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Electrophilic Reactivity of the (Phenyl)Cr(CO)$_3$-Substituted α-Propargyl Cation

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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Abstract—The reactivity of the (phenyl)Cr(CO)$_3$-substituted α-propargyl cation **2** was quantified by measuring the kinetics of nucleophilic trapping reactions. In comparison to related dicobalthexacarbonyl alkynyl substituted carbenium ions the electrophilicity *E* of **2** is by 2.5 orders of magnitude larger and, thus, this species is more reactive. © 2000 Elsevier Science Ltd. All rights reserved.

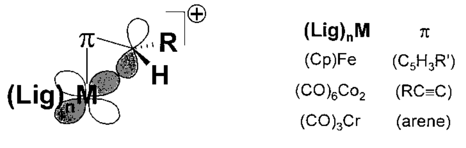
Introduction

Among numerous reactions mediated by transition metal complexation of unsaturated organic ligands the most peculiar are those occurring via the stabilization of carbenium ions by the aid of transition metal π-complexes[1] and subsequent nucleophilic trapping reactions. Due to an ideal overlap of occupied d-orbitals of the metal fragment, such as ferrocene, (alkyne)Co$_2$(CO)$_6$, or (arene)Cr(CO)$_3$ and the vacant p-orbital at the carbenium center in α-position (Scheme 1) a rate-increasing anchimeric assistance in S$_N$1 reactions can be easily explained.[1c,d,2] Stereochemically, this pronounced neighbor group effect 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.[1d,e,f]

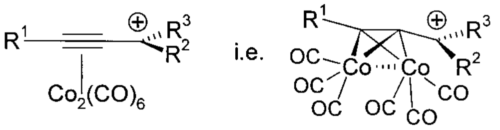
According to calculations at different levels of theory in the case of chromium carbonyl complexed benzyl cations the carbenium center is significantly distorted from coplanarity with the phenyl ring upon bending towards the metal center.[2e,3] This distortion not only results in a stabilization of the carbenium ion by the adjacent transition metal fragment but also fixes the sidechain configurationally in a rigid (at low temperatures) conformation. In particular, this peculiar feature has impressively been applied in a couple of asymmetric syntheses based upon the stabilization of benzylic cations by chromium carbonyl complexation.[1f,4]

By attaching a dicobalthexacarbonyl cluster to a triple bond Nicholas successfully achieved the activation of the propargylic position.[1e,5] The generated cation stabilized by the adjacent cobalt(0) fragment under simultaneous protection of the alkyne can be reacted with a number of nucleophiles giving rise to functionalized propargylic derivatives, interesting building blocks in complex natural product syntheses.[6] However, the so called '*Nicholas' cations*' rather can be regarded as cobalt cluster stabilized carbenium ions than propargyl cations, especially, since the triple bond is permanently complexed by the dicobalt hexacarbonyl fragment and even the precursors for ionizations display bond lengths for the 'triple bond' that strongly deviate from those of alkynes (Scheme 2).[5]

Recently, we have reported on the electronic structures and spectroscopic characterization of (phenyl)Cr(CO)$_3$-stabilized α- and γ-propargyl cations[7] and anions.[8] Additionally, we have found that various nucleophiles regioselectively add to planar chiral complex substituted α-propargyl cations with excellent diastereoselectivity.[9] Now we wish to disclose our investigations on the quantification of the reactivity of a (phenyl)Cr(CO)$_3$-substituted α-propargyl cation as determined by measuring the kinetics



Scheme 1. Stabilization of carbenium ions by π-complex fragments.



Scheme 2. Alkynyl cobalt complex substituted carbenium ions (*Nicholas' cations*).

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of nucleophilic trapping reactions and compare its electrophilicity parameter to the related *Nicholas' cations*.

Results and Discussion

Propargylic cations are most conveniently generated from a suitable propargylic precursor upon ionization with a Brønsted or Lewis acid. Recently, we have studied the ionization kinetics of the (phenyl)Cr$(CO)_3$-substituted propargyl acetate **1** with boron trifluoride etherate in dichloromethane at −65°C to furnish the (phenyl)-Cr$(CO)_3$-substituted α-propargyl cation **2** that was unambiguously characterized spectroscopically.[7a] In contrast to its free ligand[10] this organometallic species is stable at low temperatures and readily reacts with various nucleophiles. Thus, the nucleophilic addition of hydride donors (triethylsilane, dimethylphenylsilane) or π-nucleophiles such as allyltrimethylsilane, allylchlorodimethylsilane, anisole, and trimethylsiloxy cyclohex-1-ene gives rise to the formation of propargylated products **3** as pale yellow crystalline solids (**3a**, **3c**, **3d**) or an oil (**3b**), respectively, in moderate to good yields (Scheme 3).

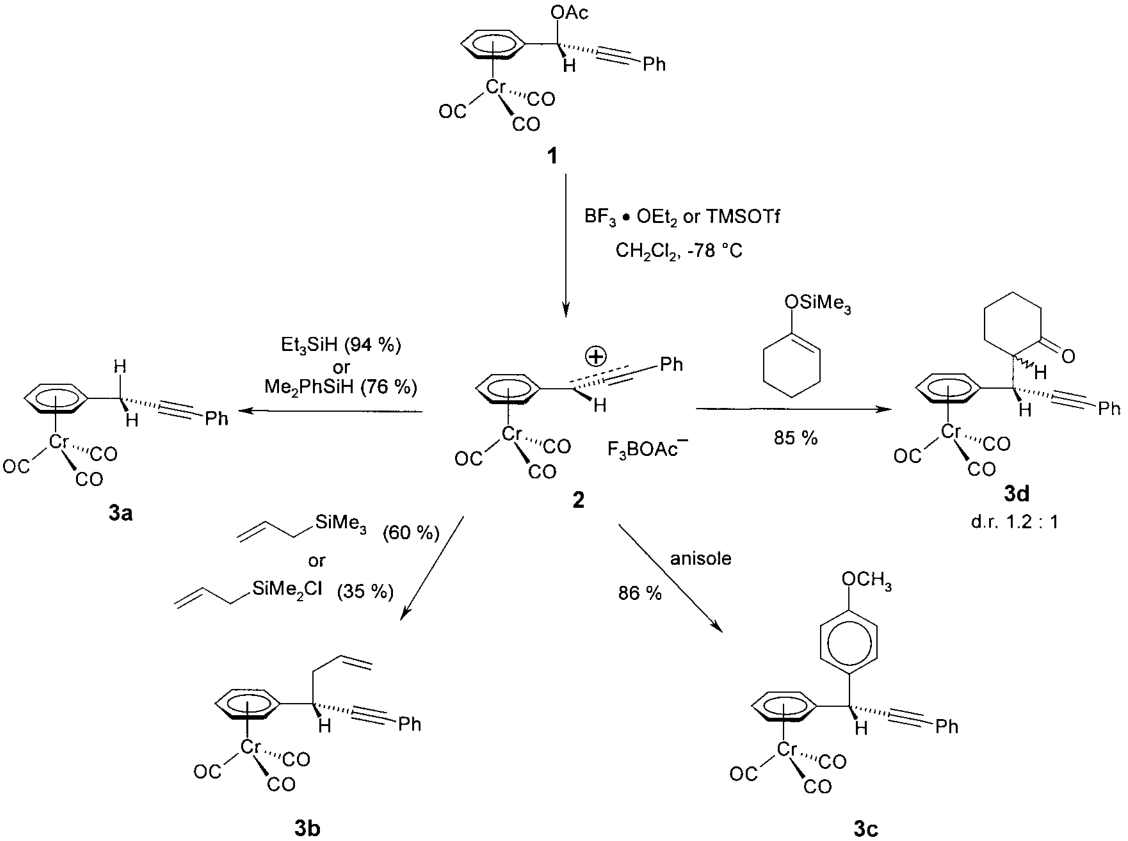
The structures of the propargylated compounds **3** are unambiguously supported by the characteristic appearance of the alkynyl carbon resonances in the ^{13}C NMR spectra between δ 83.4 and 88.7. Due to the π-complexation and the adjacent benzylic chirality center in the compounds **3b**, **3c**, and **3d** in the ^{13}C and ^{1}H NMR spectra the resonances of the complexed *ortho* and *meta* phenyl protons and carbons are diastereotopic with the expected spin splitting of the proton signals. The simple facial diastereoselectivity (d.r.=1.2:1) in the case of the trapping reaction of **2** with the prochiral silyl enol ether to give **3d** is rather unspectacular, presumably due to small steric biases in the trapping nucleophile. Interestingly, in the mass spectra the indicative fragment at m/z=191 resulting from a propargyl cleavage that can be assigned to the 1,3-diphenylpropargyl cation, i.e. the hydrocarbon ligand of **2** can be detected for all compounds **3**.

According to the UV/vis studies[7a] the cation **2** is stable from −70 to 0°C (for several hours). Therefore, a semiquantitative treatment Eq. (1) of the reactivity of **2** according to *Mayr's electrophilicity-nucleophilicity equation*[11,12]

$$\lg k(20°C) = s(E + N) \qquad (1)$$

where s: nucleophile dependent slope parameter, E: electrophilicity parameter and N: nucleophilicity parameter was pursued by determining the kinetics of the nucleophilic trapping reactions of **2** with an excess of four well characterized nucleophiles (allyltrimethylsilane, allylchlorodimethylsilane, anisole, and dimethylphenyl-silane).[11] Thus, the time-dependent decrease of the long wavelength absorption band of **2a** at 490 or 510 nm, respectively, was measured at various temperatures and found to follow a pseudo-first order rate law. The results of the kinetic measurements are summarized in Table 1.[13]

Along with the rate constants at various temperatures an Eyring-plot[12] ($\ln\frac{k}{T} = -\frac{\Delta H^{\neq}}{R}\cdot\frac{1}{T} + \frac{\Delta S^{\neq}}{R} + \ln\frac{k_B}{h}$) gives the



Scheme 3.

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 2.

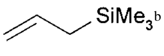
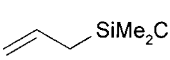
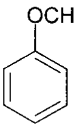
From the kinetics of the trapping reactions allyltrimethylsilane, allyldimethylchlorosilane, and anisole for the cation **2** an average electrophilicity parameter $\bar{E} = 1.24 \pm 0.39$ can be calculated. The electrophilicity as determined from the trapping reaction with the hydride donor dimethylphenylsilane deviates by 1.8 orders of magnitude from the average parameter for the π-nucleophiles. A similar deviation was also found for the (phenyl)Cr(CO)$_3$-substituted γ-propargyl cation **4**[7b] where the electrophilicity parameter for the silylhydride addition ($E=-1.36$) was one order of magnitude smaller than the average electrophilicity parameter ($\bar{E}=-0.35\pm0.18$) as determined from the kinetics of π-nucleophiles. Regarding the Eyring activation entropy terms $\Delta S^{\neq}$ the transition states for the attack of the π-nucleophiles are significantly higher ordered than for the attack of the silylhydride. Since a nucleophilic attack to the cation **2** very likely occurs in an *anti*-fashion with respect to the chromium carbonyl tripod a significant participation of steric effects can not be fully excluded. This also suggests for the incoming π-nucleophile a coplanar alignment of its π-orbitals with those of the propargyl cation in order to maximize the stabilizing interactions. However, due to the less ordered transition state (according to the magnitude of $\Delta S^{\neq}$) in the case of the silylhydride trapping reaction another reaction pathway, presumably via a precoordination at the chromium center,[14] can also be conceived.

In comparison to the related *Nicholas' cation* **5** ($\bar{E}=-1.34$)[15] the reactivity of the phenyl chromium carbonyl stabilized α-propargyl cation **2** is enhanced by 2.6 orders of magnitude. Therefore, (aryl)Cr(CO)$_3$-substituted α-propargyl cations, complementary to Nicholas' systems, appear to be synthetically useful propargyl cation equivalents setting the stage for more sophisticated diastereo- and enantioselective cationic propargylations (Scheme 4).

Conclusion

Arene chromium carbonyl complex substituted α-propargyl cations are related to the corresponding *Nicholas' cations* only at first sight. In particular, they represent a class of organometallically substituted de facto propargyl cations without simultaneous complexation of the triple bond. In

Table 1. Kinetics of the nucleophilic trapping reactions of **2** with selected nucleophiles

Nucleophile	No.	T (°C)	c$_0$(BF$_3$ OEt$_2$)[a] (mol L^{-1})	c$_0$(**1**) (mol L^{-1})	c$_0$(Nucleophile) (mol L^{-1})	Conv. (%)	k_{obs} (L mol^{-1} s^{-1})
 [b]	1	−67.7	3.85×10^{-3}	7.71×10^{-5}	1.89×10^{-3}	82	2.875
	2	−58.0	4.15×10^{-3}	8.32×10^{-5}	1.63×10^{-3}	86	5.059
	3[c]	−48.1	5.20×10^{-4}	7.06×10^{-5}	1.37×10^{-3}	84	1.032×10^{1}
	4	−47.6	4.06×10^{-3}	8.13×10^{-5}	9.95×10^{-4}	94	1.023×10^{1}
	5[c]	−38.7	6.47×10^{-4}	6.14×10^{-5}	1.71×10^{-3}	76	1.754×10^{1}
	6	−38.0	3.00×10^{-3}	4.01×10^{-5}	1.38×10^{-3}	91	1.772×10^{1}
	7	−28.6	2.64×10^{-3}	3.53×10^{-5}	8.64×10^{-4}	73	3.093×10^{1}
 [d]	1	−32.7	5.40×10^{-3}	8.92×10^{-5}	4.61×10^{-3}	45	7.108×10^{-1}
						47–71	5.056×10^{-1}
	2	−23.3	5.67×10^{-3}	6.24×10^{-5}	2.26×10^{-3}	48	1.202
						48–73	8.333×10^{-1}
	3	−14.5	5.71×10^{-3}	6.28×10^{-5}	2.27×10^{-3}	46	1.772
						47–75	1.246
	4	−4.5	5.23×10^{-3}	5.76×10^{-5}	1.49×10^{-3}	50	2.868
						53–79	1.741
 [e]	1	−48.6	3.16×10^{-3}	6.65×10^{-5}	1.94×10^{-3}	78	3.360×10^{-2}
	2	−38.6	3.57×10^{-3}	7.41×10^{-5}	9.66×10^{-4}	98	6.276×10^{-2}
	3	−28.3	6.01×10^{-3}	1.00×10^{-4}	4.61×10^{-3}	84	1.261×10^{-1}
	4	−19.0	3.16×10^{-3}	6.69×10^{-5}	1.36×10^{-3}	68	1.897×10^{-1}
	5	−9.0	2.48×10^{-3}	8.27×10^{-5}	3.81×10^{-3}	85	4.225×10^{-1}
	6	−8.9	1.57×10^{-3}	6.66×10^{-5}	1.93×10^{-3}	79	3.534×10^{-1}
	7	−0.2	2.47×10^{-3}	5.12×10^{-5}	1.90×10^{-3}	66	5.883×10^{-1}
H–SiMe$_2$Ph[f]	1	−67.8	4.24×10^{-3}	8.35×10^{-5}	2.12×10^{-3}	96	1.951×10^{-1}
	2	−56.5	3.33×10^{-3}	8.61×10^{-5}	1.67×10^{-3}	98	4.892×10^{-1}
	3	−48.3	3.56×10^{-3}	7.02×10^{-5}	1.42×10^{-3}	88	1.008
	4	−47.8	2.63×10^{-3}	6.80×10^{-5}	1.32×10^{-3}	99	1.083
	5	−38.4	1.89×10^{-3}	3.72×10^{-5}	1.89×10^{-3}	63	2.459
	6	−37.5	3.79×10^{-3}	4.89×10^{-5}	1.89×10^{-3}	98	2.648
	7	−30.1	3.87×10^{-3}	9.99×10^{-5}	7.74×10^{-4}	96	5.102

[a] 0.13 M solution of BF$_3$ OEt$_2$ in dry and degassed dichloromethane.

[b] 2.03×10^{-3} M solution of **1** in dry and degassed dichloromethane; 0.53 M solution of allyltrimethylsilane in dichloromethane.

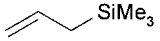
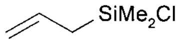
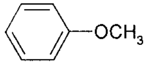
[c] 0.13 M solution of TMSOTf in dry and degassed dichloromethane.

[d] 1.66×10^{-3} M solution of **1** in dry and degassed dichloromethane; 0.86 M solution of allylchlorodimethylsilane in dichloromethane.

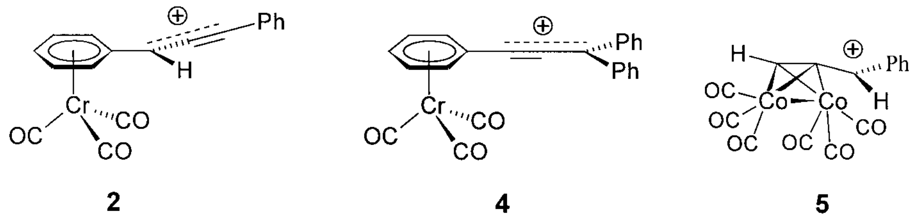
[e] 2.12×10^{-3} M solution of **1** in dry and degassed dichloromethane; 0.58 M solution of anisole in dichloromethane.

[f] 2.28×10^{-3} M solution of **1** in dry and degassed dichloromethane; 0.50 M solution of dimethylphenylsilane in dichloromethane.

Table 2. Activation and electrophilicity parameters from the evaluation of the Eyring plot and Mayr's equation

Nucleophile	Activation energy E_a (kJ mol^{-1})	lg (A)	Activation enthalpy $\Delta H^{\neq}$ (kJ mol^{-1})	Activation entropy $\Delta S^{\neq}$ (JK^{-1} mol^{-1})	k(20°C) (L mol^{-1} s^{-1})	Nucleophilicity N	Parameter s	Electrophilicity E
	25.73±0.50	6.97±0.12	23.87±0.49	−117.46±2.15	249.66	1.62	1.01	0.75[a]
	26.22±0.75	5.55±0.16	24.11±0.75	−145.66±2.96	7.597	−0.45	1.07	1.27[a]
	23.61±1.06	4.85±0.22	21.50±1.08	−159.18±4.27	4.366			1.05
	30.44±1.04	5.58±0.22	28.38±1.03	−144.75±4.13	1.469	−1.56	1.17	1.70[a]
H–SiMe$_2$Ph	36.02±1.12	8.41±0.26	34.17±1.10	−89.91±4.88	99.86	3.39	0.72	−0.61

[a] Electrophilicity parameters used for calculating the average value $\bar{E}$.



Scheme 4.

many ways, the chromium complexes are complementary to the dicobalt carbonyl complexed alkynyl systems and due to their enhanced electrophilic reactivity they also can prove to be valuable synthetic equivalents for cationic propargylations. Cationic propargylations with simple and facial diastereoselectivity as well as the methodological application to the syntheses of norlignans are now currently underway.

Experimental

General

All reactions involving chromiumtricarbonyl 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.[16] 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 chromiumcarbonyl complexed diphenyl propargyl acetate **1** was prepared according to our previously published protocol.[7a] 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.

General procedure (GP) for the nucleophilic trapping reactions of the propargyl cation 1 with nucleophiles

To a degassed solution of 1 equiv. of the propargyl acetate **1** in 15 mL of dichloromethane, cooled to -78°C were added dropwise a solution of 1.4 equiv. of boron trifluoride diethyl etherate over a period of 1 min. The reaction mixture was stirred at -78°C for 55 min before the trapping nucleophile, neat or as a solution, was added dropwise. After the addition the reaction time indicated 20 mL of diethyl ether and 20 mL of water were added to the mixture and the external cooling was removed to allow the mixture to come to room temperature. The aqueous phase was extracted twice with diethyl ether (2×25 mL) and the combined organic phases were dried with magnesium sulfate. After evaporation of the solvents in vacuo the residue was chromatographed on silica gel (diethyl ether/pentane). The yellow band was collected. Further purification was achieved by recrystallization from diethyl ether/pentane.

Tricarbonyl[η^6-(1-phenylprop-1-yn-3-yl)benzene]chromium(0) (3a). According to the GP 150 mg (0.39 mmol) of acetate **1** and 0.22 mL (1.41 mmol) of triethylsilane dissolved in 0.9 mL of dichloromethane were reacted for 140 min to give after workup and chromatography 120 mg (94%) of **3a** as pale yellow crystals, mp 90°C. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ=3.74 (s, 2H), 5.61 (m, 1H), 5.80 (m, 4H), 7.37–7.45 (m, 5H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ=24.2 (CH_2), 83.4 ($C_{quat.}$), 86.1 ($C_{quat.}$), 93.5 (CH), 94.5 (CH), 95.6 (CH), 110.5 ($C_{quat.}$), 122.6 ($C_{quat.}$), 128.6 (CH), 128.8 (CH), 131.5 (CH), 234.0 ($C_{quat.}$, CO). MS (EI, 70 eV), *m/z* (%): 328 (M^+, 10), 272 (M^+-2 CO, 5), 244 (M^+-3 CO, 100), 192 ($M^+-Cr(CO)_3$, 9), 191 ($PhCHC{\equiv}CPh^+$, 10), 52 (Cr^+, 28). IR (KBr): $\tilde{\nu}$= 1968 cm^{-1}, 1884, 1856. UV/vis (DMSO): λ_{max} (ϵ)= 315 nm (8900). $C_{18}H_{12}CrO_3$ (328.3) calcd C 65.86, H 3.68; found C 65.58, H 4.00.

Tricarbonyl[η^6-(1-phenylhex-5-en-1-yn-3-yl)benzene]chromium(0) (3b). According to the GP 200 mg (0.52 mmol) of acetate **1** and 0.17 mL (1.04 mmol) of allyltrimethylsilane were reacted for 15 min to give after workup and chromatography 115 mg (60%) of **3b** as a yellow oil. ^{1}H NMR ([D_6]DMSO, 400 MHz): δ=2.56–2.59 (m, 2H), 3.84–3.85 (m, 1H), 5.10 (d, *J*=11.8 Hz, 2H), 5.64–5.69 (m, 2H), 5.75 (m, 1H), 5.84–5.92 (m, *J*=11.3 Hz, 3H), 7.36–7.44 (m, 5H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ=36.62 (CH), 42.34 (CH_2), 84.57 ($C_{quat.}$), 88.66 ($C_{quat.}$), 93.87 (CH), 94.34 (CH), 94.35 (CH), 94.55 (CH), 95.52 (CH), 113.86 ($C_{quat.}$), 118.26 (CH_2), 122.65 ($C_{quat.}$), 128.55 (CH), 128.68 (CH), 131.51 (CH), 134.57 (CH), 233.90 ($C_{quat.}$, CO). MS (EI, 70 eV), *m/z* (%): 368 (M^+, 17), 312 (M^+-2 CO, 5), 284 (M^+-3 CO, 100), 191 ($PhCHC{\equiv}CPh^+$, 19). IR (KBr): $\tilde{\nu}$=1963 cm^{-1}, 1880. UV/vis (DMSO): λ_{max} (ϵ)=315 nm (9700). $C_{21}H_{16}CrO_3$ (368.4) calcd C 68.48, H 4.38; found C 68.98, H 4.49.

Tricarbonyl{η^6-[3-(p-methoxyphenyl)-1-phenylprop-1-yn-3-yl]benzene}chromium(0) (3c). According to the GP 100 mg (0.26 mmol) of acetate **1** and 0.10 mL (0.92 mmol) of anisole dissolved in 0.8 mL of dichloromethane were reacted for 160 min to give after workup and chromatography 97 mg (86%) of **3c** as pale yellow crystals, mp 135°C. ^{1}H NMR ([D_6]DMSO, 400 MHz): δ=3.72 (s, 3H), 5.11 (s, 1H), 5.61–5.67 (m, 2H), 5.74 (t, *J*=6.2 Hz, 1H), 5.88 (d, *J*=6.3 Hz, 1H), 5.93 (d, *J*=6.4 Hz, 1H), 6.92 (d, *J*=8.7 Hz, 2H), 7.37–7.39 (m, 3H), 7.47 (d, *J*=8.7 Hz, 2H), 7.49–7.51 (m, 2H). ^{13}C NMR ([D_6]DMSO, 100 MHz):

δ=40.13 (CH), 55.10 (CH_3), 84.67 ($C_{quat.}$), 88.41 ($C_{quat.}$), 93.01 (CH), 94.07 (CH), 94.28 (CH), 94.54 (CH), 95.13 (CH), 114.21 (CH), 115.45 ($C_{quat.}$), 122.33 ($C_{quat.}$), 128.53 (CH), 128.55 (CH), 131.38 (CH), 132.78 ($C_{quat.}$), 158.63 ($C_{quat.}$), 233.67 ($C_{quat.}$, CO). MS (EI, 70 eV), *m/z* (%): 434 (M^+, 7), 350 (M^+-3 CO, 100), 298 ($M^+-Cr(CO)_3$, 21), 197 (12), 191 ($PhCHC{\equiv}CPh^+$, 3), 52 (Cr^+, 7). IR (KBr): $\tilde{\nu}$=1957 cm^{-1}, 1904, 1868. UV/vis (DMSO): λ_{max} (ϵ)=317 nm (10200). $C_{25}H_{18}CrO_4$ (434.4) calcd C 69.12, H 4.18; found C 69.13, H 4.29.

Tricarbonyl{η^6-[3-(2-oxocyclohexyl)-1-phenylprop-1-yn-3-yl]benzene}chromium(0) (3d). According to the GP 100 mg (0.26 mmol) of acetate **1** and 0.99 mL (5.14 mmol) of trimethylsiloxy cyclohex-1-ene were reacted for 75 min to give after workup and chromatography 93 mg (85%) of **3d** as a 1.2: 1 mixture of diastereomers as pale yellow crystals, mp 116°C. ^1H NMR ([D_6]DMSO, 400 MHz): δ=0.82–2.44 (m, 6H), 2.78–2.81 (m, 1H), 2.96–3.03 (m, 1H), 3.96 (d, *J*=5.1 Hz, 1H), 5.65–5.71 (m, 2H), 5.77 (t, *J*=6.2 Hz, 1H), 5.86 (m, 2H), 6.00 (d, *J*=6.6 Hz, 1H), 7.36–7.42 (m, 5H); minor diastereomer: δ=4.25 (d, *J*=3.5 Hz, 1H). ^{13}C NMR ([D_6]DMSO, 100 MHz): δ=24.34 (CH_2), 27.28 (CH_2), 31.59 (CH_2), 37.05 (CH), 41.80 (CH_2), 55.94 (CH), 83.89 ($C_{quat.}$), 88.51 ($C_{quat.}$), 94.02 (CH), 94.60 (CH), 95.70 (CH), 96.96 (CH), 113.26 ($C_{quat.}$), 122.71 ($C_{quat.}$), 128.50 (CH), 128.74 (CH), 131.51 (CH), 209.12 ($C_{quat.}$), 234.06 ($C_{quat.}$, CO); minor diastereomer: δ=24.01 (CH_2), 26.76 (CH_2), 28.37 (CH_2), 36.26 (CH), 41.39 (CH_2), 56.01 (CH), 85.18 ($C_{quat.}$), 87.07 ($C_{quat.}$), 94.26 (CH), 94.45 (CH), 94.70 (CH), 96.01 (CH), 112.40 ($C_{quat.}$), 122.87 ($C_{quat.}$), 128.59 (CH), 128.74 (CH), 131.55 (CH), 208.47 ($C_{quat.}$), 233.95 ($C_{quat.}$, CO). MS (EI, 70 eV), *m/z* (%): 424 (M^+, 2), 368 (M^+-2 CO, 9), 340 (M^+-3 CO, 100), 288 ($M^+-Cr(CO)_3$, 12), 244 (35), 191 ($PhCHC{\equiv}CPh^+$, 26), 52 (Cr^+, 23). IR (KBr): $\tilde{\nu}$= 1963 cm^{-1}, 1889, 1703. UV/vis (DMSO): λ_{max} (ϵ)= 315 nm (7600). $C_{24}H_{20}CrO_4$ (424.4) calcd C 67.92, H 4.75; found C 68.25, H 5.02.

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12. Normalized rate constant *k*.

13. The evaluation of the kinetic measurements was computed according to a second order kinetics. Integration of the differential equation

$$\frac{d[R^+]}{dt} = -k\cdot[Nu]\cdot[R^+] \tag{2}$$

gives

$$kt = \frac{1}{[Nu]_0 - [R^+]_0}\cdot\ln\left(\frac{[R^+]_0}{[Nu]_0}\cdot\frac{[Nu]_0 - [P]_t}{[R^+]_0 - [P]_t}\right) \tag{3}$$

Substitution with the following expressions Eqs (4)–(6)

$$\Delta = [Nu]_0 - [R^+] \tag{4}$$

$$[Nu]_t = [Nu]_0 - [P]_t \tag{5}$$

$$[R^+]_t = [R^+]_0 - [P]_t \tag{6}$$

where $[Nu]_0$, $[R^+]_0$: initial concentration of nucleophile and cation, resp., at t=0; $[Nu]_t$, $[R^+]_t$: concentration of nucleophile and cation, resp., at t; $[P]_t$: concentration of product at t; into Eq (3) gives Eq (7). The rate constant k is evaluated as the slope of the straight line

from the plot of the right half of Eq (7) against t

$$kt = \frac{1}{\Delta}\cdot\ln\left(\frac{[\mathrm{R}^+]_0}{[\mathrm{R}^+]_0 + \Delta}\cdot\frac{\Delta + [\mathrm{R}^+]_t}{[\mathrm{R}^+]_t}\right) \tag{7}$$

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