Spectroscopic Characterization, Reactivity, and Reactions of (Arene)$Cr(CO)_3$-Stabilized γ-Propargyl−Allenyl Cations

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(Arene)$Cr(CO)_3$-stabilized γ-propargyl−allenyl cations $Cr(CO)_3(\eta^6\text{-}R^1C_6H_4)C{\equiv}CC^+R^2R^3$ (**2**) are reactive intermediates in the synthesis of arene-complex-substituted allenes or propargyl derivatives using mild in situ ionizations of the corresponding propargyl derivatives $Cr(CO)_3(\eta^6\text{-}R^1C_6H_4)C{\equiv}CCXR^2R^3$ (X = OH, OAc). The regioselectivity of the nucleophilic attack is strongly dependent on the substitution pattern on the propargyl side chain, i.e., steric and electronic factors. In a representative case of a stable cation (**2a**; $R^1 = H$, $R^2 = R^3 = Ph$) the structure investigation of this ambident electrophile by NMR spectroscopy and UV/vis spectroscopy reveals that a considerable contribution of the allenylium resonance structure accounts for a strong participation of the chromium carbonyl fragment in the efficient stabilization. The reactivity of **2a** was studied by measuring the UV/vis kinetics for the nucleophilic trapping reactions revealing that the complexed cation **2a** is by 2 orders of magnitude less reactive than the corresponding free ligand.

Introduction

Benzylic carbenium ions stabilized by $Cr(CO)_3$ complexation have successfully been applied to a couple of syntheses in the sense of nucleophilic substitutions.[1] Thermodynamically, the $Cr(CO)_3$-complexed benzyl cation is stabilized[2] by at least 8 orders of magnitude compared to the free ligand, the benzyl cation, and some time ago the structure of (arene)$Cr(CO)_3$-stabilized benzyl cations had been elucidated unambiguously by ^1H and ^{13}C NMR spectroscopy.[2d,3] Concerning the reactivity in numerous nucleophilic substitutions on $Cr(CO)_3$-complexed benzyl derivatives, the benzyl stabilization has also been found responsible for a rate-increasing anchimeric assistance.[1] Although, the $Cr(CO)_3$ complexation is generally used to exercise a strong net electron-withdrawing effect, this peculiar feature can be readily explained by taking into account an ideal overlap of filled d-orbitals of the chromium carbonyl fragment and the vacant p_z-orbital of the sp^2-hybridized benzylic carbenium ion.[1a,2a,d] Last but not least this remarkable effect plays its key role in the conservation of the stereochemical integrity of an asymmetric benzylic center in stereoselective transformations.[1a,d] Thus, chromium carbonyl-complexed benzyl cations are accessible, both thermodynamically and kinetically. From these general considerations the intriguing question arises whether $Cr(CO)_3$-complexed arenes would also stabilize sp-hybridized positive charges such as α-allenyl cations, i.e., if the generation of the cation occurs at the remote γ-propargyl position. In particular, upon ionization propargylic derivatives form ambident propargylium−allenylium ions[4] that can be very interesting intermediates for more sophisticated arene side chain functionalizations[5] via aryl propargylic or allenyl derivatives. So far, there are only ferrocenyl-substituted γ-propargyl−α-allenyl cations among organometallic π-complex representatives of stabilized propargylium−allenylium ions.[6] Recently, we have investigated the electronic structure and ambident reactivity of a (benzene)$Cr(CO)_3$-stabilized α-propargylium ion.[7] Here we report on the NMR and UV/vis spectroscopic characterization and the reactivity of a (phenyl)$Cr(CO)_3$-substituted γ-propargyl cation and nucleophilic trapping reactions of several (arene)$Cr(CO)_3$-stabilized γ-pro-

(1) (a) For stabilization of positive charge in the benzyl chromium carbonyl derivatives see, for example: Davies, S. G.; Donohoe, T. J. *Synlett* **1993**, 323−332. (b) For stereoselective C−C-bond forming reactions via η^6-arene chromium tricarbonyl cations see, for example: Uemura, M.; Kobayashi, T.; Hayashi, Y. *Synthesis* **1986**, 386. (c) Reetz, M. T.; Sauerwald, M. *Tetrahedron Lett.* **1983**, *24*, 2837. (d) Corey, E. J.; Helal, C. J. *Tetrahedron Lett.* **1996**, *37*, 4837.

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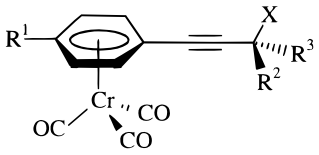
pargylium ions, some generated as stable species, others by in situ ionization techniques.

Results and Discussion

Generation of the Propargylic Cation. Propargylic cations are most conveniently generated from a suitable propargylic precursor upon ionization with a Brønstedt or Lewis acid. Recently, we have found a fairly general access to arene$Cr(CO)_3$-substituted propargylic derivatives **1** using the Sonogashira coupling of terminal prop-2-yn-1-ols with $Cr(CO)_3$-complexed chloroarenes.[8] Thus, the complexed 1,1,3-triphenyl allenyl cation (**2a**) (R^1 = H, R^2 = R^3 = Ph) is formed in a dichloromethane solution from the complex-substituted propargyl alcohol (**1a**) in the presence of a 1.3-fold excess of HBF_4 diethyl etherate at −78 °C (Scheme 1) as a stable, deep green intermediate (<20 °C) that can be identified and characterized by NMR and UV/vis spectroscopy. Some time ago, the free ligand systems, i.e., the propargyl alcohol **3** and the cation **4**, were thoroughly studied by ^{13}C NMR spectroscopy in superacidic media[9] and can now be used for direct comparison with chromium carbonyl-complexed systems, in particular, to evaluate the electronical influence of the chromium carbonyl fragment on the stabilization and, ultimately, on the reactivity of the propargyl cation.

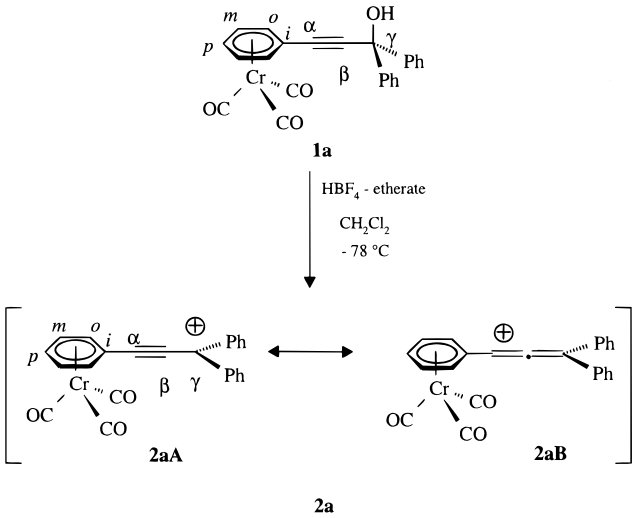
Chart 1



1

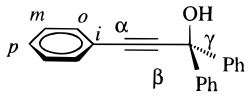
1a R_1 = H, R_2 = R_3 = Ph, X = OH
1b R_1 = H, R_2 = R_3 = CH_3, X = OH
1c R_1 = R_2 = R_3 = CH_3, X = OH
1d R_1 = R_2 = R_3 = H, X = OH
1e R_1 = R_2 = H, R_3 = Ph, X = OH
1f R_1 = R_2 = H, R_3 = Ph, X = OAc

Scheme 1

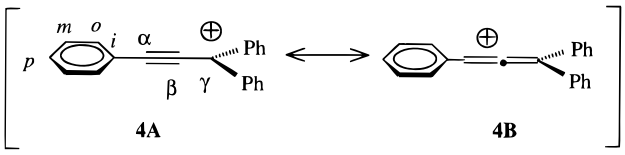


2a

Chart 2



3



4

^{13}C NMR Spectra of 1a and 2a. Most significantly no splitting of the carbonyl resonance can be found in the ^{13}C NMR spectrum (proton-decoupled and DEPT) of **2a** (231.0 ppm; Table 1), although the carbonyl signal of the propargyl alcohol **1a** (232.5 ppm) experiences a modest shift to high field upon ionization, indicating the generation of an electron-withdrawing substituent.[10] Surprisingly, the low-field shift of the *para*-carbon resonances of the uncomplexed phenyl rings with Δ_I = 9 (**1a**, 127.6, and **2a**, 136.4) is considerably smaller in comparison to the corresponding ionization shift of Δ_I = 16.6 for the free ligand pair **3**/**4**, indicating a significant resonance participation of the complexed arene substituent at the remote allenyl position.

Applying a simple model,[7,9] the relative contributions of mesomeric forms to the stabilization of a resonance-stabilized cation can be estimated. The benzhydryl cation (**5**)[11] was considered as a model for the C_γ-localized carbenium ion as depicted in structure **2aA**, whereas 1,1-diphenyl ethene (**6**)[12] serves as a model for an allenylium structure (**2aB**) assuming the γ-carbon atom does not bear positive charge. The substitution of the corresponding carbon resonances (**2a**, δ = 161.5; **5**,[11] δ = 191.1; **6**,[12] δ = 141.0) in eq 1 reveals a 59% contribution of the resonance structure **2aB** to the stabilization of the cation **2a**.

Chart 3

5 **6**

$$\text{rel contrib of } \mathbf{2aB} = \frac{\delta(\mathbf{C}\gamma - \mathbf{5}) - \delta(\mathbf{C}\gamma - \mathbf{2a})}{\delta(\mathbf{C}\gamma - \mathbf{5}) - \delta(\mathbf{C}\gamma - \mathbf{6})} \times 100\% = \frac{191.1 - 161.5}{191.1 - 141.0} \times 100\% = 59\% \quad (1)$$

Interestingly, the contribution of the corresponding allenyl resonance form **4B** of the free ligand[9] using the same procedure is estimated to be only 9%. Thus, although the chromium carbonyl arene fragment is placed at a remote position with respect to the leaving

Table 1. Assignments and Ionization Shifts Δ_I of the Alcohols (1a,[a] 3[b]) − Cations (2a,[c] 4[d])

	1a	2a	Δ_I		3[9]	4[9]	Δ_I
para (compl.)	91.5	97.5	6.0	*para* (allenyl terminus)	128.0	137.6	9.6
meta (compl.)	92.6	95.9	3.3	*meta* (allenyl terminus)	131.4	130.7	−0.7
ortho (compl.)	95.1	103.4	7.9	*ortho* (allenyl terminus)	128.0	138.7	10.7
ipso (compl.)	89.3	82.4	−6.9	*ipso* (allenyl terminus)	121.9	119.9	−2.0
α	82.4	150.4	68.0	α	86.6	159.1	72.5
β	90.8	120.8	30.0	*β*	91.5	105.9	14.4
γ	73.8	161.5	87.7	*γ*	74.5	186.8	112.3
ipso	143.9	138.3	−5.6	*ipso*	144.6	138.7	−5.9
ortho	128.2	133.9	5.7	*ortho*	125.7	139.4	13.7
meta	125.1	130.2	5.1	*meta*	128.0	131.4	3.4
para	127.6	136.5	8.9	*para*	127.4	144.0	16.6
CO	232.5	231.0	−1.5				

[a] Recorded at −70 °C in CD_2Cl_2 (100 MHz). [b] Recorded at 35 °C in $CDCl_3$ (25 MHz).[9] [c] Recorded at −70 °C in CD_2Cl_2/HBF_4 (100 MHz). [d] Recorded at −60 °C in $FSO_3H/SbF_5/SO_2$ (25 MHz).[9]

Table 2. Complexation Shifts Δ_C for the Alcohols 1a and 3 and the Cations 2a and 4 (for Recording Conditions See Table 1)

	3[9]	1a	Δ_C	4[9]	2a	Δ_C
para (allenyl terminus)	128.0	91.5	−36.5	137.6	97.5	−40.1
meta (allenyl terminus)	131.4	92.6	−38.8	130.7	95.9	−34.8
ortho (allenyl terminus)	128.0	95.1	−32.9	138.7	103.4	−35.3
ipso (allenyl terminus)	121.9	89.3	−32.6	119.9	82.4	−37.5
α	86.6	82.4	−4.2	159.1	150.4	−8.7
β	91.5	90.8	−0.7	105.9	120.8	14.9
γ	74.5	73.8	−0.7	186.8	161.5	−25.3
ipso	144.6	143.9	−0.7	138.7	138.3	−0.4
ortho	125.7	128.2	2.5	139.4	133.9	−5.5
meta	128.0	125.1	−2.9	131.4	130.2	−1.2
para	127.4	127.6	0.2	144.0	136.5	−7.5
		232.5			231.0	
$\Sigma\Delta_C$			−219.4			−258.2

group, it still participates to a considerable extent in the stabilization of the positive charge. The inspection of the complexation shifts (Table 2) of **1a** and **2a** reveals that the positive charge is as well delocalized onto the chromium atom[3a] to a certain extent ($\Delta\Sigma(\Delta_C) = 38.8 \approx 15\%\ \Delta_C$(cation)). The allenyl cation resonance form is stabilized by the anchimeric assistance of the chromium carbonyl tripod, causing a decrease of the strong deshielding of the carbon resonance at C_α and C_γ.

According to molecular orbital calculations on a η^6-phenylCr(CO)$_3$-substituted *γ*-propargyl cation **2d** as a model at the extended Hückel level of theory,[7,13] the bending of the propargyl fragment by an angle of 4° toward the chromium carbonyl tripod results only in a small gain of ∼0.33 kcal/mol. The overlap of the p_z-orbital at the sp-hybridized carbon atom with the chromium-centered $d_{x^2-y^2}$-orbital is significantly lower compared to the sp^2-hybridized η^6-phenylCr(CO)$_3$-substituted α-propargyl cation.

UV/Vis Spectra of the Cation 2a. The successful NMR studies prompted us to investigate the electronic spectrum of the cationic intermediate **2a**. Upon ionization with tetrafluoroboric acid etherate solution of a dichloromethane solution of **1a** at −70 °C, a color change from light yellow to deep green can be monitored by following the characteristic appearance of a long-wavelength absorption bands with maxima at 440, 515, and 880 nm. According to calculations on a MM2 optimized structure[13] of **2a** using the ZINDO/CI formalism with INDO/1 parameters,[13] the absorptions at 880 nm (calcd 674 nm; chromium-centered d_{z^2}-orbital HOMO to the propargyl moiety localized LUMO), at 515 nm (calcd 541 nm; $d_{x^2-y^2}$-orbital HOMO-1 to the LUMO), and at 440 nm (calcd 401 nm, $\pi-\pi^*$ transitions within the propargyl fragment (HOMO-5 to LUMO) and from the uncomplexed phenyl rings to the propargyl fragment (HOMO-6 to LUMO)) are readily reproduced.

Nucleophilic Trapping Reactions and Electrophilicity of 2a. At −78 °C the trapping reactions of the complex-substituted propargyl cation **2a** with a slight excess of various *π*- and n-nucleophiles give a facile access to allenyl- and propargyl-substituted arene complexes **7** in good yields and with excellent regioselectivity as yellow-orange crystalline solids (Scheme 2). In any case only the depicted isomer can be isolated. The spectroscopic data support the suggested structural assignments showing for the allenyl derivatives in the ^{13}C NMR spectra most significantly by the appearance of the characteristic resonance of the *β*-allenyl carbon atoms between $\delta = 205$ and 219 depending on the electronic nature of the substituent at the α-position.[14] Additionally, the structure of the allylated complex **7d** was confirmed by an X-ray crystal structure analysis[15] (Figure 1, Table 3).

Especially remarkable is the straightforward alternative synthesis of an allenylamine derivative **7f** from the propargyl alcohol **1a** via the stable cation **2a**. Starting from the uncomplexed propargyl alcohol **3,** this synthetic pathway to allenylamines is not feasible even under in-situ-ionization conditions in acidic media,[16] and classically, allenylamines are prepared by a base-

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(9) Olah, G. A.; Spear, R. J.; Westerman, P. W.; Denis, J.-M. *J. Am. Chem. Soc.* **1974**, *96*, 5855.

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(11) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C NMR Spektroskopie*; Georg Thieme Verlag: Stuttgart, New York, 1984; p 371.

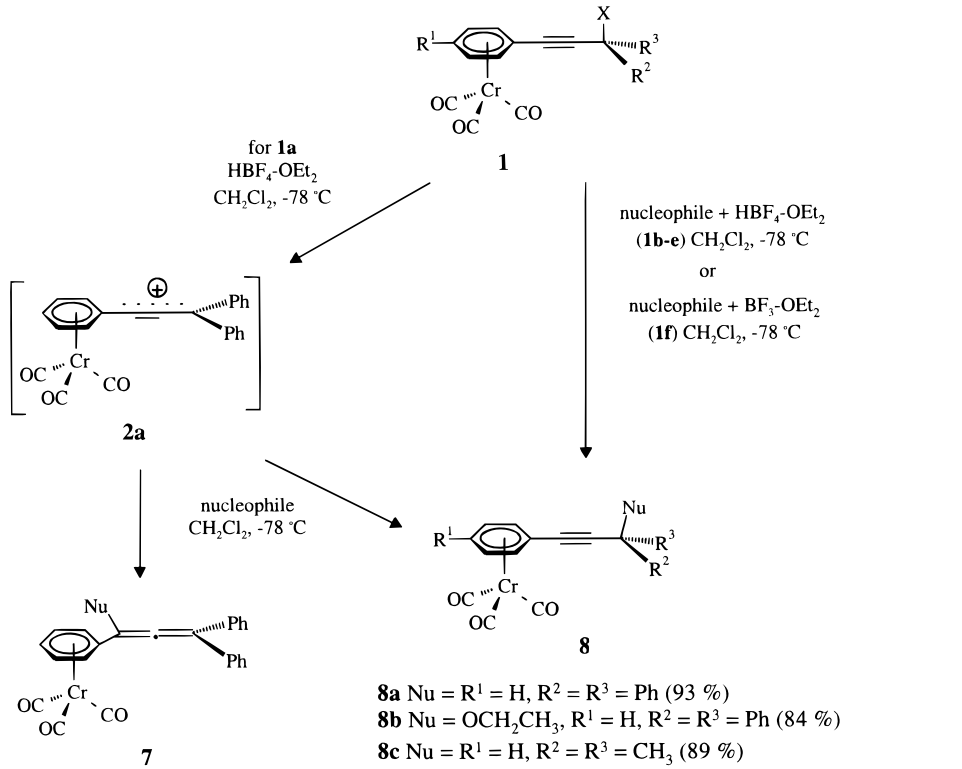
(12) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C NMR Spektroskopie*, Georg Thieme Verlag: Stuttgart, New York, 1984, p 144.

(13) *Quantum CAChe 3.0 Program*; Oxford Molecular Group, 1997.

(14) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C NMR Spektroskopie*; Georg Thieme Verlag: Stuttgart, New York, 1984; p 273.

(15) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-114222 (**7d**) and CCDC-114223 (**9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax + 44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk).

Scheme 2



7a Nu = $Ph_3P^+BF_4^-$ (55 %)
7b Nu = $C(CH_3)_2CO_2CH_3$ (87 %)
7c Nu = 2-oxocyclohexanyl (46 %)
7d Nu = allyl (89 %)
7e Nu = 2,4-dimethoxyphenyl (73 %)
7f Nu = N^iPr_2 (91 %)

8a Nu = R^1 = H, R^2 = R^3 = Ph (93 %)
8b Nu = OCH_2CH_3, R^1 = H, R^2 = R^3 = Ph (84 %)
8c Nu = R^1 = H, R^2 = R^3 = CH_3 (89 %)
8d Nu = 2,4-dimethoxyphenyl, R^1 = H, R^2 = R^3 = CH_3 (86 %)
8e Nu = $PPh_3^+BF_4^-$, R^1 = H, R^2 = R^3 = CH_3 (67 %)
8f Nu = 2,4-dimethoxyphenyl, R^1 = R^2 = R^3 = CH_3 (86 %)
8g Nu = allyl, R^1 = R^2 = R^3 = CH_3 (93 %)
8h Nu = allyl, R^1 = R^2 = H, R^3 = Ph (84 %)
8i Nu = R^1 = R^2 = H, R^3 = Ph (61 %)
8j Nu = $C(CH_3)_2CO_2CH_3$, R^1 = R^2 = H, R^3 = Ph (98 %)
8k Nu = $CH_2C(O)Ph$, R^1 = R^2 = H, R^3 = Ph (86 %)

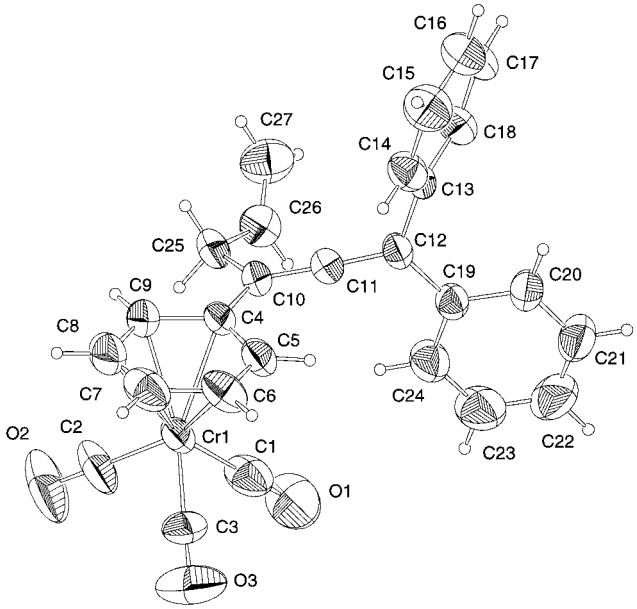


Figure 1. ORTEP plot of **7d** and selected bond lengths [Å], bond angles [deg], and torsional angles [deg]: C(4)−C(10) 1.482(5), C(10)−C(11) 1.306(4), C(11)−C(12) 1.317(4), C(10)−C(11)−C(12) 176.5(4), C(5)−C(4)−C(10)−C(11) −14.1(5), C(9)−C(4)−C(10)−C(25) 165.8(3).

catalyzed rearrangement of the corresponding propargylamines.[17] Furthermore, this arene complex-substituted allenylamine is fairly acid sensitive. Even on silica gel (thin-layer chromatography) a complete conversion via a violet, strongly polar intermediate, presumably the allyl cation, proceeds readily to give 50% of the hydrolysis product, the enone **9**, as red crystals (Scheme 3). Independently, **9** can be synthesized by the acid-catalyzed *Meyer−Schuster rearrangement*[18] from the propargyl alcohol **1a** in 73% yield. The structure of **9** was unambiguously corroborated by X-ray crystallography[15] (Figure 2, Table 3). Due to the torsional strain imposed on the enone by the two geminal phenyl groups at the γ-terminus of the side chain, the enone strongly deviates from coplanarity, as indicated by the torsional angles.

In all trapping reactions with carbon π, phosphorus, and nitrogen nucleophiles exclusively allenes were formed. Ethanol and the hydride donor triethylsilane, however, regioselectively gave rise to the formation of

(16) For reactions with propargyl alcohols under in-situ ionization conditions see, for example: Mayr, H.; Bäuml, E. *Tetrahedron Lett.* **1984**, *25*, 1127.

(17) See, for example: (a) Normant, H.; Mantione, R.; *C. R. Hebd. Seances Acad. Sci.* **1964**, *259*, 1635. (b) Pourcelot, G.; Cadiot, P.; Georgoulis, C.; *Tetrahedron* **1982**, *38*, 2123.

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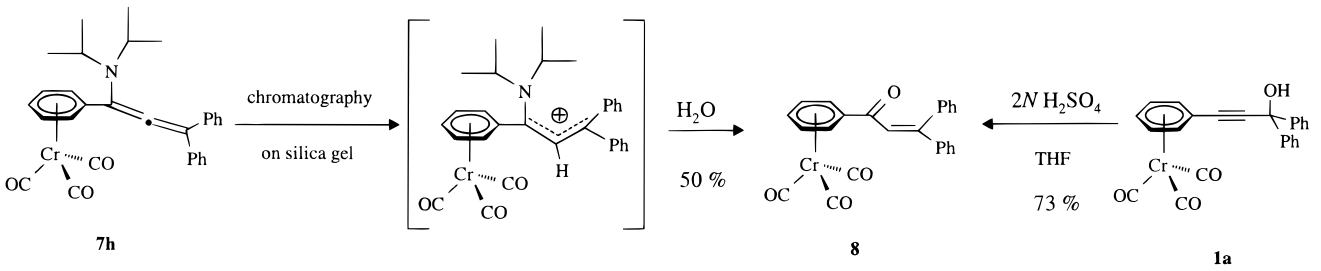
Table 3. Crystal Data and Structure Refinements for 7d and 9

	7d	9
empirical formula	$C_{27}H_{20}CrO_3$	$C_{24}H_{16}CrO_4$
color, form	yellow plates	red plates
fw	444.43	420.37
temperature (K)	295(2)	294(2)
wavelength (Å), radiation	0.71073 (Mo Kα)	0.71073 (Mo Kα)
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
unit cell dimens (Å, deg),	a = 9.9946(15); α = 82.246 (14)	a = 18.5944(21); α = 90.00(13)
	b = 10.277(2); β = 84.525(15)	b = 7.3122(17); β = 96.487(9)
	c = 11.3709(15); γ = 84.94(2)	c = 29.2020(34); γ = 90.000(14)
volume (Å^3)	1148.6(3)	3945.0(1)
Z	2	8
density (calcd) (g/cm^3)	1.285	1.416
absorption coeff (mm^{-1})	0.522	0.608
F(000)	460	1728
crystal size (mm)	0.17 × 0.27 × 0.43	0.10 × 0.33 × 0.66
θ range for data collection (deg)	2.53−23.97	2.20−23.98
index ranges	$-11 \le h \le 11$	$-20 \le h \le 21$
	$-11 \le k \le 11$	$0 \le k \le 8$
	$0 \le l \le 12$	$-33 \le l \le 0$
no. of reflns collected	3798	3178
no. of indep reflns	3592 [R(int) = 0.0200]	3103 [R(int) = 0.0117]
no. obsd ($I > 2\sigma(I)$)	2465	2617
absorption corr	semiempirical from ψ-scans	semiempirical from ψ-scans
max. and min. transmission	0.8917 and 0.9998	0.9298 and 0.9997
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	3592/24/368	3103/0/262
goodness-of-fit on F^2	1.099	1.096
final R indices [$I > 2\sigma(I)$]		
R1	0.0532	0.0322
wR2	0.1140	0.0781
R indices (all data)		
R1	0.0827	0.0435
wR2	0.1298	0.0858
largest diff. peak and hole (e/Å^3)	0.249 and −0.164	0.218 and −0.277

Scheme 3



propargyl derivatives. This prompted us to look in more detail into the nucleophile-dependent ambident reactivity of the cation **2a**.

According to the UV/vis studies, the ambident cation **2a** is stable from −70 °C (for several hours) to room temperature (rapid decomposition over 20 °C). Therefore, a semiquantitative treatment of the reactivity of **2a** according to *Mayr's electrophilicity−nucleophilicity equation*,[19]

$$\log k(20\ °C) = s(E + N) \qquad (2)$$

where s is the nucleophile-dependent slope parameter, E is the electrophilicity parameter, and N is the nucleophilicity parameter, was pursued by determining the kinetics of the nucleophilic trapping reactions of **2a** with an excess of four well-characterized nucleophiles (allyltrimethylsilane, 1,3-dimethoxybenzene, allyltriphenylstannane, and triphenylsilane).[19] Thus, the time-dependent decrease of the long-wavelength absorption band of **2a** at 460 nm was measured at various temperatures and found to follow a pseudo-first-order rate

(19) Mayr, H.; Patz, M. *Angew. Chem.* **1994**, *106*, 990.

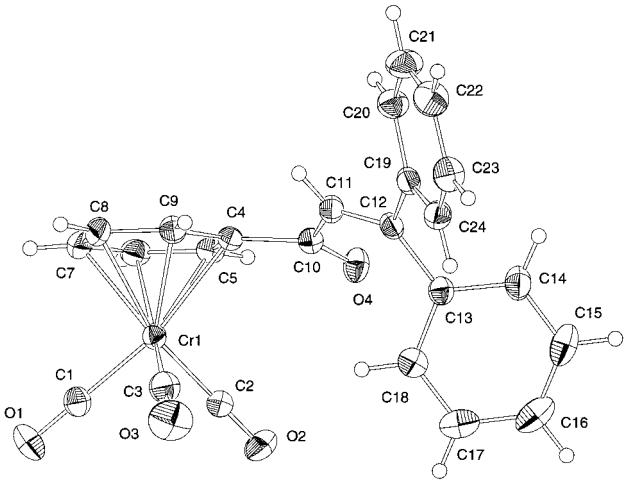
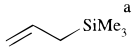
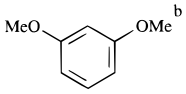
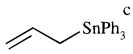
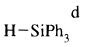


Figure 2. ORTEP plot of **9** and selected bond lengths [Å], bond angles [deg], and torsional angles [deg]: C(4)−C(10) 1.498(3), C(10)−C(11) 1.474(3), C(11)−C(12) 1.344 (3), O(4)−C(10) 1.218(3), C(10)−C(11)−C(12) 127.2(2), C(9)−C(4)−C(10)−C(11) −19.5(3), C(9)−C(4)−C(10)−O(4) 163.4-(2), O(4)−C(10)−C(11)−C(12) −26.9(4), C(4)−C(10)−C(11)−C(12) 156.1(2).

Table 4. Kinetics of the Nucleophilic Trapping Reaction of 2a with Selected Nucleophiles

Nucleophile	no.	T [°C]	$[\mathbf{1a}]_0$ [molL^{-1}]	$[\text{nucleophile}]_0$ [molL^{-1}]	$[HBF_4]_0$ [molL^{-1}]	conv.	k_{obs} [Lmol^{-1}s^{-1}]
 [a]	1	-40	$8.69 \cdot 10^{-5}$	$8.27 \cdot 10^{-3}$	$1.46 \cdot 10^{-3}$	69 %	$2.49 \cdot 10^{-1}$
	2	-30	$8.74 \cdot 10^{-5}$	$1.65 \cdot 10^{-2}$	$1.47 \cdot 10^{-3}$	76 %	$4.94 \cdot 10^{-1}$
	3	-20	$7.67 \cdot 10^{-5}$	$1.45 \cdot 10^{-2}$	$1.29 \cdot 10^{-3}$	72 %	1.26
	4	-10	$7.67 \cdot 10^{-5}$	$1.45 \cdot 10^{-2}$	$1.29 \cdot 10^{-3}$	90 %	2.65
 [b]	1	-70	$8.08 \cdot 10^{-5}$	$4.12 \cdot 10^{-3}$	$1.44 \cdot 10^{-3}$	44 %	6.50
	2	-60	$8.27 \cdot 10^{-5}$	$2.11 \cdot 10^{-3}$	$1.48 \cdot 10^{-3}$	51 %	15.71
	3	-50	$7.67 \cdot 10^{-5}$	$2.34 \cdot 10^{-3}$	$1.37 \cdot 10^{-3}$	49 %	23.83
	4	-40	$7.95 \cdot 10^{-5}$	$4.05 \cdot 10^{-3}$	$1.42 \cdot 10^{-3}$	76 %	39.02
 [c]	1	-66	$6.68 \cdot 10^{-5}$	$1.58 \cdot 10^{-2}$	$5.10 \cdot 10^{-4}$	35 %	1.523
	2	-60	$7.45 \cdot 10^{-5}$	$1.32 \cdot 10^{-2}$	$5.69 \cdot 10^{-4}$	52 %	2.247
	3	-50	$7.39 \cdot 10^{-5}$	$1.31 \cdot 10^{-2}$	$5.64 \cdot 10^{-4}$	42 %	5.184
	4	-38	$7.03 \cdot 10^{-5}$	$1.25 \cdot 10^{-2}$	$5.37 \cdot 10^{-4}$	34 %	10.89
 [d]	1	-20	$7.74 \cdot 10^{-5}$	$6.14 \cdot 10^{-3}$	$1.39 \cdot 10^{-3}$	69 %	$8.86 \cdot 10^{-2}$
	2	-10	$7.23 \cdot 10^{-5}$	$5.74 \cdot 10^{-3}$	$1.30 \cdot 10^{-3}$	64 %	$2.12 \cdot 10^{-1}$
	3	0	$7.41 \cdot 10^{-5}$	$2.94 \cdot 10^{-3}$	$1.33 \cdot 10^{-3}$	61 %	$4.54 \cdot 10^{-1}$
	4	10	$7.91 \cdot 10^{-5}$	$2.19 \cdot 10^{-3}$	$1.42 \cdot 10^{-3}$	57 %	1.38
	5	20	$8.11 \cdot 10^{-5}$	$2.12 \cdot 10^{-3}$	$1.46 \cdot 10^{-3}$	63 %	2.48

[a] 1.08×10^{-3} M solution of **1a** in dry and degassed dichloromethane; neat allyl trimethylsilane (6.26 M). [b] 1.02×10^{-3} M solution of **1a** in dry and degassed dichloromethane; neat 1,3-dimethoxybenzene (1.045 M). [c] 9.51×10^{-4} M solution of **1a** in dry and degassed dichloromethane; 1.126 M solution of allyltriphenylstannane in dichloromethane. [d] 1.01×10^{-3} M solution of **1a** in dry and degassed dichloromethane; 1.61 M solution of triphenylsilane in dichloromethane.

law. The results of the kinetic measurements are summarized in Table 4.

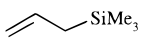
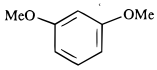
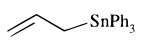
Along with the rate constants at various temperatures an Eyringplot ($\ln(k/T) = -(\Delta H^{\ddagger}/R)(1/T) + (\Delta S^{\ddagger}/R) + \ln(k_B/h)$) gives the activation parameters (Arrhenius and Eyring parameters) of the nucleophilic trapping reactions and allows the extrapolation to a rate constant at 20 °C. The results of the Eyring plots and the calculated electrophilicity parameters E are summarized in Table 5.

From the kinetics of the trapping reactions with allyl trimethylsilane, 1,3-dimethoxybenzene, and allyltriphenylstannane an average electrophilicity parameter $\bar{E} = -0.36 \pm 0.18$ can be calculated. The electrophilicity as determined from the trapping reaction with the hydride donor triphenyl silane deviates by 1 order of magnitude from the average parameter for the π-nucleophiles. Since all types of π-nucleophiles attack the ambident cation **2a** at the α-position giving rise to allenyl derivatives (vide supra) and triphenylsilane reacts with **2a** at the γ-position to give a propargyl derivative, the assumption lies at hand that there exists a nucleophile-dependent reactivity of the two reaction centers. However, since a nucleophilic attack to the cation **2a** very likely occurs in an *anti*-fashion with respect to the chromium carbonyl tripod, a strong participation of steric rather than electronic effects cannot be fully excluded. Regarding the Eyring activation entropy terms, the transition states for the attack at the α-position (π-nucleophiles) are significantly higher ordered than for those for the attack at the γ-position (triphenyl silane). This also suggests for an incoming π-nucleophile a coplanar orientation of its π-orbitals with those of the propargyl−allenyl cation in order to maximize the stabilizing interactions. Thus, the π-nucleophiles tend to react rather by orbital control and by minimization of steric strain, whereas the hydride donor triphenylsilane reacts by charge control, i.e., at the γ-position. In comparison to the free ligand **4** ($\bar{E} = 1.64$)[20] the reactivity of the chromium carbonyl-stabilized γ-propargyl−allenyl cation **2a** is lowered by 2 orders of magnitude.

***In-Situ* Ionizations with Arene Complex-Substituted Propargyl Alcohols.** Unfortunately, all at-

(20) Siegmund, T.; Mayr, H. Unpublished results.

Table 5. Activation and Electrophilicity Parameters from the Evaluation of the Eyring Plot and Mayr's Equation

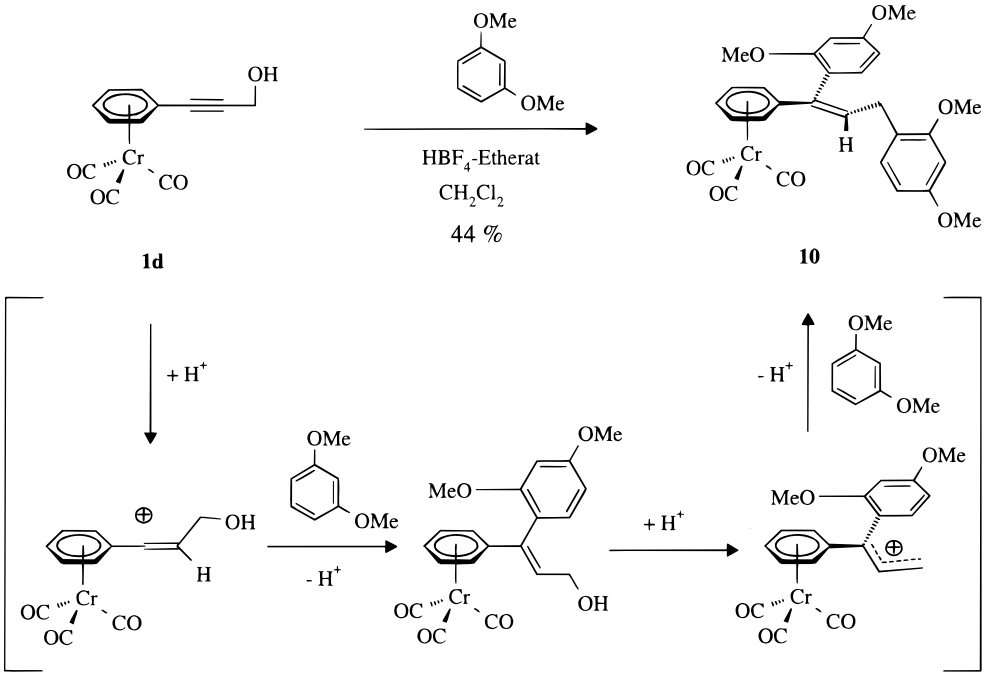
nucleophile	activation energy E_a [kJmol^{-1}]	lg(A)	activation enthalpy $\Delta H^{\neq}$ [kJmol^{-1}]	activation entropy $\Delta S^{\neq}$ [JK^{-1}mol^{-1}]	k(20 °C) [Lmol^{-1}s^{-1}]	nucleophilicity N	s parameter	electrophilicity E
	40.902 ± 2.225	8.530 ± 0.470	38.844 ± 2.206	-88.410 ± 8.917	17.6	1.62	1.01	-0.38
	22.921 ± 2.302	6.747 ± 0.553	21.114 ± 2.322	-121.481 ± 10.688	476.8	2.40	1.20	-0.17
	30.971 ± 0.788	7.966 ± 0.189	29.145 ± 0.772	-98.212 ± 3.535	291.9	3.29	0.89	-0.52
H-SiPh$_3$	52.666 ± 2.446	9.791 ± 0.470	50.404 ± 2.438	-65.063 ± 8.962	2.48	1.91	0.72	-1.36

tempts to generate stable cationic intermediates from the propargyl alcohols **1b** and **1c** where the two stabilizing phenyl goups have been replaced by methyl groups were unsuccessful. Although, a short-lived deep blue species was observed when adding the propargyl alcohol **1b** to a solution of tetrafluoroboric acid in dichloromethane at −78 °C, it was not possible to trap this intermediate prior to decomposition with a nucleophile. However, if the nucleophilic trapping reactions are conducted under in-situ ionization conditions (the propargyl alcohol and the nucleophile are added to HBF_4 etherate in dichloromethane at −78 °C) with acid-stable nucleophiles such as allyltrimethylsilane, triethylsilane, 1,3-dimethoxybenzene, or triphenylphosphane, the propargyl derivatives **8c**−**g** are formed regioselectively as yellow crystals with moderate to good yields (Scheme 2) and it seems to be very likely that the product formation proceeds through a nucleophilic addition to an intermediate propargyl cation.

Therefore, we were intrigued to investigate the regioselectivity of the nucleophilic attack if only one phenyl substituent was present at the γ-position. A model system such as **1e** also would rule out steric biases. Under the conditions of the in-situ ionization for either the alcohol **1e** with tetrafluoroboric acid and acid-stable nucleophiles or the acetate **1f** with boron trifluoride and acid-labile nucleophiles exclusively the propargylic derivatives **8h**−**k** were found and isolated in good to excellent yields (Scheme 2).

Finally, omitting any stabilizing substituents at the γ-position should lead to a very reactive cationic intermediate that forms upon the protonation of complexed 3-phenylprop-2-yn-1-ol (**1d**) under the conditions of in-situ ionization in the presence of 1,3-dimethoxybenzene. A 2:1 product **10** can be isolated in 44% yield as a yellow solid (Scheme 4), and its structure was unambiguously confirmed by 2D-NMR spectroscopy (NOESY, HETCOR). Presumably, the reaction path here does not proceed via a propargyl cation, but, in analogy with ferrocenyl-substituted propargyl alcohols[6a] the formation of a (benzene)Cr(CO)$_3$-stabilized vinyl cation (in analogy with ref 6c) seems to be reasonable. Therefore,

Scheme 4



a sequence based upon the different reactivity of vinyl and allyl cations that commences with a triple-bond protonation, followed by an electrophilic aromatic substitution with a vinyl cation, followed by an acidic allyl alcohol ionization to give a allyl cation, and concludes with another electrophilic aromatic substitution rationalizes the formation of **10**.

Based upon this methodology, regioselective functionalizations at the γ-position of arene complex-substituted γ-propargyl derivatives easily can be envisioned. However, a control of the stereochemistry at this remote position still remains a challenge in the field of side chain functionalizations. Presumably, a stronger stabilization of the propargyl−allenyl cation by an electron-richer chromium fragment would allow fine-tuning of the regioselectivity, i.e., propargyl vs allenyl substitution.

Conclusion

The chromium carbonyl complexation has a significant effect on the electronic nature of the triphenyl propargylium ion **4**. This stable species **2a** can be studied by NMR and UV/vis spectroscopy, and its reactivity was investigated by kinetic measurements. Compared with its free ligand **4**, the cation **2a** is by 2 orders of magnitude less reactive in nucleophilic addition reactions. The nucleophilic trapping reactions occurred with a predominant regioselectivity at the allenyl position due to steric biases imposed by the γ-terminal phenyl substituents. However, the corresponding dialkyl- or monophenyl-substituted systems were found to react under the conditions of the in-situ ionization to give regioselectively the propargyl derivatives. Nevertheless, these findings represent an extension of the well-established benzyl cation stabilization by chromium arene complexation to conjugated side chains. Further studies directed to control and reverse the regioselectivity of the nucleophilic additions by ligand substitutions on the chromium carbonyl tripod for fine-tuning the side chain functionalizations are currently under way.

Experimental Section

All reactions involving tricarbonyl chromium 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.[21] Column chromatography: silica gel 60 (0.063−0.2 mm/70−230 mesh, Firma Merck). TLC: silica gel plates (60 F_{254} Merck, Darmstadt). Melting points (uncorrected values): Reichert-Jung Thermovar. The chromium carbonyl-complexed aryl propargylic alcohols **1** were prepared according to our previously published protocols.[8] The trapping nucleophiles were purchased from Merck, Aldrich, or Fluka and used without further purification. ^{1}H 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 diodes array spectrometer) with a Hellma low-temperature quartz probe and J&M Spektralys program 1.5.5 for evaluation, Schölly UV-spectrometer KGS III Intraphotometer (UV/vis kinetics). 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.

$Cr(CO)_3(\eta^6\text{-}C_6H_5)C{\equiv}CCHOH(C_6H_5)$ (1e). Over 2 min 2.6 mL (4.20 mmol) of a 1.6 M BuLi solution was added dropwise to a solution of 1.0 g (4.20 mmol) of the $Cr(CO)_3$-complexed phenylacetylene in 25 mL of THF at −78 °C. The reaction mixture was stirred for 1 h, and then over 2 min a solution of 447 mg (4.20 mmol) of benzaldehyde in 5 mL of THF was added dropwise. Then the mixture was allowed to come to room temperature and was stirred for 1 h. After the addition of 10 mL of a saturated ammonium chloride solution to the reaction mixture the aqueous phase was extracted several times with diethyl ether. The combined organic phases were washed with distilled water and dried over magnesium sulfate. After evaporation of the solvents on the rotovap the residue was chromatographed on silica gel (gradient diethyl ether/pentane, 1:3, to diethyl ether) 1.11 g (77%) of the analytically pure propargyl alcohol **1e** is isolated as a yellow oil. ^{1}H NMR ([D_6]-DMSO, 300 MHz): δ = 5.57 (d, J = 4.9 Hz, 1 H), 5.66 (t, J = 6.0 Hz, 1 H), 5.72 (t, J = 6.4 Hz, 2 H), 5.84 (d, J = 6.2 Hz, 2 H), 6.23 (d, J = 4.8 Hz, 1 H), 7.29 (m, 1 H), 7.36 (t, J = 6.8 Hz, 2 H), 7.51 (d, J = 7.1 Hz, 2 H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 62.15 (CH), 80.11 ($C_{quat.}$), 90.72 ($C_{quat.}$), 90.74 ($C_{quat.}$), 93.23 (CH), 93.64 (CH, double intensity), 96.38 (CH), 96.42 (CH), 126.03 (CH), 127.26 (CH), 127.76 (CH), 140.86 ($C_{quat.}$), 232.68 ($C_{quat.}$, CO). MS (EI, 70 eV), m/z (%): 344 (M^+, 2), 260 (M^+ − 3 CO, 8), 52 (Cr^+, 100). IR (KBr): $\tilde{\nu}$ = 3560 cm^{-1}, 3369, 3089, 3033, 2924, 1966, 1889, 1524, 1493, 1455, 1408, 1285, 1247, 1189, 1151, 1079, 1025, 993, 957, 918, 815, 763, 722, 699, 672, 653, 627, 580, 532, 471. UV/vis (DMSO): λ_{max} (ϵ) = 321 nm (9400). Anal. Calcd for $C_{18}H_{12}CrO_4$ (344.28): C, 62.79; H, 3.51. Found: C, 62.79; H, 3.59.

$Cr(CO)_3(\eta^6\text{-}C_6H_5)C{\equiv}CCH[OC(O)CH_3](C_6H_5)$ (1f). The procedure followed the preceding to give the propargyl alcoholate. The reaction mixture was then allowed to come to 0 °C over 30 min before being recooled to −78 °C. To the mixture was added 0.85 mL (9.0 mmol) of acetic anhydride. After stirring the solution for 2 h at − 78 °C water was added and the aqueous phase was extracted several times with diethyl ether and then dried over magnesium sulfate. After evaporation of the solvents on the rotovap the residue was chromatographed on silica gel (gradient of diethyl ether/pentane, 1:4 to 1:2) 1.06 g (65%) of the acetate **1f** was isolated as yellow crystals. Mp: 118−120 °C. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ = 2.09 (s, 3 H), 5.68 (t, J = 6.4 Hz, 1 H), 5.74 (t, J = 6.1 Hz, 2 H), 5.88−5.91 (m, 2 H), 6.61 (s, 1 H), 7.40−7.45 (m, 3 H), 7.55−7.58 (m, 2 H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ = 20.79 (CH_3), 65.09 (CH), 82.95 ($C_{quat.}$), 86.17 ($C_{quat.}$), 89.82 ($C_{quat.}$), 94.00 (CH), 94.29 (CH), 94.30 (CH), 97.05 (CH), 97.12 (CH), 127.82 (CH), 128.87 (CH), 129.26 (CH), 136.42 ($C_{quat.}$), 169.30 ($C_{quat.}$), 233.16 ($C_{quat.}$). MS (EI, 70 eV), m/z (%): 386 (M^+, 20), 330 (M^+ − 2 CO, 1), 302 (M^+ − 3 CO, 100), 244 (M^+ − 3 CO − OAc, 37), 191 (M^+ − $Cr(CO)_3$ − OAc, 52), 52 (Cr^+, 31). IR (KBr): $\tilde{\nu}$ = 3094 cm^{-1}, 1968, 1915, 1895, 1740, 1637, 1527, 1495, 1457, 1430, 1409, 1368, 1348, 1307, 1291, 1280, 1224, 1190, 1149, 1017, 983, 952, 931, 891, 819, 756, 696, 673, 653, 631, 565, 544, 529, 470, 413. UV/vis (DMSO): λ_{max} (ϵ) = 322 nm (9700). Anal. Calcd for $C_{20}H_{14}CrO_5$ (386.32): C, 62.18; H, 3.65. Found: C, 62.32; H, 3.73.

Generation of the Cation 2a and Nucleophilic Trapping Reactions (General Procedure). To a degassed solution of 100 μL (0.62 mmol) of HBF_4 diethyl etherate in 10 mL of dichloromethane was added a solution of 0.20 g (0.48 mmol) of complex **1a** in 5 mL of dichloromethane dropwise and under nitrogen at −78 °C. Instantaneously, a dark green solution of the propargyl cation was formed, which was stirred for 60 min at −78 °C before a solution of 1.0−7.0 mmol of the nucleophile in 5 mL of dichloromethane was added to the reaction mixture. After stirring for 40 min at −78 °C the reaction mixture was allowed to come to room temperature, and after 2 h at room temperature 10 mL of water was added. The aqueous layer

(21) Various editors, *Organikum*, 14th ed.; VEB Deutscher Verlag der Wissenschaften: Berlin, 1993.

was extracted several times with dichloromethane. The combined organic phases were dried over magnesium sulfate, and the solvents were removed in vacuo (water bath 25 °C). The residue (with exception of **7a** and **7f**) was chromatographed on silica gel (diethyl ether/pentane, 1:1), and the yellow to orange band was isolated to give the allenyl (**7**) or propargyl derivatives (**8a,b**) as crystalline products. Further purification was achieved by recrystallization from suitable solvents.

$Cr(CO)_3(\eta^6\text{-}C_6H_5)C[P^+(C_6H_5)_3]{=}C{=}C(C_6H_5)_2BF_4^-$ (7a). According to the GP, the reaction with 0.262 g (1.0 mmol) of triphenylphosphane gave rise to 200 mg (55%) of pure **7a** after recrystallization of the crude residue from dichloromethane/diethyl ether. Mp: 197−200 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 5.09−5.19 (m, 5 H), 6.85−7.46 (m, 25 H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 90.90 (CH), 90.90 (C$_{quat.}$, 2 signals), 92.84 (C$_{quat.}$, $J_{P,C}$ = 87.5 Hz), 94.09 (CH), 94.40 (CH, $J_{P,C}$ = 3.3 Hz), 98.79 (C$_{quat.}$), 117.08 (C$_{quat.}$, $J_{P,C}$ = 88.2 Hz), 128.73 (CH, $J_{P,C}$ = 2.6 Hz), 129.53 (CH), 130.92 (CH), 131.08 (C$_{quat.}$), 131.09 (CH), 134.54 (CH, $J_{P,C}$ = 10.6 Hz), 136.41 (CH, $J_{P,C}$ = 3.3 Hz), 218.61 (C$_{quat.}$, $J_{P,C}$ = 3.9 Hz), 231.41 (C$_{quat.}$, CO). ^{31}P NMR (CD_2Cl_2, 121 MHz): δ = 22.9 ppm. MS (FAB), *m*/*z* (%): 665 ($M^+ - BF_4^-$, 17), 581 ($M^+ - BF_4^- - 3$ CO, 10), ($M^+ - BF_4^- - Cr(CO)_3$, 12). IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1}, 2924, 1967, 1890, 1629, 1586, 1483, 1453, 1439, 1407, 1309, 1187, 1123, 1108, 1062, 997, 901, 817, 770, 753, 725, 695, 656, 629, 576, 531, 519, 503. UV/vis (DMSO): λ_{max} (ϵ) = 340 nm (6300), 430 (1600). Anal.Calcd for $[C_{42}H_{30}CrO_3P]^+[BF_4]^-$ (752.46): C, 67.04; H, 4.01. Found: C, 66.93; H, 3.90.

$Cr(CO)_3(\eta^6\text{-}C_6H_5)C[C(CH_3)_2CO_2CH_3]{=}C{=}C(C_6H_5)_2$ (7b). According to the GP, the reaction with 0.30 mL (1.50 mmol) of 1-methoxy-2,2-dimethyl-1-(trimethylsiloxy)ethene gave rise to 210 mg (87%) of pure **7b**. Mp: 141−143 °C. ^{1}H NMR ([D$_6$]-DMSO, 300 MHz): δ = 1.41 (s, 6 H), 3.65 (s, 3 H), 5.69−5.78 (m, 5 H), 7.23−7.43 (m, 10 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 26.05 (CH$_3$), 48.79 (C$_{quat.}$), 52.78 (CH$_3$), 93.58 (CH), 95.07 (CH, broad, 2 signals), 106.15 (C$_{quat.}$), 111.24 (C$_{quat.}$), 114.18 (C$_{quat.}$), 128.19 (CH), 128.20 (CH), 128.91 (CH), 135.08 (C$_{quat.}$), 175.70 (C$_{quat.}$), 205.18 (C$_{quat.}$), 233.52 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 504 (M^+, 1), 448 ($M^+ - 2$ CO, 1), 420 ($M^+ - 3$ CO, 100), 368 ($M^+ - Cr(CO)_3$, 3), 52 (Cr^+, 16). IR (KBr): $\tilde{\nu}$ = 1956 cm^{-1}, 1893, 1872, 1727, 1629, 1524, 1492, 1454, 1413, 1388, 1355, 1258, 1184, 1145, 1079, 821, 770, 747, 696, 659, 631, 585, 536, 475. UV/vis (DMSO): λ_{max} (ϵ) = 324 nm (9100). Anal. Calcd for $C_{29}H_{24}CrO_5$ (504.49): C, 69.04; H, 4.79. Found: C, 69.11; H, 4.79.

$Cr(CO)_3(\eta^6\text{-}C_6H_5)C$(2-cyclohexan-1-onyl)$=C=C(C_6H_5)_2$ (7c). According to the GP, the reaction with 0.19 mL (1.00 mmol) of 1-(trimethylsiloxy)cyclohexene gave rise to 110 mg (46%) of pure **7c**. Mp: 122−125 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.60−3.65 (m, 9 H), 5.62−5.80 (m, 5 H), 7.37−7.32 (m, 10 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 24.58 (CH$_2$), 27.50 (CH$_2$), 33.13 (CH$_2$), 41.65 (CH$_2$), 50.63 (CH), 92.38 (CH), 92.53 (CH), 93.51 (CH), 95.34 (CH), 95.84 (CH), 106.73 (C$_{quat.}$), 107.68 (C$_{quat.}$), 115.42 (C$_{quat.}$), 128.03 (CH), 128.11 (CH), 128.18 (CH), 128.85 (CH), 134.96 (C$_{quat.}$), 135.00 (C$_{quat.}$), 205.75 (C$_{quat.}$), 209.01 (C$_{quat.}$), 234.02 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 500 (M^+, 4), 472 ($M^+ - CO$, 1), 444 ($M^+ - 2$ CO, 1), 416 ($M^+ - 3$ CO, 76), 364 ($M^+ - Cr(CO)_3$, 40), 52 (Cr^+, 3). IR (KBr): $\tilde{\nu}$ = 2939 cm^{-1}, 2862, 1962, 1883, 1707, 1629, 1523, 1492, 1449, 1312, 1127, 1073, 771, 697, 659, 630, 532, 473. UV/vis (DMSO): λ_{max} (ϵ) = 324 nm (9200). Anal. Calcd for $C_{30}H_{24}CrO_4$ (500.51): C, 71.99; H, 4.83. Found: C, 72.06; H, 5.00.

$Cr(CO)_3(\eta^6\text{-}C_6H_5)C[CH_2CH{=}CH_2]{=}C{=}C(C_6H_5)_2$ (7d). According to the GP, the reaction with 0.24 mL (1.50 mmol) of allyltrimethylsilane gave rise to 190 mg (89%) of pure **7d**. Mp: 136−138 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 3.21 (d, *J* = 5.1 Hz, 2 H), 5.11−5.26 (m, 2 H), 5.68 (m, 1 H), 5.80−5.84 (m, 5 H), 7.35 (m, 10 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 33.7 (CH$_2$), 92.6 (CH), 94.1 (CH), 95.4 (CH), 105.3 (C$_{quat.}$), 107.0 (C$_{quat.}$), 114.7 (C$_{quat.}$), 117.7 (CH$_2$), 128.2 (CH), 128.2 (CH), 129.0 (CH), 134.7 (CH), 135.4 (C$_{quat.}$), 205.6 (C$_{quat.}$), 234.1 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 444 (M^+, 8), 360 ($M^+ - 3$ CO, 100), 308 ($M^+ - Cr(CO)_3$, 8), 52 (Cr^+, 3). IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1}, 1967, 1903, 1884, 1644, 1597, 1522, 1492, 1454, 1415, 1268, 1072, 1029, 991, 912, 819, 772, 754, 700, 681, 657, 629, 580, 531, 474. UV/vis (DMSO): λ_{max} (ϵ) = 325 nm (10500). Anal. Calcd for $C_{27}H_{20}CrO_3$ (444.44): C, 72.96; H, 4.54. Found: C, 73.37; H, 4.72.

$Cr(CO)_3(\eta^6\text{-}C_6H_5)C[o,p\text{-}C_6H_3(OCH_3)_2]{=}C{=}C(C_6H_5)_2$ (7e). According to the GP, the reaction with 0.26 mL (2.0 mmol) of 1,3-dimethoxybenzene gave rise to 190 mg (73%) of pure **7e**. Mp: 174−178 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 3.73 (s, 3 H), 3.78 (s, 3 H), 5.55 (d, *J* = 6.0 Hz, 2 H), 5.66−5.73 (m, 3 H), 6.64 (d, *J* = 8.2 Hz, 1 H), 6.69 (s, 1 H), 7.19 (d, *J* = 8.0 Hz, 1 H), 7.38 (m, 10 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 55.50 (CH$_3$), 55.65 (CH$_3$), 93.19 (CH), 94.25 (CH), 94.73 (CH), 99.21 (CH), 105.09 (C$_{quat.}$), 105.61 (CH), 107.03 (C$_{quat.}$), 112.86 (C$_{quat.}$), 114.08 (C$_{quat.}$), 128.18 (CH), 128.33 (CH), 128.86 (CH), 131.14 (CH), 134.95 (C$_{quat.}$), 157.98 (C$_{quat.}$), 161.26 (C$_{quat.}$), 206.37 (C$_{quat.}$), 233.97 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 540 (M^+, 10), 456 ($M^+ - 3$ CO, 100), 404 ($M^+ - Cr(CO)_3$, 64), 52 (Cr^+, 9). IR (KBr): $\tilde{\nu}$ = 3059 cm^{-1}, 2937, 2837, 1959, 1889, 1606, 1578, 1505, 1492, 1455, 1441, 1414, 1306, 1282, 1246, 1209, 1170, 1157, 1095, 1073, 1032, 927, 900, 836, 769, 745, 696, 659, 631, 581, 534, 475. UV/vis (DMSO): λ_{max} (ϵ) = 315 nm (11600). Anal. Calcd for $C_{32}H_{24}CrO_5$ (540.53): C, 71.10; H, 4.47. Found: C, 71.47; H, 4.57.

$Cr(CO)_3(\eta^6\text{-}C_6H_5)C\{N[CH(CH_3)_2]_2\}{=}C{=}C(C_6H_5)_2$ (7f). Deviating from the GP, the reaction with 1.0 mL (7.0 mmol) of diisopropylamine was subjected to an aqueous workup with saturated sodium bicarbonate solution. After extraction of the aqueous phase with ether the combined organic extracts were dried over magnesium sulfate and the solvents were removed on the rotovap. The residue was recrystallized from pentane to give 220 mg (91%) of pure **7f**. Mp: 134−136 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.01 (d, *J* = 6.4 Hz, 12 H), 3.41 (sept, *J* = 6.4 Hz, 2 H), 5.66 (t, *J* = 6.3 Hz, 2 H), 5.77 (t, *J* = 6.1 Hz, 1 H), 6.07 (d, *J* = 6.4 Hz, 2 H), 7.31−7.42 (m, 10 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 21.31 (CH$_3$), 49.72 (CH), 92.71 (CH), 95.03 (CH), 96.36 (CH), 109.26 (C$_{quat.}$), 115.65 (C$_{quat.}$), 116.33 (C$_{quat.}$), 128.11 (CH), 128.24 (CH), 128.78 (CH), 135.96 (C$_{quat.}$), 206.05 (C$_{quat.}$), 233.92 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 503 (M^+, 7), 447 ($M^+ - 2$ CO, 7), 419 ($M^+ - 3$ CO, 100), 367 ($M^+ - Cr(CO)_3$, 5), 52 (Cr^+, 15). IR (KBr): $\tilde{\nu}$ = 3081 cm^{-1}, 2971, 2929, 1958, 1892, 1869, 1653, 1596, 1520, 1491, 1452, 1413, 1381, 1364, 1247, 1183, 1145, 1119, 1073, 1030, 897, 920, 827, 768, 737, 696, 661, 631, 605, 533, 476. UV/vis (DMSO): λ_{max} (ϵ) = 322 nm (11800). Anal. Calcd for $C_{30}H_{29}CrNO_3$ (503.55): C, 71.55; H, 5.80, N: 2.78. Found: C, 71.57; H, 5.76, N: 2.63.

$Cr(CO)_3(\eta^6\text{-}C_6H_5)C(=O)C=C(C_6H_5)_2$ (9). (a) Hydrolysis of the Allenylamine 7f on Silica Gel. The crude allenylamine (from a 0.48 mmol scale reaction, vide supra) was chromatographed on wet silica gel (gradient ether to dichloromethane) to give 100 mg (50%) of pure **9** as dark red needles (from dichloromethane/pentane).

(b) Meyer−Schuster Rearrangement of 1a. To a degassed solution of 0.3 g (0.7 mmol) of **1a** in 20 mL of THF was added 6 mL of degassed 25% aqueous sulfuric acid. The reaction mixture was heated to reflux temperature for 3 h. After cooling the mixture was neutralized with a 2 N aqueous sodium hydroxide solution, and the aqueous phase was extracted several times with diethyl ether. The combined organic extracts were washed with a saturated sodium bicarbonate solution and dried over magnesium sulfate. The solvents were removed on the rotovap, and the residue was chromatographed on silica gel (gradient diethyl ether/pentane, 1:4, to ether) to 220 mg (73%) of pure **9** as dark red needles (from dichloromethane/pentane).

Mp: 143−145 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.64 (t, *J* = 6.5 Hz, 2 H), 6.07 (t, *J* = 6.3 Hz, 1 H), 6.44 (d, *J* = 6.5

Hz, 2 H), 7.17−7.37 (m, 11 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 91.98 (CH), 96.98 (CH), 98.54 (CH), 99.18 (C$_{quat.}$), 121.05 (CH, olefin.), 128.28 (CH), 128.40 (CH), 128.61 (CH), 128.77 (CH), 129.36 (CH), 129.96 (CH), 139.01 (C$_{quat.}$), 140.61 (C$_{quat.}$), 155.36 (C$_{quat.}$), 187.89 (C$_{quat.}$), 232.33 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 420 (M$^+$, 3), 392 (M$^+$ − CO, 3), 364 (M$^+$ − 2 CO, 8), 336 (M$^+$ − 3 CO, 100), 284 (M$^+$ − Cr(CO)$_3$, 10), 52 (Cr$^+$, 94). IR (KBr): $\tilde{\nu}$ = 1970 cm^{-1}, 1888, 1651, 1587, 1569, 1445, 1367, 1266, 1205, 1147, 1021, 955, 865, 750, 698, 657, 619. UV/vis (DMSO): λ_{max} (ϵ) = 317 nm (15500), 438 (3800). Anal. Calcd for $C_{24}H_{16}CrO_4$ (420.38): C, 68.57; H, 3.84. Found: C, 68.33; H, 3.74.

Cr(CO)$_3$(η^6-C$_6$H$_5$)C≡CCH(C$_6$H$_5$)$_2$ (8a). According to the GP, the reaction with 0.24 mL (1.50 mmol) of triethylsilane gave rise to 180 mg (93%) of pure **8a**. Mp: 94−97 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 5.44 (s, 1 H), 5.65 (m, 1 H), 5.74−5.76 (m, 2 H), 5.90−5.92 (m, 2 H), 7.22−7.55 (m, 10 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 42.19 (CH), 80.59 (C$_{quat.}$), 91.14 (C$_{quat.}$), 92.19 (C$_{quat.}$), 93.62 (CH), 94.69 (CH), 97.07 (CH), 127.15 (CH), 127.66 (CH), 128.84 (CH), 141.42 (C$_{quat.}$), 233.54 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 404 (M$^+$, 12), 348 (M$^+$ − 2 CO, 3), 320 (M$^+$ − 3 CO, 100), 268 (M$^+$ − Cr(CO)$_3$, 13), 52 (Cr$^+$, 3). IR (KBr): $\tilde{\nu}$ = 2981 cm^{-1}, 1968, 1895, 1720, 1627, 1492, 1455, 1437, 1369, 1326, 1241, 1153, 1049, 1022, 866, 772, 745, 701, 673, 655, 628, 535, 470. UV/vis (DMSO): λ_{max} (ϵ) = 322 nm (9100). Anal. Calcd for $C_{24}H_{16}CrO_3$ (404.38): C, 71.28; H, 3.98. Found: C, 71.53; H, 4.38.

Cr(CO)$_3$(η^6-C$_6$H$_5$)C≡CCOC$_2$H$_5$(C$_6$H$_5$)$_2$ (8b). According to the GP, the reaction with 117 μL (2.0 mmol) of ethanol gave rise to 180 mg (84%) of pure **8b**. Mp: 98−100 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.22 (t, *J* = 6.7 Hz, 3 H), 3.52 (q, *J* = 6.8 Hz, 2 H), 5.70 (t, *J* = 6.1 Hz, 1 H), 5.78 (t, *J* = 6.3 Hz, 2 H), 6.02 (d, *J* = 6.2 Hz, 2 H), 7.26 (t, *J* = 7.1 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 4 H), 7.55 (d, *J* = 7.4 Hz, 4 H). ^{13}C NMR ([D$_6$]-DMSO, 75 MHz): δ = 15.35 (CH$_3$), 60.23 (CH$_2$), 79.99 (C$_{quat.}$), 85.24 (C$_{quat.}$), 88.91 (C$_{quat.}$), 90.21 (C$_{quat.}$), 94.11 (CH), 94.39 (CH), 97.34 (CH), 126.09 (CH), 127.91 (CH), 128.50 (CH), 143.25 (C$_{quat}$), 233.33 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 448 (M$^+$, 9), 392 (M$^+$ − 2 CO, 1), 364 (M$^+$ − 3 CO, 18), 52 (Cr$^+$, 14). IR (KBr): $\tilde{\nu}$ = 3082 cm^{-1}, 2976, 2927, 2881, 1968, 1897, 1628, 1524, 1489, 1451, 1407, 1392, 1318, 1259, 1180, 1157, 1114, 1091, 1067, 1030, 1003, 940, 924, 815, 795, 760, 702, 672, 655, 630, 562, 532, 471. UV/vis (DMSO): λ_{max} (ϵ) = 323 nm (9600). Anal. Calcd for $C_{26}H_{20}CrO_4$ (448.43): C, 69.63; H, 4.49. Found: C, 70.25; H, 4.52.

General Procedure for the *in-Situ* Ionization of 1b and 1c. To a cooled solution (−78 °C) of 150 μL (0.93 mmol) of HBF$_4$ diethyl etherate and 3.2 mmol of the acid-stable nucleophile in 10 mL of dichloromethane was added dropwise a solution of 0.64 mmol of the complex **1b** or **1c** in 5 mL of dichloromethane over a period of 5 min. After 30 min of stirring at −78 °C 10 mL of water was added to the reaction mixture. The mixture was extracted several times with diethyl ether, and the combined organic phases were dried over magnesium sulfate. The residue was chromatographed on silica gel (1:3 diethyl ether/pentane) to give the pure propargylic products (**8c**−**g**).

Cr(CO)$_3$(η^6-C$_6$H$_5$)C≡CCH(CH$_3$)$_2$ (8c). According to the GP, the reaction with 0.50 mL (3.2 mmol) of triethylsilane gave rise to 160 mg (89%) of pure **8c**. Mp: 57−60 °C. ^{1}H NMR ([D$_6$]-DMSO, 300 MHz): δ = 1.16 (d, *J* = 6.7 Hz, 6 H), 2.76 (sept, *J* = 6.8 Hz, 1 H), 5.52−5.76 (m, 5 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 22.65 (CH$_3$), 31.23 (CH), 65.16 (C$_{quat.}$), 76.01 (C$_{quat.}$), 92.94 (CH), 93.53 (C$_{quat.}$), 95.09 (CH), 96.53 (CH), 233.64 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 280 (M$^+$, 24), 252 (M$^+$ − CO, 2), 224 (M$^+$ − 2 CO, 17), 196 (M$^+$ − 3 CO, 87), 144 (M$^+$ − Cr(CO)$_3$, 9), 52 (Cr$^+$, 100). IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1}, 2976, 2931, 1872, 2235, 1968, 1900, 1869, 1635, 1527, 1454, 1408, 1383, 1365, 1322, 1254, 1151, 1098, 1047, 1011, 996, 936, 813, 673, 656, 628, 528, 512, 470. UV/vis (DMSO): λ_{max} (ϵ) = 322 nm (9100). Anal. Calcd for $C_{14}H_{12}CrO_3$ (280.24): C, 60.00; H, 4.31. Found: C, 60.04; H, 4.40.

Cr(CO)$_3$(η^6-C$_6$H$_5$)C≡CC[*o*,*p*-C$_6$H$_3$(OCH$_3$)$_2$](CH$_3$)$_2$ (8d). According to the GP the reaction with 0.20 g (0.64 mmol) of complex **1c** and 0.42 mL (3.2 mmol) of 1,3-dimethoxybenzene gave rise to 230 mg (86%) of pure **8d**. Mp: 79−81 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.61 (s, 6 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 5.60−5.76 (m, 5 H), 6.45 (d, *J* = 8.5 Hz, 1 H), 6.58 (s, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 29.16 (CH$_3$), 34.57 (C$_{quat.}$), 55.30 (CH$_3$), 55.64 (CH$_3$), 77.07 (C$_{quat.}$), 93.03 (CH), 93.76 (C$_{quat.}$), 95.07 (CH), 96.64 (CH), 98.37 (C$_{quat.}$), 99.99 (CH), 104.32 (CH), 124.71 (C$_{quat.}$), 127.39 (CH), 158.52 (C$_{quat.}$), 159.77 (C$_{quat.}$), 233.69 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 416 (M$^+$, 19), 360 (M$^+$ − 2 CO, 3), 332 (M$^+$ − 3 CO, 100), 280 (M$^+$ − Cr(CO)$_3$, 5), 52 (Cr$^+$, 12). IR (KBr): $\tilde{\nu}$ = 3076 cm^{-1}, 2970, 2934, 2838, 2238, 1968, 1886, 1610, 1582, 1524, 1503, 1455, 1415, 1378, 1357, 1311, 1290, 1262, 1209, 1159, 1085, 1039, 995, 938, 842, 808, 724, 674, 655, 630, 573, 532, 472. UV/vis (DMSO): λ_{max} (ϵ) = 323 nm (9100). Anal. Calcd for $C_{22}H_{20}CrO_5$ (416.39): C, 63.46; H, 4.84. Found: C, 63.27; H, 4.71.

Cr(CO)$_3$(η^6-C$_6$H$_5$)C≡CC[P$^+$(C$_6$H$_5$)$_3$](CH$_3$)$_2$BF$_4^-$ (8e). According to the previous protocol, the reaction with 335 mg (1.28 mmol) of triphenylphosphane gave rise to 270 mg (67%) of **8e** after aqueous workup and recrystallization of the crude product from dichloromethane/diethyl ether. Mp: 145−148 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 1.73 (d, $^3J_{P,H}$ = 6.2 Hz, 6 H), 5.11−5.33 (m, 5 H), 7.56−7.85 (m, 15 H). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ = 26.83 (CH$_3$), 34.23 (C$_{quat.}$, $J_{P,C}$ = 50.4 Hz), 86.08 (C$_{quat.}$, $J_{P,C}$ = 3.7 Hz), 87.43 (C$_{quat.}$, $J_{P,C}$ = 7.5 Hz), 91.37 (C$_{quat.}$), 91.37 (CH), 93.42 (CH), 96.27 (CH, $J_{P,C}$ = 2.2 Hz), 116.61 (C$_{quat.}$, $J_{P,C}$ = 82.2 Hz), 131.01 (CH, $J_{P,C}$ = 11.9 Hz), 134.25 (CH, $J_{P,C}$ = 12.6 Hz), 134.79 (CH, $J_{P,C}$ = 8.6 Hz), 232.10 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 541 (M$^+$ − BF$_4^-$, 100), 513 (M$^+$ − BF$_4^-$ − CO, 3), 457 (M$^+$ − BF$_4^-$ − 3 CO, 34), 405 (M$^+$ − BF$_4^-$ − Cr(CO)$_3$, 89). IR (KBr): $\tilde{\nu}$ = 3068 cm^{-1}, 2925, 1964, 1883, 1635, 1586, 1525, 1483, 1454, 1439, 1407, 1393, 1371, 1309, 1283, 1191, 1123, 1107, 1083, 1061, 996, 948, 913, 885, 840, 821, 755, 725, 693, 672, 654, 630, 618, 543, 532, 522, 510, 490. UV/vis (DMSO): λ_{max} (ϵ) = 324 nm (6900). Anal. Calcd for [$C_{32}H_{26}CrO_3P$]$^+$[BF$_4$]$^-$ (628.32): C, 61.17; H, 4.17. Found: C, 61.87; H, 4.44.

Cr(CO)$_3$(η^6-*p*-H$_3$CC$_6$H$_4$)C≡CC[*o*,*p*-C$_6$H$_3$(OCH$_3$)$_2$](CH$_3$)$_2$ (8f). According to the GP, the reaction with 0.42 mL (3.2 mmol) of 1,3-dimethoxybenzene gave rise to 190 mg (69%) of pure **8f**. Mp: 122−124 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.59 (s, 6 H), 2.10 (s, 3 H), 3.73 (s, 3 H), 3.81 (s, 3 H), 5.62 (d, *J* = 6.7 Hz, 2 H), 5.87 (d, *J* = 6.6 Hz, 2 H), 6.43 (dd, ^3J = 8.7 Hz, ^4J = 2.4 Hz, 1 H), 6.57 (d, ^4J = 2.4 Hz, 1 H), 7.38 (d, ^3J = 8.5 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 20.02 (CH$_3$), 29.15 (CH$_3$), 34.54 (C$_{quat.}$), 55.30 (CH$_3$), 55.66 (CH$_3$), 76.81 (C$_{quat.}$), 90.43 (C$_{quat.}$), 94.71 (CH), 97.55 (C$_{quat.}$), 98.10 (CH), 100.02 (CH), 104.29 (CH), 109.81 (C$_{quat.}$), 124.83 (C$_{quat.}$), 127.38 (CH), 158.53 (C$_{quat.}$), 159.75 (C$_{quat.}$), 233.87 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 430 (M$^+$, 18), 374 (M$^+$ − 2 CO, 2), 346 (M$^+$ − 3 CO, 100), 294 (M$^+$ − Cr(CO)$_3$, 4), 52 (Cr$^+$, 12). IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1}, 3013, 2974, 2936, 2241, 1965, 1906, 1891, 1610, 1581, 1504, 1457, 1439, 1387, 1357, 1310, 1291, 1271, 1258, 1209, 1160, 1139, 1085, 1044, 1028, 923, 887, 848, 798, 700, 676, 660, 644, 630, 574, 528, 471. UV/vis (DMSO): λ_{max} (ϵ) = 324 nm (9400). Anal. Calcd for $C_{23}H_{22}CrO_5$ (430.41): C, 64.18; H, 5.15. Found: C, 64.25; H, 5.27.

Cr(CO)$_3$(η^6-*p*-H$_3$CC$_6$H$_4$)C≡CC(CH$_2$CH=CH$_2$)(CH$_3$)$_2$ (8g). To a cooled solution (−78 °C) of 150 μL (0.93 mmol) of HBF$_4$ diethyl etherate in 10 mL of dichloromethane was added dropwise a solution of 200 mg (0.64 mmol) of **1c** and 0.51 mL (3.2 mmol) of allyltrimethylsilane in 5 mL of dichloromethane over a period of 5 min. After stirring at −78 °C for 15 min the reaction mixture was allowed to come to room temperature and was stirred for a further 15 min. The mixture was extracted several times with diethyl ether, and the combined

organic phases were dried over magnesium sulfate. The residue was chromatographed on silica gel (1:3 diethyl ether/pentane) to give 200 mg (93%) of pure **8g** as yellow crystals. Mp: 41−45 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.18 (s, 6 H), 2.09 (s, 3 H), 2.18 (d, J = 7.3 Hz, 2 H), 5.10 (d, J = 12.8 Hz, 2 H), 5.62 (d, J = 6.6 Hz, 2 H), 5.81 (d, J = 6.7 Hz, 2 H), 5.86−5.97 (m, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 19.99 (CH$_3$), 28.43 (CH$_3$), 31.24 (C$_{quat.}$), 46.88 (CH$_2$), 76.68 (C$_{quat.}$), 90.17 (C$_{quat.}$), 94.80 (CH), 96.91 (C$_{quat.}$), 97.87 (CH), 109.56 (C$_{quat.}$), 118.19 (CH$_2$), 134.80 (CH), 233.79 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 334 (M$^+$, 26), 278 (M$^+$ − 2 CO, 2), 250 (M$^+$ − 3 CO, 86), 198 (M$^+$ − Cr(CO)$_3$, 1), 52 (Cr$^+$, 34). IR (KBr): $\tilde{\nu}$ = 3079 cm^{-1}, 2973, 2926, 2235, 1966, 1891, 1641, 1540, 1466, 1443, 1384, 1363, 1314, 1298, 1156, 1096, 1035, 997, 919, 843, 815, 661, 626, 532, 472. UV/vis (DMSO): λ_{max} (ϵ) = 324 nm (9400). Anal. Calcd for $C_{18}H_{18}CrO_3$ (334.33): C, 64.66; H, 5.42. Found: C, 64.59; H, 5.45.

***In-Situ* Ionization of the Propargyl Alcohol 1e (General Procedure).** To a cooled solution (−78 °C) of 1.4 equiv of 54% HBF_4 etherate in 10 mL of dichloromethane was added dropwise a solution of 1 equiv of **1e** and 4 equiv of the acid-stable nucleophile in 5 mL of dichloromethane over 2 min. After stirring for 30 min at −78 °C 10 mL of distilled water was added and the reaction mixture was allowed to come to room temperature. The aqueous phase was extracted several times with diethyl ether, the combined organic phases were dried over magnesium sulfate, and the solvents were removed on the rotovap. Chromatography of the residue on silica gel (diethyl ether/pentane) afforded the pure substitution products (**8h,i**).

Cr(CO)$_3$(η^6-C$_6$H$_5$)C≡CCH(CH$_2$CH=CH$_2$)(C$_6$H$_5$) (8h). According to the GP, 90 mg (0.26 mmol) of **1e**, 0.16 mL (1.0 mmol) of allyltrimethylsilane, and 60 μL (0.37 mmol) of tetrafluoroboric acid gave rise to 80 mg (84%) of **8h** as a yellow oil. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 2.46−2.53 (m, 2 H), 4.04 (t, J = 7.5 Hz, 1 H), 5.03−5.10 (m, 3 H), 5.63 (t, J = 6.2 Hz, 1 H), 5.75 (t, J = 6.3 Hz, 2 H), 5.82 (d, J = 6.2 Hz, 2 H), 7.24 (t, J = 7.0 Hz, 1 H), 7.33 (t, J = 7.1 Hz, 2 H), 7.40 (d, J = 7.1 Hz, 2 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 37.07 (CH), 42.04 (CH$_2$), 79.77 (C$_{quat.}$), 92.00 (C$_{quat.}$), 92.59 (C$_{quat.}$), 93.44 (CH), 94.72 (CH, double intensity), 96.94 (CH), 96.98 (CH), 117.74 (CH$_2$), 127.09 (CH), 127.59 (CH), 128.34 (CH), 135.08 (CH), 140.46 (C$_{quat.}$), 233.55 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 368 (M$^+$, 13), 312 (M$^+$ − 2 CO, 1), 284 (M$^+$ − 3 CO, 100), 232 (M$^+$ − Cr(CO)$_3$, 1), 52 (Cr$^+$, 16). IR (KBr): $\tilde{\nu}$ = 3083 cm^{-1}, 2917, 2238, 1969, 1892, 1641, 1600, 1524, 1493, 1455, 1408, 1343, 1306, 1261, 1181, 1150, 1075, 1046, 1030, 994, 920, 813, 759, 699, 672, 653, 627, 531, 471. UV/vis (DMSO): λ_{max} (ϵ) = 322 nm (9000). Anal. Calcd for $C_{21}H_{16}CrO_3$ (368.35): C, 68.47; H, 4.37. Found: C, 69.55; H, 4.85.

Cr(CO)$_3$(η^6-C$_6$H$_5$)C≡CCH$_2$(C$_6$H$_5$) (8i). According to the GP, 140 mg (0.40 mmol) of **1e**, 0.19 mL (1.20 mmol) of triethylsilane, and 93 μL (0.58 mmol) of tetrafluoroboric acid gave rise to 80 mg (61%) of **8i** as a yellow crystals. Mp: 60−62 °C. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 3.88 (s, 2 H), 5.64 (t, J = 6.2 Hz, 1 H), 5.74 (t, J = 6.4 Hz, 2 H), 5.86 (d, J = 5.9 Hz, 2 H), 7.22−7.26 (m, 5 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 24.57 (CH$_2$), 78.51 (C$_{quat.}$), 89.08 (C$_{quat.}$), 92.67 (C$_{quat.}$), 93.64 (CH), 94.67 (CH), 97.13 (CH), 126.88 (CH), 128.03 (CH), 128.70 (CH), 136.05 (C$_{quat.}$), 233.59 (C$_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 328 (M$^+$, 16), 272 (M$^+$ − 2 CO, 7), 244 (M$^+$ − 3 CO, 100), 192 (M$^+$ − Cr(CO)$_3$, 16), 52 (Cr$^+$, 35). IR (KBr): $\tilde{\nu}$ = 3086 cm^{-1}, 3031, 1969, 1887, 1629, 1525, 1495, 1455, 1408, 1338, 1289, 1183, 1151, 1075, 1047, 1029, 1012, 999, 939, 813, 737, 716, 696, 673, 654, 628, 532, 474. UV/vis (DMSO): λ_{max} (ϵ) = 322 nm (9600). Anal. Calcd for $C_{18}H_{12}CrO_3$ (328.28): C, 65.85; H, 3.68. Found: C, 65.76; H, 3.25.

***In-Situ* Ionization of the Propargyl Acetate 1f (General Procedure).** To a cooled solution (−78 °C) of 2 equiv of boron trifluoride etherate in 10 mL of dichloromethane was added a solution of 1 equiv of **1f** and 4 equiv of the acid-labile nucleophile in 5 mL of dichloromethane dropwise over 2 min. After stirring for 30 min at −78 °C 10 mL of distilled water was added, and the reaction mixture was allowed to come to room temperature. The aqueous phase was extracted several times with diethyl ether, and the combined organic phases were dried over magnesium sulfate; the solvents were removed on the rotovap. Chromatography of the residue on silica gel (diethyl ether/pentane) afforded the pure substitution products (**8j,k**).

Cr(CO)$_3$(η^6-C$_6$H$_5$)C≡CCH[C(CH$_3$)$_2$CO$_2$CH$_3$](C$_6$H$_5$) (8j). According to the GP, 100 mg (0.26 mmol) of **1f**, 0.20 mL (1.0 mmol) of 1-methoxy-2,2-dimethyl-1-(trimethylsiloxy)ethene, and 63 μL (0.50 mmol) of boron trifluoride etherate gave rise to 110 mg (98%) of **8j** as a yellow oil. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 1.09 (s, 3 H), 1.27 (s, 3 H), 3.59 (s, 3 H), 4.27 (s, 1 H), 5.65−5.83 (m, 5 H), 7.31 (m, 5 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 21.58 (CH$_3$), 23.27 (CH$_3$), 45.68 (CH), 47.20 (C$_{quat.}$), 51.99 (CH$_3$, OMe), 80.53 (C$_{quat.}$), 89.69 (C$_{quat.}$), 91.87 (C$_{quat.}$), 93.76 (CH), 94.52 (CH, double intensity), 97.14 (CH), 97.19 (CH), 127.75 (CH), 128.21 (CH), 129.36 (CH), 136.60 (C$_{quat.}$), 175.50 (C$_{quat.}$), 233.50 (C$_{quat.}$), CO). MS (EI, 70 eV), *m*/*z* (%): 428 (M$^+$, 13), 372 (M$^+$ − 2 CO, 2), 344 (M$^+$ − 3 CO, 66), 292 (M$^+$ − Cr(CO)$_3$, 1), 52 (Cr$^+$, 21). IR (KBr): $\tilde{\nu}$ = 3087 cm^{-1}, 3031, 2981, 2950, 2234, 1965, 1887, 1731, 1601, 1524, 1493, 1455, 1434, 1408, 1388, 1367, 1343, 1303, 1243, 1191, 1150, 1126, 1079, 1047, 1017, 985, 917, 867, 815, 770, 752, 737, 703, 672, 654, 628, 532, 472. UV/vis (DMSO): λ_{max} (ϵ) = 323 nm (8000). Anal. Calcd for $C_{23}H_{20}CrO_5$ (428.40): C, 64.48; H, 4.71. Found: C, 65.02; H, 5.26.

Cr(CO)$_3$(η^6-C$_6$H$_5$)C≡CCH(CH$_2$COC$_6$H$_5$](C$_6$H$_5$) (8k). According to the GP, 200 mg (0.52 mmol) of **1f**, 0.42 mL (2.05 mmol) of 1-phenyl-1-(trimethylsiloxy)ethene silylenol ether, and 126 μL (1.0 mmol) of boron trifluoride etherate gave rise to 192 mg (86%) of **8k** as a yellow oil. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 3.53 (dd, J = 5.9 Hz, J = 17.2 Hz, 1 H), 3.68 (dd, J = 8.3 Hz, J = 17.2 Hz, 1 H), 4.50 (dd, J = 5.9 Hz, J = 8.1 Hz, 1 H), 5.60−5.72 (m, 5 H), 7.23−8.05 (m, 10 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 32.87 (CH), 46.20 (CH$_2$), 78.90 (C$_{quat}$), 92.32 (C$_{quat.}$), 92.56 (C$_{quat.}$), 93.25 (CH), 94.73 (CH), 96.69 (CH), 127.24 (CH), 127.77 (CH), 128.26 (CH), 128.71 (CH), 128.86 (CH), 133.52 (CH), 136.54 (C$_{quat.}$), 140.38 (C$_{quat.}$), 196.87 (C$_{quat.}$), 233.46 (C$_{quat.}$). MS (70 eV, EI), *m*/*z* (%): 446 (M$^+$, 8), 362 (M$^+$ − 3 CO, 100), 319 (M$^+$ − Cr(CO)$_3$, 16), 52 (Cr$^+$, 17). IR (KBr): $\tilde{\nu}$ = 2239 cm^{-1}, 1965, 1887, 1687, 1597, 1580, 1525, 1493, 1449, 1407, 1351, 1308, 1258, 1240, 1206, 1181, 1151, 1077, 1047, 1002, 988, 970, 912, 814, 750, 699, 672, 653, 627, 589, 532, 471. UV/vis (DMSO): λ_{max} (ϵ) = 321 nm (7300). Anal. Calcd for $C_{26}H_{18}CrO_4$ (446.42): C: 69.95, H: 4.06. Found: C: 69.47, H: 4.78.

***E*-Cr(CO)$_3$(η^6-C$_6$H$_5$)C[*o*,*p*-C$_6$H$_3$(OCH$_3$)$_2$]=CHCH$_2$[*o*,*p*-C$_6$H$_3$-(OCH$_3$)$_2$] (10).** To a cooled solution (−78 °C) of 173 μL (1.07 mmol) of HBF_4 diethyl etherate and 0.48 mL (3.70 mmol) of 1,3-dimethoxybenzene in 10 mL of dichloromethane was added dropwise a solution of 200 mg (0.74 mmol) of **1d** in 5 mL of dichloromethane over a period of 5 min. After stirring at −78 °C for 15 min the reaction mixture was allowed to come to room temperature and was stirred for a further 90 min. The mixture was extracted several times with diethyl ether, the combined organic phases were dried over magnesium sulfate, and the solvents were removed in vacuo (water bath 25 °C). The residue was chromatographed on silica gel (1:2 diethyl ether/pentane) to give 170 mg (44%) of pure **10** as a yellow oil that solidifies as a foam under vacuum. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 3.03 (d, J = 7.1 Hz, 2 H), 3.69 (s, 3 H), 3.71 (br, 6 H), 3.79 (s, 3 H), 5.49−5.71 (m, 5 H), 6.41 (d, J = 8.3 Hz, 1 H), 6.47−6.48 (m, 2 H), 6.61−6.65 (m, 2 H), 6.95 (d, J = 8.3 Hz, 1 H), 7.0 (d, J = 8.1 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 29.18 (CH$_2$), 55.02 (CH$_3$), 55.12 (CH$_3$), 55.16 (CH$_3$), 55.26 (CH$_3$), 94.27 (CH, br, 2 signals), 94.58 (CH), 98.40 (CH), 98.80 (CH), 104.47 (CH), 105.16 (CH), 111.32 (C$_{quat.}$), 117.46 (C$_{quat.}$), 119.64 (C$_{quat.}$), 129.54 (CH), 130.83 (CH), 131.27

(CH), 133.39 ($C_{quat.}$), 157.76 ($C_{quat.}$), 157.95 ($C_{quat.}$), 159.28 ($C_{quat.}$), 160.66 ($C_{quat.}$), 234.36 ($C_{quat.}$, CO). MS (EI, 70 eV), *m*/*z* (%): 526 (M^+, 9), 442 ($M^+ - 3$ CO, 100), 390 ($M^+ - Cr(CO)_3$, 13), 52 (Cr^+, 6). IR (KBr): $\tilde{\nu} = 3084$ cm^{-1}, 3001, 2936, 2836, 1959, 1878, 1505, 1458, 1414, 1333, 1303, 1291, 1261, 1208, 1177, 1156, 1118, 1035, 935, 828, 697, 661, 631, 581, 534, 477. UV/vis (DMSO): λ_{max} (ϵ) = 276 nm (11000), 323 (9400). Anal. Calcd for $C_{28}H_{26}CrO_7$ (526.50): C, 63.87; H, 4.97. Found: C, 63.75; H, 5.08.

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Supporting Information Available: Figures of the ^{13}C NMR and UV/vis spectra of the propargyl alcohol **1a** and the cation **2a**, the Walsh plots on the extended Hückel calculations on the cation **2d**, the MO plots of the ZINDO/CI calculations on the cation **2a**, and tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **7d** and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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