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Unexpected Consecutive Propargyl−Allenyl Isomerization in Nucleophilic Trapping Reactions of (arene)$Cr(CO)_3$-Substituted Propargyl Cations

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Summary: Instead of giving rise to the expected propargylated phosphonium salts ***4****, the addition of triphenylphosphane to (arene)$Cr(CO)_3$-substituted α-propargyl cations furnishes allenyl phosphonium salts* ***3*** *via a prototropic isomerization.*

Among several organometallic substituents, $Cr(CO)_3$-complexed arenes[1] are the most interesting functional groups, since they allow an efficient stabilization of both positive[2] and negative[3] benzylic charges.[4] This peculiar feature results in an electronically "hermaphroditic"[2b] or amphoteric behavior and has been exploited in quite some elegant syntheses of complex molecules.[5] In the past years we have demonstrated that conjugated substituents on $Cr(CO)_3$-complexed arenes[6] can be successfully applied for charge stabilization, even if the charge is generated at a remote position.[7] In particular, stabilized propargyl cations[7a,b] and anions[8] have been generated, structurally characterized, and selectively trapped with nucleophiles[9] and electrophiles,[8] respectively. Here, we wish to communicate an unusual prototropic propargyl−allene isomerization in Lewis acidic medium to give solely (arene)$Cr(CO)_3$-substituted allenyl phosphonium salts as addition products of the reaction of triphenylphosphane with (arene)$Cr(CO)_3$-substituted α-propargyl cations.

The base-catalyzed propargyl−allene isomerization (Scheme 1) proceeding via a resonance-stabilized propargyl anion is a well-documented and synthetically useful procedure to obtain allenes,[10] in particular, since alkynes are readily available by several approaches.[11] However, the alternative isomerization process in acidic media proceeding via a highly reactive and elusive vinyl cation intermediate (Scheme 1) is almost unknown.[12]

In the course of our studies of cationic propargylations with (arene)$Cr(CO)_3$-substituted α-propargyl cations we have investigated various trapping nucleophiles.[7,9] Although for planar chiral (arene)$Cr(CO)_3$-substituted α-propargyl cations the trapping reactions with π-, S-, O-, and N-nucleophiles give exclusively the propargylated products with high diastereoselectivity,[9a] we have now observed a deviating behavior for the reaction with phosphanes such as triphenylphosphane. Upon ionization of the propargyl acetates **1** according to our standard procedure[7−9] with a slight excess of trimethylsilyl triflate (TMSOTf) in dichloromethane at −78 °C the deeply colored propargyl cations **2** are subsequently trapped with an excess of triphenylphosphane (Scheme 2). Instantaneously, the deeply colored solutions of **2** are decolorized, and after neutral aqueous workup, surprisingly, exclusively the allenyl phosphonium salts **3** are obtained in good yields as yellow crystalline solids (**3a**

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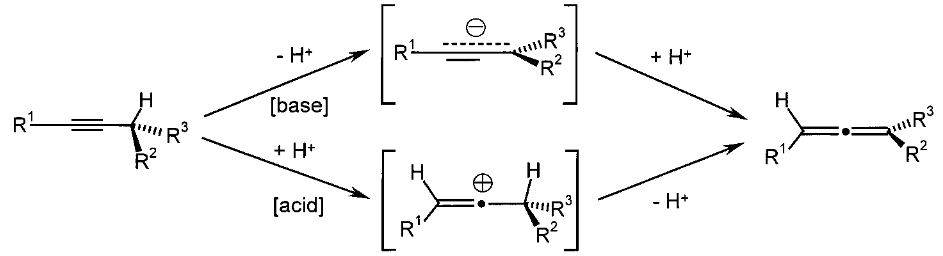
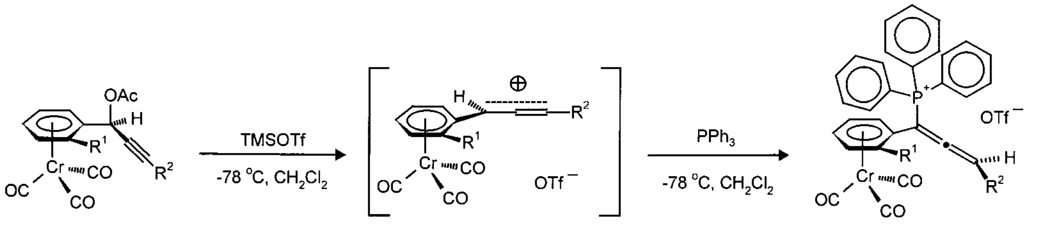
Scheme 1. Base- and Acid-Catalyzed Propargyl–Allenyl Isomerizations



Scheme 2



1a: $R^1 = H$, $R^2 = Ph$
1b: $R^1 = CH_3$, $R^2 = p\text{-}C_6H_4OCH_3$
1c: $R^1 = OCH_3$, $R^2 = n\text{-butyl}$

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3a: $R^1 = H$, $R^2 = Ph$ (69 %)
3b: $R^1 = CH_3$, $R^2 = p\text{-}C_6H_4OCH_3$ (73 %)
3c: $R^1 = OCH_3$, $R^2 = n\text{-butyl}$ (77 %)

and **3b**) or as a yellow foam (**3c**).[13] Trapping the configurationally stable racemic planar chiral propargyl cations **2b** and **2c** with triphenylphosphane gives rise to the isolation of a racemic mixture of the diastereomers of **3b** (diastereomeric ratio (dr) = 61:39) and **3c** (dr = 60:40). The diastereomeric ratio can be readily reproduced by MM2 calculations[14] on both diastereomers of **3b** with a difference in steric energy of 0.14 kcal/mol (T = 195 K; K = 59:41), indicating a thermodynamically controlled formation of the diastereomeric allenyl phosphonium salts **3**.

According to the NMR spectra the structure of the unexpectedly formed allenyl derivatives is supported by the characteristic appearance of the allenyl proton resonances in the ^1H NMR spectra as doublets between δ 7.01 and 7.12 (the allenyl proton resonance in the spectrum of **3c** is found between δ 5.89 and 6.01 as a multiplet due to vicinal coupling) with large phosphorus proton coupling constants ^4J (11.3–11.5 Hz). In the carbon NMR spectra the characteristic signals for the α-allenyl carbon atoms are found between δ 86.3 and 93.9 ($^1J_{PC}$ = 83.8–92.6 Hz), for the central β-allenyl resonances between δ 216.5 and 219.7 ($^2J_{PC}$ = 4.1–7.3 Hz), and for the terminal γ-allenyl nuclei between δ 98.5 and 104.3 ($^3J_{PC}$ = 12.0–13.8 Hz).[15] In the ^{31}P NMR spectra the characteristic singlets for the phosphorus nuclei in phosphonium salts can be found between δ 20.64 and 23.05.[16] By the aid of 2D NOESY experiments of **3b** a geminal orientation of the (arene)Cr(CO)3 and the triphenylphosphonium substituents at the α-position is supported by the appearance of strong cross-peaks for the *meta* anisyl and allenyl protons. Additionally, cross-peaks are found for the *ortho* methyl protons on the complexed arene ring and the *ortho* phenyl protons of the triphenylphosphane moiety. Additionally, the structure of the allenes **3** was unambiguously corroborated by X-ray crystal structure analyses for both **3a** (Figure 1) and **3b** (Figure 2).[17,18] Furthermore, the bond lengths in the allenyl fragments (**3a**, C(10)–C(11) = 1.304 Å, C(11)–C(12) = 1.297 Å; **3b**, C(11)–C(12) = 1.303 Å, C(12)–C(13) = 1.307 Å) are in agreement with those of other allenyl-substituted (arene)chromium carbonyl complexes.[19] Therefore, the formation of **3** can be rationalized by a regioselective attack of the phosphane at the propargylic position followed by a subsequent prototropic rearrangement[20] to give the allenyl derivative **3**. In particular, this propargyl–allenyl rearrangement is rather unusual, since it proceeds in a Lewis

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(13) **Synthesis of the allenyl phosphonium salts 3:** To a solution of 1 equiv (0.5 mmol) of the acetate **1** in 5 mL of dry dichloromethane was added dropwise 1.3 equiv of TMSOTf at −78 °C. Immediately a deeply colored solution of the propargyl cation **2** was formed, which was stirred at that temperature for 40–60 min. To this reaction mixture was then added a solution of 2.2 equiv of triphenylphosphane in 3 mL of dichloromethane at −78 °C. The reaction can be followed by a color change from deep purple to yellow. After 55–65 min subsequently 20 mL of diethyl ether and 20 mL of water were added and the external cooling was removed. After extraction of the aqueous phase with dichloromethane (2 × 25 mL) the combined organic layers were dried with magnesium sulfate and filtered and the solvents were evaporated in vacuo. The residue was dried in vacuo and triturated with diethyl ether to give as a yellow crystalline solid. Further purification was achieved by recrystallization from dichloromethane/diethyl ether. **3a**: yield 270 mg (69%); yellow crystals; mp >185 °C dec. **3b**: yield 270 mg (73%, dr = 61:39); yellow crystals (dichloromethane/diethyl ether); mp >183 °C dec. **3c**: yield 219 mg (77%, dr = 60:40); yellow foam.

(14) Quantum CAChe 3.0 Program, Oxford Molecular Group, 1997.

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(18) The crystals suitable for the X-ray structure analysis of **3b** showed a modest enrichment of the major diastereomer (dr = 70.5:29.5), as determined from the displacement of the *ortho* methyl group in positions C5 and C9 with a distribution of 70.5% to 29.5%.

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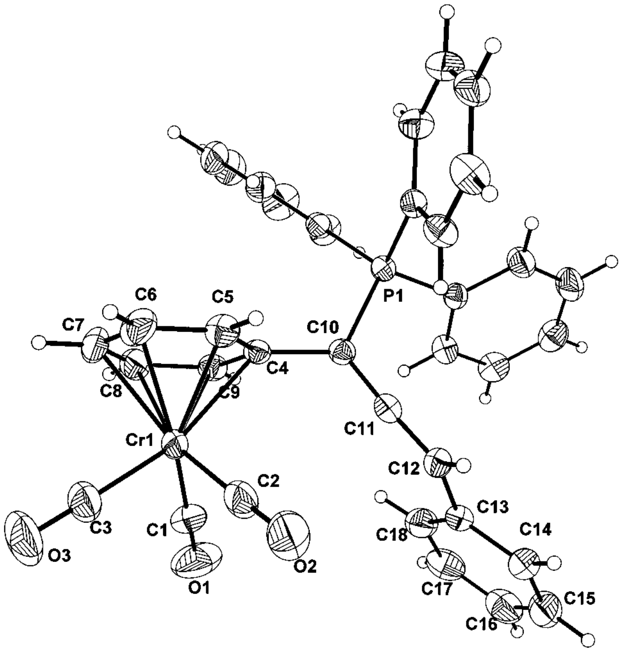


Figure 1. ORTEP plot of **3a**. Selected bond lengths (Å) and dihedral and torsional angles (deg): C(4)−C(10) = 1.488, C(10)−C(11) = 1.304, C(11)−C(12) = 1.297, C(12)−C(13) = 1.462, C(10)−P(1) = 1.812; C(12)−C(11)−C(10) = 176.41, C(5)−C(4)−C(10)−C(11) = 84.72, C(18)−C(13)−C(12)−C(11) = 10.06.

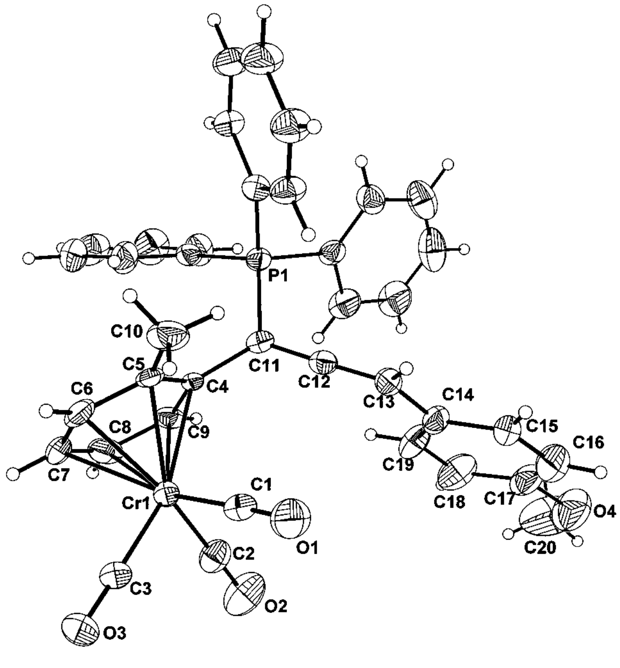
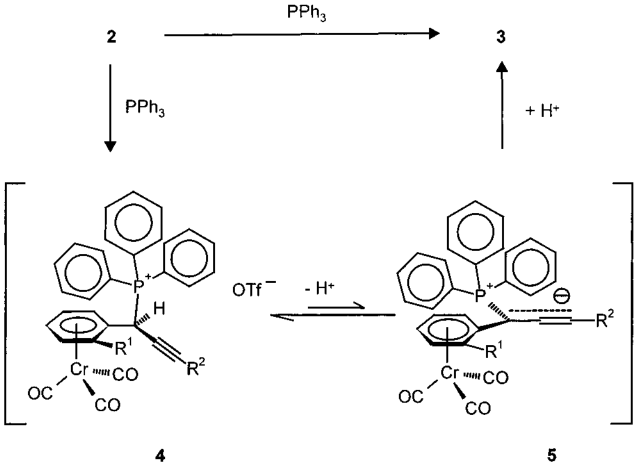


Figure 2. ORTEP plot of **3b** (only the major diastereomer is depicted). Selected bond lengths (Å) and dihedral and torsional angles (deg): C(4)−C(11) = 1.496, C(11)−C(12) = 1.303, C(12)−C(13) = 1.307, C(13)−C(14) = 1.457, C(11)−P(1) = 1.817; C(11)−C(12)−C(13) = 178.20, C(5)−C(4)−C(11)−C(12) = 84.37, C(12)−C(13)−C(14)−C(19) = 4.80.

acidic medium in a nonprotic solvent. However, the peculiar isomerization can be rationalized on the basis of the amphoteric electronic nature of the (arene)chromium carbonyl substituent (Scheme 3). This means that the propargylic proton of the initially formed propargyl phosphonium salt **4** is acidified due to the enhanced cooperative electron-withdrawing nature of the chromium carbonyl complexed arene and the cationic phosphonium substituent. Obviously, even the weakly basic phosphane present in excess now affords a deprotonation, at least in equilibrium, to give the highly resonance stabilized propargyl Wittig ylide[21] **5** that is irreversibly protonated to furnish the thermodynamically more stable allene isomer **3**.

Scheme 3



In conclusion, we have observed that the addition of a phosphane to (arene)Cr(CO)$_3$-substituted α-propargyl cations results in an unusual propargyl−allenyl isomerization in a Lewis acidic medium. This process takes advantage of the electronically amphoteric nature of the (arene)chromium carbonyl substituent, which stabilizes not only the propargyl cation **2** but also the presumed propargyl anion intermediate **5**. Recently, we have demonstrated the benefits of (arene)chromium carbonyl substituted allenyl phosphonic acid ester metal-templated synthesis of heterocycles,[7c] and thus, the consecutive phosphane addition, propargyl−allenyl isomerization sequence allows an alternative approach to allenyl phosphorus species. The reactions of this novel class of organometallic allenes will be the goal of future investigations.

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Supporting Information Available: Text giving experimental procedures and characterization data for **3a**, **3b**, and **3c** and tables giving data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[21] For stable propargyl ylides see, e.g.: Pommer, H. *Angew. Chem.* **1960**, *72*, 811.