion we have explained the deviating behavior of thiols in the nucleophilic trapping reactions with the (phenyl)chromiumcarbonyl-substituted propargyl cation furnishing allenes instead of propargyl derivatives. This peculiar sequence is related to previously reported addition-isomerization sequences of phosphanes and is caused by the synergism of an anion-stabilizing substituent and the amphoteric (phenyl)-chromiumcarbonyl fragment [11]. Two representative reactions, i.e. a thermal [2 + 2]-cycloaddition at low temperature in a polar solvent and a nucleophilic thiolate addition have shown that these organometallic



Scheme 8. Selected nOe contacts (dotted line: weak contact) in the spectrum of **15**.



Scheme 9. Extended Hückel calculations on the four allyl anion diastereomers **14**, **16**, **17**, and **18** (relative energies) and the two allyl derivatives **15** and **19** (relative energies).

allenes behave largely like related organic compounds. Most significantly, the (phenyl)chromiumcarbonyl fragment exerts its electron withdrawing nature and its steric bulk giving rise to highly regio- and stereoselective allylations. Further studies with these organometallic allenes will be directed towards 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 [19]. (a) Column chromatography: silica gel 60 (0.063–0.2 mm/70–230 mesh, Firma Merck Darmstadt). (b) TLC: silica gel plates (60 F_{254} Merck, Darmstadt); (c) Melting points (uncorrected values): Reichert–Jung Thermovar. (d) The propargyl acetate complex **3** was prepared according to our published procedure [7a]. The thiols were purchased from Merck, Aldrich or Fluka, and used without further purification. (e) ^{1}H-and ^{13}C-NMR spectra: Bruker WM 300, Bruker AC 300, Bruker ARX 300 or Varian VXR 400S DMSO-d_6. (f) IR: Perkin-Elmer FT-IR spectrometer 1000 or Perkin-Elmer FT-IR Paragon 1000 PC. The samples were pressed into KBr pellets or recorded on NaCl plates, (g) UV–Vis: Beckman DK-2-a or Beckman UV 5240. (h) MS: Finnigan MAT 311-A/100MS, Finnigan MAT 90 and MAT 95 Q; (i) Elemental analysis were carried out in the Microanalytical Laboratories of the Department Chemie, Ludwig–Maximilians-Universität München.

4.1. Generation of the cation 4 and nucleophilic trapping reactions (General Procedure, GP).

To a solution of the acetate **3** in 18 ml of dichloromethane, cooled to −78 °C, were added dropwise 1.4 equivalents of boron trifluoride etherate. The purple red solution was stirred at −78 °C for 50 min and then the corresponding thiol 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 derivatives **5**.

*4.1.1. $Cr(CO)_3(\eta^6\text{-}C_6H_5)C[SCH(CH_3)_2]{=}C{=}CHC_6H_5$ (**5a**)*

According to the GP 150 mg (0.39 mmol) of **3** were 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 (diethyl ether/pentane 1:2) and recrystallization from pentane to give 112 mg (72%) of pure **5a** as a yellow powder. Mp: 97–98 °C. ^{1}H-NMR ([D$_6$]Me$_2$SO, 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$_6$]Me$_2$SO, 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$^+$ − 2 CO, 12), 318 (M$^+$ − 3 CO, 44), 244 (C$_{15}$H$_{12}$Cr$^+$, 100), 243 (C$_{15}$H$_{11}$Cr$^+$, 6), 191 (C$_6$H$_5$CHCCC$_6$H$_5^+$, 50), 52 (Cr$^+$, 22). IR (KBr): = 1964 cm^{-1}, 1901, 1875. UV–Vis (Me$_2$SO): λ_{max} (ε) = 319 nm (10300). 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.

*4.1.2. $Cr(CO)_3(\eta^6\text{-}C_6H_5)C(SCH_2CH_3CO_2CH_3){=}C{=}CHC_6H_5$ (**5b**)*

According to the GP 150 mg (0.39 mmol) of **3** were ionized and allowed to react for 50 min with 0.11 ml (0.85 mmol) of methyl 3-mercapto propionate. After workup the crude product was purified by flash chromatography on silica gel (diethyl ether–pentane 1:5-1:1) to give 129 mg (74%) of pure **5b** as a yellow oil.-^{1}H-NMR ([D$_6$]Me$_2$SO, 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 (DMSO-d_6, 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$^+$ − 3 CO, 51), 310 (M$^+$-Cr(CO)$_3$, 1), 244 (C$_{15}$H$_{12}$Cr$^+$, 70), 243 (C$_{15}$H$_{11}$Cr$^+$, 12), 191 (C$_6$H$_5$CHCCC$_6$H$_5^+$, 100), 52 (Cr$^+$, 25). IR (KBr): = 1965 cm^{-1}, 1887, 1732. UV–Vis (Me$_2$SO): 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.

*4.1.3. $Cr(CO)_3(\eta^6\text{-}C_6H_5)C(S\text{-}p\text{-}C_6H_4Cl){=}C{=}CHC_6H_5$ (**5c**)*

According to the GP 100 mg (0.26 mmol) of **3** were ionized and allowed to react for 90 min with 85 mg (0.59 mmol) of *p*-chloro thiophenol. After workup the crude product was purified by crystallization from diethyl ether/pentane to give 98 mg (80%) of pure **3c** as yellow crystals. Mp: 85 °C. ^{1}H-NMR ([D$_6$]Me$_2$SO, 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 (DMSO-d_6, 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$^+$ − 3 CO, 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$_6$H$_5$CHCCC$_6$H$_5^+$, 93), 52 (Cr$^+$, 43).-IR (KBr): = 1966 cm^{-1}, 1883.-UV–Vis (Me$_2$SO): λ_{max}(ε) = 320 nm (11200). Anal. Calcd. for $C_{24}H_{15}ClCrO_3S$ (470.9): C, 61.22; H, 3.21; Cl, 7.53; S, 6.81. Found: C, 61.45; H, 3.24; Cl, 7.22; S, 6.86.

*4.2. $Cr(CO)_3(\eta^6\text{-}C_6H_5)CH(S\text{-}p\text{-}C_6H_4Cl)C[SCH(CH_3)_2]{=}CHC_6H_5$ (**15**)*

To a suspension of 14 mg (0.54 mmol) of NaH in 10 ml of THF under nitrogen was added dropwise 50 μl (0.53 mmol) of 2-propanethiol and the mixture was stirred for 35 min until the evolution of hydrogen had ceased. Then a solution of 100 mg (0.21 mmol) of the allene **5c** in 5 ml of THF were added to the cooled suspension (−9 °C) and the reaction mixture was stirred for 45 min at −9 °C before 10 ml of a saturated aqueous solution of sodium bicarbonate were added. The aqueous layer was extracted twice with diethylether (2 × 30 ml). After drying with magnesium sulfate and evaporation of the solvents in vacuo the residue crystallized from diethylether–pentane (1:1) to furnish 91 mg (78%) of **15** as yellow needles. Mp.

121 °C.-^{1}H-NMR (DMSO-d_6, 400 MHz): δ 0.70 (d, $J = 5.4$ Hz, 3 H), 0.81 (d, $J = 5.5$ Hz, 3 H), 2.73 (m, 1 H), 5.09 (s, 1 H), 5.63–5.68 (m, 2 H), 5.76 (m, 1 H), 5.96 (d, $J = 5.1$ Hz, 1 H), 6.01 (d, $J = 5.1$ Hz, 1 H), 7.23 (m, 2 H), 7.31 (m, 2 H), 7.42 (d, $J = 7.3$ Hz, 2 H), 7.51 (m, 2 H), 7.58 (d, $J = 7.2$ Hz, 2 H). ^{13}C-NMR (DMSO-d_6, 100 MHz): δ 22.60 (CH_3), 22.72 (CH_3), 36.18 (CH), 60.12 (CH), 92.41 (CH), 92.66 (CH), 95.69 (CH), 96.18 (CH), 96.80 (CH), 110.59 ($C_{quat.}$), 127.95 (CH), 128.31 (CH), 128.91 (CH), 129.19 (CH), 132.41 ($C_{quat.}$), 133.19 ($C_{quat.}$), 134.28 ($C_{quat.}$), 135.05 (CH), 135.49 (CH), 135.87 ($C_{quat.}$), 233.65 ($C_{quat.}$, CO).-MS (70 eV, EI), m/z (%): 548/546 (M^+, 0.4/0.9), 520/518 ($M^+ - CO$, 1/2), 492/490 ($M^+ - 2$ CO, 12/23), 464/462 ($M^+ - 3$ CO, 50/100), 388/368 ($M^+ - 3$ CO,–HSCH(CH_3)$_2$; 20/43), 320 ($M^+ - 3$ CO,–HSC_6H_4Cl; 65), 278 ($M^+ - 3$ CO,–HSC_6H_4Cl,–CH_2=CHCH_3; 65), 267 ($M^+ -$ $Cr(CO)_3$,–SC_6H_4Cl; 48), 192 ($M^+ - Cr(CO)_3$,–SC_6H_4Cl,–SCH(CH_3)$_2$; 73), 191 ($M^+ - Cr(CO)_3$,–SC_6H_4Cl,–HSCH(CH_3)$_2$; 91). IR (KBr): 1989 cm^{-1}, 1969, 1876, 1475, 1094, 1013, 660, 630, 534. UV–Vis (Me_2SO): $\lambda_{max}(\varepsilon)$ 318 nm (14900). Anal. Calcd. for $C_{27}H_{23}ClCrO_3S_2$ (547.06): C, 59.28; H, 4.24; Cl, 6.48; S, 11.72. Found: C, 59.34; H, 4.31; Cl, 6.34; S, 11.40.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 160434 for compound **10**. 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).

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References

[1] For reviews see e.g.: (a) L. Haynes, R. Pettit, in: G.A. Olah, P.v.R. Schleyer (Eds.), Carbonium Ions, Wiley, New York, 1975, p. 5;
(b) W.E. Watts, G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 8, Pergamon, Oxford, 1982, p. 1051, Chapter 59;
(c) A. Solladié-Cavallo, Polyhedron 4 (1985) 901;
(d) G. Jaouen, Pure Appl. Chem. 58 (1986) 597;
(e) K.M. Nicholas, Acc. Chem. Res. 20 (1987) 207. For stabilization of positive charge in benzylic positions by chromium carbonyl fragments;
(f) S.G. Davies, T.J. Donohoe, Synlett (1993) 323.

[2] (a) D.K. Wells, W.S. Trahanovsky, J. Am. Chem. Soc. 91 (1969) 5870;
(b) G.A. Olah, S.H. Yu, J. Org. Chem. 41 (1976) 1694;
(c) D. Seyferth, S. Merola, C.S. Eschbach, J. Am. Chem. Soc. 100 (1978) 4124;
(d) D.W. Clack, L.A.P. Kane-Maguire, J. Organomet. Chem. 145 (1978) 201;
(e) P.A. Downton, B.G. Sayer, M.J. McGlinchey, Organometallics 11 (1992) 3281.

[3] (a) M.T. Reetz, M. Sauerwald, Tetrahedron Lett. 24 (1983) 2837;
(b) M.T. Reetz, M. Sauerwald, J. Organomet. Chem. 382 (1990) 121;
(c) M. Uemura, T. Kobayashi, Y. Hayashi, Synthesis (1986) 386;
(d) S.G. Davies, T.D. McCarthy, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, 1995, p. 1039;
(e) For side chain activation, see e.g.: E.J. Corey, C.J. Helal, Tetrahedron Lett. 37 (1996) 4837;
(f) T. Tanaka, H. Mikamiyama, K. Maeda, C. Iwata, Y. In, T. Ishida, J. Org. Chem. 63 (1998) 9782.

[4] (a) For recent computational studies on the DFT level of theory, see e.g.: A. Pfletschinger, T.K. Dargel, J.W. Bats, H.-G. Schmalz, W. Koch, Chem. Eur. J. 5 (1999) 537;
(b) C.A. Merlic, J.C. Walsh, D.J. Tantillo, K.N. Houk, J. Am. Chem. Soc. 121 (1999) 3596.

[5] (a) M. Murray, in: Methoden zur Herstellung und Umwandlung von Allenen bzw. Kumulenen (Eds.), Houben-Weyl, Georg Thieme Verlag, Stuttgart, Vol. 5/2a (1977) 991;
(b) H. Mayr, E. Bäuml, Tetrahedron Lett. 24 (1983) 357;
(c) E. Bäuml, H. Mayr, Chem. Ber. 118 (1985) 694;
(d) J.-P. Dau-Schmidt, H. Mayr, Chem. Ber. 127 (1994) 205;
(e) S.M. Lukyanov, A.V. Koblik, L.A. Muradyan, Russ. Chem. Rev. 67 (1998) 81.

[6] (a) T.J.J. Müller, H.J. Lindner, Chem. Ber. 129 (1996) 607;
(b) T.J.J. Müller, Tetrahedron Lett. 38 (1997) 1025;
(c) T.J.J. Müller, M. Ansorge, K. Polborn, J. Organomet. Chem. 578 (1999) 252;
(d) M. Ansorge, T.J.J. Müller, J. Organomet. Chem. 585 (1999) 174;
(e) T.J.J. Müller, J. Organomet. Chem. 578 (1999) 95;
(f) T.J.J. Müller, A. Netz, M. Ansorge, E. Schmälzlin, C. Bräuchle, K. Meerholz, Organometallics 18 (1999) 5066.

[7] (a) T.J.J. Müller, A. Netz, Organometallics 17 (1998) 3609;
(b) T.J.J. Müller, M. Ansorge, K. Polborn, Organometallics 18 (1999) 3690;
(c) A. Netz, T.J.J. Müller, Organometallics 19 (2000) 1452;
(d) M. Ansorge, K. Polborn, T.J.J. Müller, Eur. J. Inorg, Chem. (2000) 2003.

[8] A. Netz, T.J.J. Müller, Tetrahedron 56 (2000) 4149.

[9] (a) T.J.J. Müller, A. Netz, Tetrahedron Lett. 40 (1999) 3145;
(b) A. Netz, K. Polborn, T.J.J. Müller, J. Am. Chem. Soc. 123 (2001) 3441.

[10] This aspect has initially been misinterpreted in [7a].

[11] A. Netz, T.J.J. Müller, Organometallics 20 (2001) 376.

[12] H.-O. Kalinowski, S. Berger, S. Braun, ^{13}C-NMR Spektroskopie, Georg Thieme Verlag, Stuttgart, New York, 1984, p. 273.

[13] For (arene)chromiumcarbonyl stabilized propargyl anions, see [7c].

[14] Recrystallization from diethylether or dichloromethane only gives crystals of **5c** in poor quality.

[15] QUANTUM CACHE 3.0 Program, Oxford Molecular Group, 1997.

[16] (a) For comprehensive reviews of allene chemistry, see e.g.: D.R. Taylor, Chem. Rev. 67 (1967) 317;

(b) T.F. Rutledge, Acetylenes and Allenes, Reinhold Book Corporation, New York, Amsterdam, London, parts 1–3 (1969);
(c) W.T. Brady, in: S. Patai (Ed.), The Chemistry of Ketenes, Allenes and Related Compounds, J. Wiley & Sons, Chichester, New York, Brisbane, Toronto, 1980, p. 298 pt. 1;
(d) H. Hopf, in: S. Patai (Ed.), The Chemistry of Ketenes, Allenes and Related Compounds, J. Wiley & Sons, Chichester, New York, Brisbane, Toronto, 1980, p. 779 pt. 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, J. Wiley & Sons, Chichester, New York, Brisbane, Toronto, 1984.

[17] (a) T.J.J. Müller, M. Ansorge, Tetrahedron 54 (1998) 1457;
(b) M. Ansorge, K. Polborn, T.J.J. Müller, Eur. J. Inorg. Chem. (1999) 225;
(c) M. Ansorge, K. Polborn, T.J.J. Müller, J. Organomet. Chem. 630 (2001) 198.

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

[19] Various editors, Organikum, 14th edition, VEB Deutscher Verlag der Wissenschaften, Berlin (1993).