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How Electrophilic Are Cobalt Carbonyl Stabilized Propargylium Ions?

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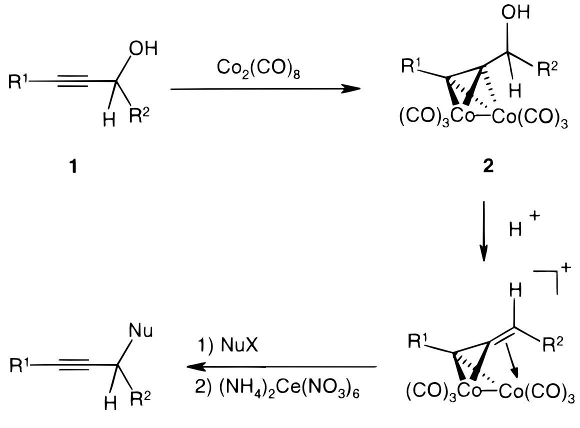
Abstract: The kinetics of the reactions of dicobalt-coordinated propargyl cations with π-nucleophiles (e.g., allylsilanes) and hydride donors (e.g., trialkylsilanes) have been studied conductometrically and/or photometrically. The reactions follow second-order kinetics with rate-determining CC-bond formation or hydride transfer. It is found that phenyl and trimethylsilyl substituents in the propargyl cation moiety reduce the electrophilic reactivities of these cations by less than a factor of 10. The electrophilicity is reduced by a factor of more than 10^5, however, when one CO ligand is replaced by PPh_3 (**3a** → **3e**). The reactions of the dicobalt-coordinated propargyl cations with allylsilanes and -stannanes, silylated enol ethers and ketene actetals, and hydride donors (R_3SiH, R_3SnH) follow the linear free enthalpy relationship $\log k = s(E + N)$, which allows one to calculate electrophilicity parameters E for these carbocations and to rationalize their synthetic potential.

Introduction

Because of the low ability of the alkynyl group to stabilize positive charge,[1] Lewis acid-catalyzed reactions of propargyl halides with π-systems are limited to propargyl halides substituted by at least two alkyl or phenyl substituents[2] or other strong electron donors.[3] This severe limitation in the use of propargyl cations as synthons has been overcome by the discovery of Nicholas and Pettit[4] that the dicobalt hexacarbonyl group can efficiently stabilize propargyl cations. Thus, even the parent dicobalt hexacarbonyl coordinated propargyl cation **3** (R^1, R^2 = H) could be isolated as a stable tetrafluoroborate. These propargyl cation equivalents react with a wide variety of nucleophiles[5] to yield alkyne complexes which can be demetalated oxidatively as described in Scheme 1.

Scheme 1



This reaction sequence, commonly referred to as the Nicholas reaction, has recently been used for the synthesis of complex biologically active compounds such as enediynes[6] (Scheme 2), tetrapyrroles,[7] (+)-begamide E,[8] cyclocolorenone,[9] and blastinomycine.[10]

Though the thermodynamic stabilities of the cobalt-coordinated propargylium ions have already been determined by Nicholas[11] and Gruselle,[12] and their fluxional structures have

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(1) For kinetic data of solvolyses of propargyl chlorides, see: (a) Burawoy, A.; Spinner, E. *J. Chem. Soc.* **1954**, 3752−3760. (b) Fenton T. L. *J. Org. Chem.* **1965**, *30*, 1808−1812. For calculations of propargyl cations, see: (c) Mayr, H.; Schneider, R. *Chem. Ber.* **1982**, *115*, 3470−3478. (d) Dorado, M.; Mò, O.; Yàñez, M. *J. Am. Chem. Soc.* **1980**, *102*, 947−950. (e) Hopkinson, A. C.; Lien, M. H. *Ibid.* **1986**, *108*, 2843−2849. For NMR-spectroscopic investigations of propargyl cations, see: (f) Richey, H. G., Jr.; Philips, J. C.; Rennick, L. E. *Ibid.* **1965**, *87*, 1381−1382. (g) Richey, H. G., Jr.; Philips, J. C.; Rennick, L. E.; Kushner, A. S; Richey J. M.; Philips, J. C. *Ibid.* **1965**, *87*, 4017−4019. (h) Olah, G. A.; Spear, R. J.; Westerman, P. W.; Denis, J.-M. *Ibid.* **1974**, *96*, 5855−5859. (i) Pittman, C. U., Jr.; Olah, G. A. *Ibid.* **1965**, *87*, 5632−5637.

(2) (a) Mayr, H.; Seitz, B.; Halberstadt-Kausch, I. K. *J. Org. Chem.* **1981**, *46*, 6, 1041−1043. (b) Mayr, H.; Schütz, F. *Tetrahedron Lett.* **1981**, *22*, 925−928. (c) Mayr, H.; Klein, H. *J. Org. Chem.* **1981**, *46*, 4097−4100. (d) Mayr, H.; Halberstadt-Kausch, I. K. *Angew. Chem.* **1980**, *92*, 840−841*; Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 184−186. (e) Mayr, H.; Klein, H. *Chem. Ber.* **1982**, *115*, 3528−3546. (f) Bäuml, E.; Mayr, H. *J. Org. Chem.* **1983**, *48*, 2600−2601.

(3) Baum, J. S.; Viehe, H. G. *J. Org. Chem.* **1976**, *41*, 183−187.

(4) Nicholas, K. M.; Pettit, R. *Tetrahedron Lett.* **1971**, 3475−3478.

(5) (a) Nicholas, K. M. *Acc. Chem. Res* **1987**, *20*, 207−214. (b) Smit, W. A.; Caple, R.; Smoliakova, I. P. *Chem. Rev.* **1994**, *94*, 2359−2382.

(6) Magnus, P.; Lewis, R. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 6921−6923.

(7) Jacobi, P. A.; Rajeswari, S. *Tetrahedron Lett.* **1989**, *30*, 6231−6234.

(8) Mukai, C.; Moharram, S. M.; Kataoka, O.; Hanaoka, M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2849−2854.

(9) Saha, M.; Bagby, B.; Nicholas, K. M. *Tetrahedron Lett.* **1986**, *27*, 915−918.

(10) Mukai, C.; Katuoka, O.; Hanaoka, M. *J. Org. Chem.* **1993**, *58*, 2946−2952.

(11) Connor, R. E.; Nicholas, K. M. *J. Organomet. Chem.* **1977**, *125*, C45−C48.

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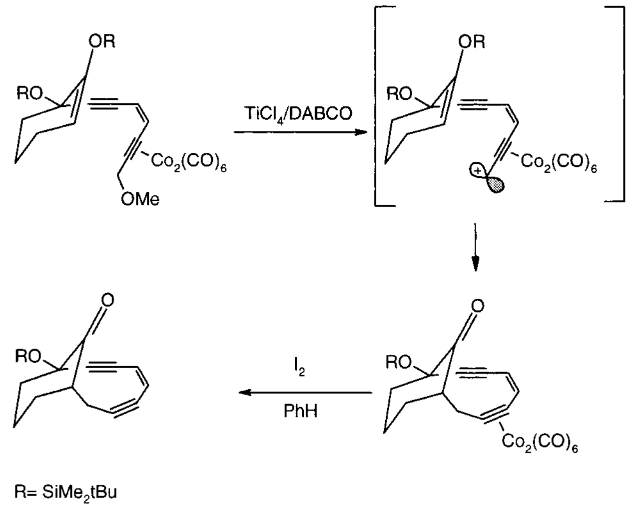
Scheme 2



been elucidated by Schreiber,[13] kinetic investigations on the electrophilic reactivities of these cations have not yet been performed.

Recently, we have demonstrated that the second-order rate constants for the reactions of cationic electrophiles with neutral nucleophiles are correlated by the linear free enthalpy relationship (1), where *E* is an electrophilicity parameter, *N* is a

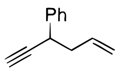
$$\log k(20\ °\mathrm{C}) = s(E + N) \tag{1}$$

nucleophilicity parameter, and *s* is a nucleophile-specific slope parameter.[14] The listed[14] *E* and *N* values lead to the rate constants being expressed in units of L $\mathrm{mol}^{-1}\ \mathrm{s}^{-1}$.

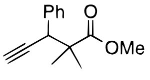
Since the parameter *s* is close to unity for most nucleophiles, the parameters *E* and *N* are usually sufficient for a rough estimate as to whether a selected electrophile is capable of reacting with a certain nucleophile at room temperature.[14] In this paper we will show that the reactions of the cations **3a**−**e** with nucleophiles (Scheme 3) roughly obey the linear free enthalpy relationship (1). It is, therefore, possible to determine electrophilicity parameters *E* for the dicobalt propargylium complexes **3a**−**e** and thus to characterize their synthetic potential.

Results

The propargylium complexes **3a,b** and **3d,e** were prepared as tetrafluoroborates by treatment of the corresponding propargylic alcohols with $HBF_4{\cdot}OEt_2$ according to literature procedures (Scheme 3).[13] Combination with the π-nucleophiles **6a**−**d** and **7a**,**b** and with the hydride donors **5a**−**c** gave the cobalt complexes **8a**−**p** which were either isolated and identified or treated with ceric ammonium nitrate to give the decomplexed alkynes **9b** and **9p** as noted in Table 1.



9b



9p

Alternatively, the acetoxy dervatives **4a**−**c** were treated with trimethylsilyl triflate to give solutions of the propargylium triflates **3-OTf** which were not isolated but combined with the nucleophiles **5**−**7** to yield the same products **8** as before. In accord with literature reports,[5] the nucleophiles generally attacked at the propargyl position with formation of alkynes, and we were not able to detect any allenes.

As shown for the reaction of **3a** with allyltrimethylsilane **6a** (Scheme 4), all reactions listed in Table 1 yield nonionic products from ionic reactants, and it is possible to follow the kinetics conductometrically. Alternatively, the reactions of the cations **3c** and **3e** were monitored photometrically by following the absorbance at 470−490 nm which usually drops to approximately 20% of the original value during the reaction.

Details of the kinetic method have been reported previously.[15] For the reactions of **3c-OTf** with **5a** and **6a** it was shown that conductometric and photometric methods yielded identical rate constants.

All reactions reported in this paper followed second-order kinetics, first-order with respect to propargylium ion and first-order with respect to nucleophile. The reactions of **3a** with **6a** and of **3b** with **5a** were studied with both OTf^- and BF_4^- as counterions. Since the measured rate constants proved to be independent of the employed counterion, one has to conclude that the anions come into play after the rate-determining step; i.e., the observed rate constant must refer to the slow, irreversible attack of **3a** at the π-system of **6a** (Scheme 4). Additionally, the appearance of long-lived UV-active intermediates can be excluded by the observation of an isosbestic point (Figure 1).

Discussion

A study of Table 2, where the nucleophiles **5**−**7** are ordered according to increasing nucleophilicity *N* from top to bottom,[14] shows that series of nucleophiles with different ranges of reativity had to be used in the kinetic investigations of the various cobalt complexes. While relatively weak nucleophiles as the allylsilanes **6a**−**c** or the hydrosilanes **5a**,**b** have been used for kinetic investigations of the hexacarbonyldicobalt coordinated propargyl cations **3a**−**d**, considerably more reactive nucleophiles such as the allylstannane **6d**, tributylstannane **5c**, or the silylketene acetal **7b** were required to obtain sufficiently fast reactions with the triphenylphosphane-coordinated cation **3e**.

The reactions of the cations **3a**−**d** with the allylsilanes **6a** and **6b** and with dimethylphenylsilane **5a** show that variation of the substituents at the propargylium fragment has little influence on reactivity (less than a factor of 10). The propargyl cation complexes **3a**−**d** thus differ considerably from the corresponding noncoordinated propargyl cations where substitution of H by phenyl influences the reactivity by more than 3.5 orders of magnitude.[1a,16]

When the rate constants for the reactions of **3a**−**e** with the nucleophiles **5**−**7** and the *N* and *s* values of the corresponding nucleophiles are substituted into eq 1, electrophilicity parameters *E* for the different cations are obtained, which show standard deviations of ±0.7, indicating that the linear free enthalpy relationship (1) is not precisely fulfilled. However, a similar order of magnitude of *E* is obtained with nucleophiles of quite different structure, indicating that the averaged *E* values can be used for roughly estimating rate constants of the reactions of

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(12) Gruselle, M.; Cordier, C.; Salmain, M.; El Amouri, H.; Guerin, C.; Vaissermann, J.; Jaouen, G. *Organometallics* **1990**, *9*, 2993−2997.

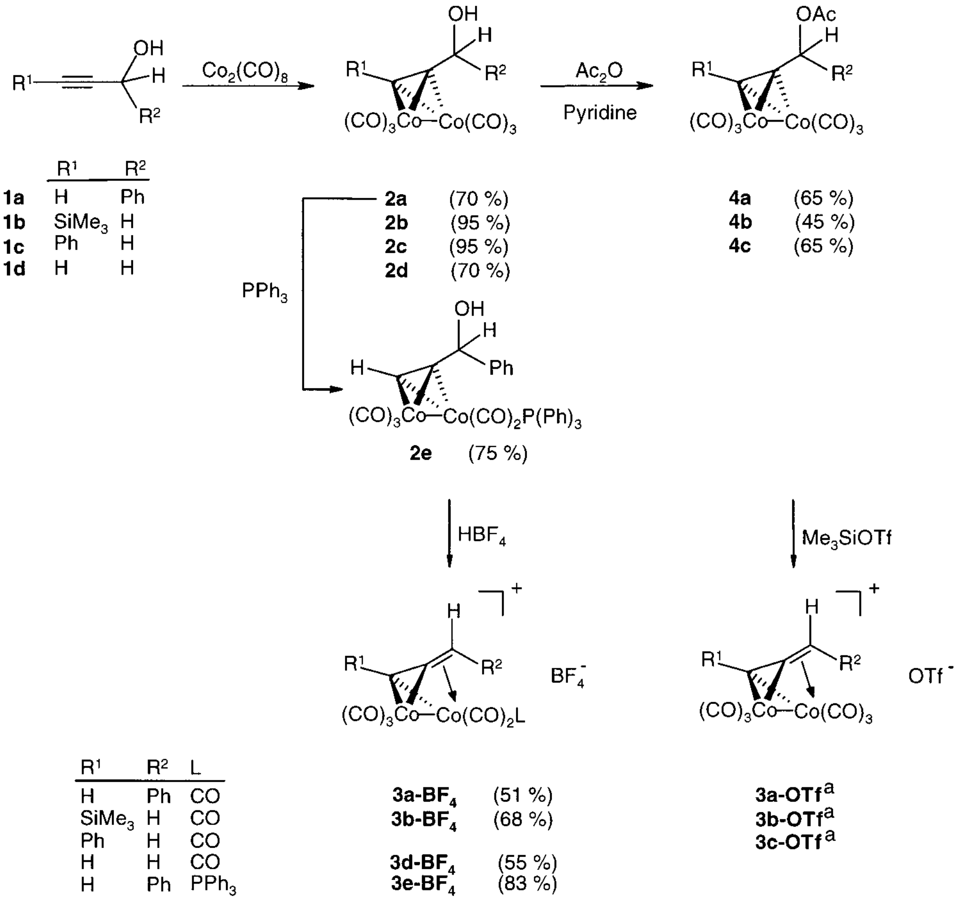
(13) Schreiber, S. L.; Klimas, M. T.; Sammakia T. *J. Am. Chem. Soc.* **1987**, *109*, 5749−5759.

(14) Mayr, H.; Patz, M. *Angew. Chem* **1994**, *106*, 990−1010; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938−957.

(15) Mayr, H.; Schneider, R.; Schade, C.; Bartl, J.; Bederke, R. *J. Am. Chem. Soc.* **1990**, *112*, 4446−4454.

(16) (a) Mayr, H.; Dau-Schmidt, J. P. *Chem. Ber.* **1994**, *127*, 205−212. (b) Dau-Schmidt, J. P. Ph.D. Thesis, Medizinische Hochschule zu Lübeck, 1992.

Scheme 3[a]



[a] The triflates **3-OTf** were generated in situ by treatment of the propargyl acetates **4a**–**c** with Me_3SiOTf.

cations **3a**–**e** with nucleophiles. Table 2 shows that calculated and experimental rate constants deviate by factors between 1.1 and 15, thus giving an idea of the accuracy of our correlations.

The graphical presentation of the electrophilicity parameters E in Figure 2 shows that all hexacarbonyldicobalt-coordinated propargyl cations **3a**–**d** are slightly less electrophilic than the dianisylmethylium ion[14] and have similar electrophilic reactivities, comparable to those of the xanthylium[14] and the ferrocenylmethylium ion.[17]

In accordance with the small influence of the substituents on the electrophilicity of the hexacarbonyldicobalt-coordinated propargyl cations **3a**–**d**, Nicholas has previously reported that the Lewis acidities (defined by pK_{R^+}) of such cations are almost unaffected by variation of the substituents at the propargylium fragment[11] (Scheme 5).

Figure 3 shows that the cobalt stabilized propargylium ion **3d**, the only system for which both E and pK_{R^+} are available, matches the moderate correlation (2) between the electrophilicity parameters E and the Lewis acidity parameter pK_{R^+}.[18]

$$E = -0.635\ pK_{R^+} - 2.78 \qquad (2)$$

Though the deviation of **3d** from the correlation line in Figure 3 is somewhat larger than the standard deviation, one can conclude that the electrophilic reactivities of the hexacarbonyldicobalt-coordinated propargylium ions are similary controlled by their affinities toward bases (pK_{R^+}) as the reactivities of other carbocations.

The dramatically reduced electrophilicity of the triphenylphosphane-coordinated cation **3e**, which has qualitatively been described by Nicholas,[19] can now be quantified: Replacement of one carbonyl group in **3a** by triphenylphosphane **(3e)** reduces the electrophilic reactivity by a factor of 10^5 (Table 2). According to Figure 2, the cation **3e** is less electrophilic than the tropylium ion and comparable to iminium ions.[20]

The low electrophilicity of cation **3e** is in accord with Nicholas' NMR- and IR-spectroscopic investigations.[19] While the ionization of hexacarbonyldicobalt-coordinated propargyl alcohols (e.g., **2a** → **3a**) is accompanied by an increase of the carbonyl wavenumber by $\Delta\nu = 50\ \mathrm{cm}^{-1}$, the corresponding ionization **2e** → **3e** causes only a blue shift of $\Delta\nu = 30\ \mathrm{cm}^{-1}$, indicating that the triphenylphosphane ligand reduces the electron demand of cobalt in **3e**.

Similar conclusions were drawn from variable-temperature NMR spectra of hexacarbonyldicobalt[13]- and pentacarbonyl(triphenylphosphane)dicobalt[19]-coordinated propargylium ions.

Conclusions

In Figure 4, electrophiles and nucleophiles are arranged in a way that electrophilic and nuleophilic reactants which are located at the same level ($E + N = -5$) will react with second-order rate constants (L $\mathrm{mol}^{-1}\ \mathrm{s}^{-1}$) governed by $\log k = -5s$ (eq 1) at 20 °C.[14] Since s is between 0.6 and 1.2 for most nucleophiles, this corresponds to slow reactions at room temperature for reactant concentrations used in practice.[14]

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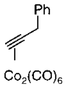
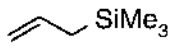
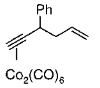
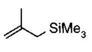
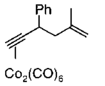
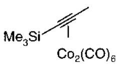
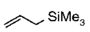
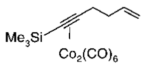
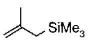
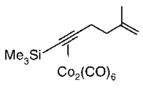
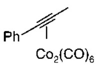
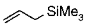
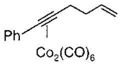
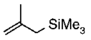
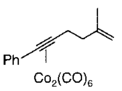
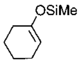
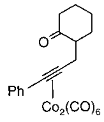
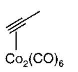
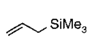
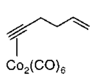
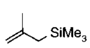
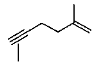
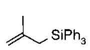
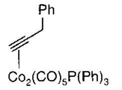
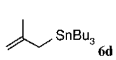
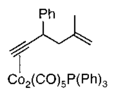
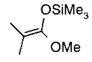
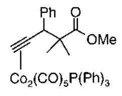
(17) Mayr, H.; Rau, D. *Chem. Ber.* **1994**, *127*, 2493–2498.

(18) Patz, M. Ph.D. Thesis, Technische Hochschule Darmstadt, 1994.

(19) Bradley, D. H.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1992**, *11*, 2598–2607.

(20) Mayr, H.; Ofial, A. R. *Tetrahedron Lett.* **1997**, *38*, 3503–3506.

Table 1. Products, Second-Order Rate Constants (k_2, CH_2Cl_2, 20 °C), and Eyring Parameters for the Reactions of the Cobalt-Stabilized Propargyl Cations **3a**−**e** with the Nucleophiles **5a**−**c**, **6a**−**d**, and **7a**,**b**

Electrophile	Nucleophile	Product	k_2, L mol^{-1} s^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J K^{-1} mol^{-1}
3a-OTf	HSiMe$_2$Ph **5a**	 **8a**	9.35	43.5± 1.8	-77 ± 7
3a-BF$_4$ **3a-OTf**	 **6a**	 **8b**[a]	4.94	28.5 ± 0.9	-134 ± 4
3a-BF$_4$	 **6b**	 **8c**[b]	2436	23.8 ± 0.8	-99 ± 4
3b-OTf **3b-BF$_4$**	HSiMe$_2$Ph **5a**	 **8d**	1.13		
3b-BF$_4$	 **6a**	 **8e**	3.26	41.4 ± 1.7	-95 ± 7
	 **6b**	 **8f**	243	29.2 ± 0.9	-98 ± 4
3c-OTf	HSiMe$_2$Ph **5a**	 **8g**[b]	1.79	48.4 ± 0.9	-75 ± 3
	HSiBu$_3$ **5b**		7.09		
	 **6a**	 **8h**	7.51	45.8 ± 0.8	-72 ± 3
	 **6b**	 **8i**	621	33.9 ± 1.0	-76 ± 4
3c-OTf	 **7a**	 **8j**	829	17.2 ± 0.9	-130 ± 4
3d-BF$_4$	HSiMe$_2$Ph **5a**	 **8k**[b]	3.95	50.5 ± 0.9	-61 ± 4
	 **6a**	 **8l**	17.4	34.1 ± 1.7	-105 ± 7
	 **6b**	 **8m**	1277	26.2 ± 0.2	-96 ± 1
	 **6c**		178	28.2 ± 0.6	106 ± 2
3e-BF$_4$	HSnBu$_3$ **5c**	 **8n**	11.0	40.3 ± 1.9	-88 ± 7
	 **6d**	 **8o**	37.5	29.9 ± 1.2	-113 ± 4
	 **7b**	 **8p**[a]	226	43.3 ± 0.7	-52 ± 3

[a] Complexes **8b** and **8p** were decomplexed to give **9b** and **9p**, respectively. [b] Products were not isolated.

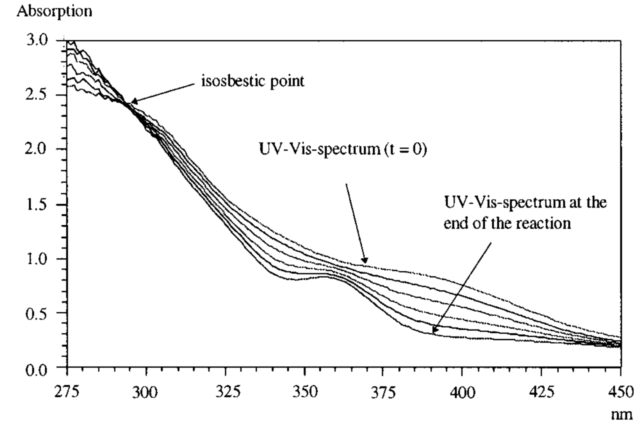


Figure 1. UV−vis spectra during the reaction of **3c**−**OTf** with allyltrimethylsilane **6a** in CH_2Cl_2.

Scheme 4

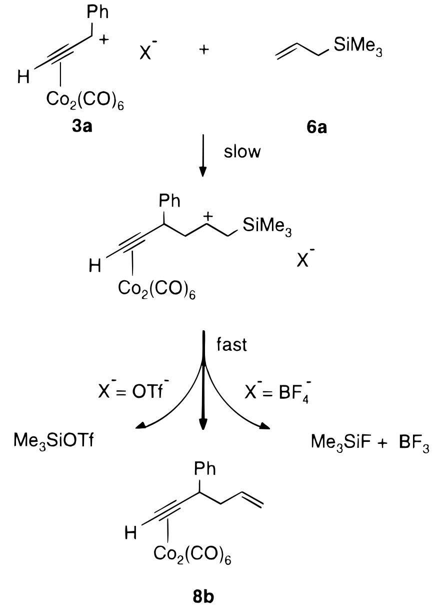


Figure 4 can, therefore, be used to describe the synthetic potential of Nicholas' cations: The hexacarbonyldicobalt-coordinated propargyl cations **3a**−**d** are expected to react with a large variety of nucleophiles ($N > -3$) while the triphenylphosphane-coordinated cation **3e** should only react with strong nucleophiles ($N > 2$).

This analysis is in accord with literature reports. While reactions of Nicholas' cations with alkylated benzenes have not been reported, the reaction of **3a** with anisole was described to give a mixture of ortho- and para-substituted propargylanisoles.[21] The reactions of **3b** with 1-heptene ($N \approx -2.0$)[14] and 2-methyl-1-octene ($N \approx 1.0$)[14] recently published by Kraft[22] are in line with the listing in Figure 4.

The nucleophilicity parameter of methyl 3-(2-furanyl)propanoate can be expected to be only insignificantly lower than that of 2-methylfuran ($N = 3.8$).[14] Its reaction with **3d**, which was employed for the synthesis of prostaglandine E analogues,[23]

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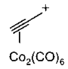
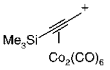
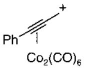
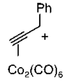
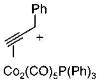
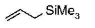
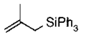
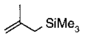
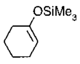
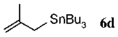
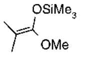
[21] Lockwood, R. F.; Nicholas, K. M. *Tetrahedron Lett.* **1977**, 4163−4166.

[22] Kraft, M. E.; Cheung, Y. Y.; Wright, C.; Cali, R. *J. Org. Chem.* **1996**, *61*, 3912−3915.

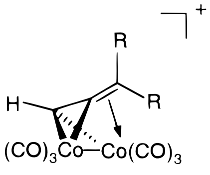
[23] Jaffer, H. J.; Pauson, P. L. *J. Chem. Res. (S)* **1983**, *10*, 244; *J. Chem. Res. (M)* **1983,** 2201−2218.

Table 2. Second-Order Rate Constants (k_2/(L mol^{-1} s^{-1}), CH_2Cl_2, 20 °C) for the Reactions of the Cobalt-Stabilized Propargyl Cations **3a**−**e** with the Nucleophiles **5a**−**c**, **6a**−**d**, and **7a**,**b** (Calculated Rate Constants (from *E*, *N*, and *s* in Eq 1) Given in Parentheses)

Nucleophile (N, s)[b]		 **3d**	 **3b**	 **3c**	 **3a**	 **3e**
	E =	-1.22 ± 0.70	-2.22 ± 0.78	-1.60 ± 0.85	-1.34 ± 0.63	-6.71 ± 0.48
 1.62, 1.01	**6a**	17.4 (2.8)	3.26 (0.25)	7.51 (1.05)	4.94 (1.92)	
HSiMe$_2$Ph 3.39, 0.72	**5a**	3.95 (36.5)	1.13 (6.96)	1.79 (19.4)	9.35 (29.9)	
 3.68,0.92	**6c**	178[a] (183)				
HSiBu$_3$ 4.48, 0.64	**5b**			7.09[a] (69.7)		
 4.90, 0.89	**6b**	1277 (1885)	243 (243)	621 (865)	2436 (1473)	(0.02)
 5.58, 0.92	**7a**			829[a] (4587)		(0.09)
 7.92, 0.87	**6d**					37.5 (11.3)
HSnBu$_3$ 9.29, 0.57	**5c**					11.0 (29.5)
 9.49, 0.93	**7b**					226 (385)

[a] Rate constants not used for the calculation of *E* in order to base the comparison of **3a**−**d** on reactions with the same nucleophiles. [b] From ref 14.

Scheme 5. pK_{R^+} Values of Hexacarbonyldicobalt Coordinated Propargyl Cations



R	H	Me	Ph
pK_{R^+}	-6.80[11] -5.50[12]	-7.20[11]	-7.40[11]

is in accord with Figure 4. Because of the high nucleophilicities of indoles ($N \approx 7.0$)[24] and enamines ($N \approx 11.0$)[25] the reported reactions of these nucleophiles with **3d**[26] and **3b**,[27] respectively, also agree with this analysis.

While **3a**−**d** were found to react readily with allyltrimethylsilane **6a**, in accord with literature reports,[28] the reaction of allyltrimethylsilane **6a** with **3e** can be expected to be very slow ($k_{\text{calcd}} = 10^{-6}$ L mol^{-1} s^{-1}). Accordingly, Nicholas and coworkers reported[19] that the reaction of cation **3e** with allyltrimethylsilane **6a** does not occur. In the same paper it was reported, however, that **3e** also did not react with 1-(trimethylsiloxy)cyclohexene **7a**. Since **7a** is located far below **3e** in Figure 4 ($k_{\text{calcd}} = 10^{-2}$ L mol^{-1} s^{-1}), we expected this reaction to take place. When combining **3e**−**BF$_4$** with **7a** at ambient temperature under the conditions described above, we were able to isolate compound **8q** in 56% yield (Scheme 6). While the reaction of **3e**−**BF$_4$** with **6d** resulted in the formation of two diastereomers **8o** in the ratio 1:0.8, only a single diastereomer of **8q** could be detected by NMR spectroscopy in the crude product.

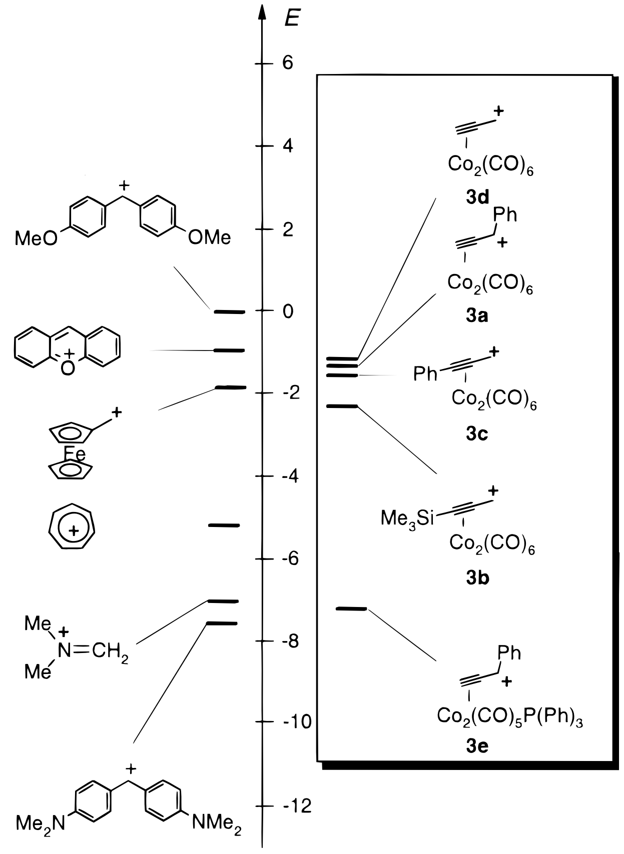


Figure 2. Comparison of the electrophilicity parameters *E* of cobalt-complexed propargyl cations **3a**−**e** and of typical carbocations.

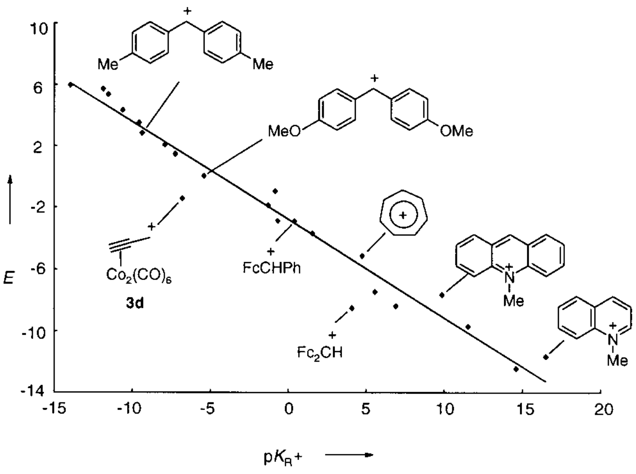


Figure 3. Correlation of the electrophilicity parameters *E* of several carbocationic entities with their pK_{R^+} values (Fc = ferrocenyl).

Figure 4 also predicts reactions of the cation **3e** with further types of carbon nucleophiles, e.g., silyl enol ethers, silylketene acetals, or allylstannanes in accord with the results reported in Table 1.

It is, therefore, suggested to examine such carbon nucleophiles for stereoselective CC-bond formation reactions with **3e**, which

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(24) Mayr, H.; Gotta, M. F. Unpublished results.

(25) Mayr, H.; Ofial, A. R.; Müller, K.-H.; Hering, N. Unpublished results.

(26) Nakagawa, M.; Ma, J.; Hino, T. *Heterocycles* **1990**, *30*, 451−462.

(27) Roth, K. D. *Synlett* **1992**, 435−438.

(28) O'Boyle, J. E.; Nicholas, K. M. *Tetrahedron Lett.* **1980**, *21*, 1595−1598.

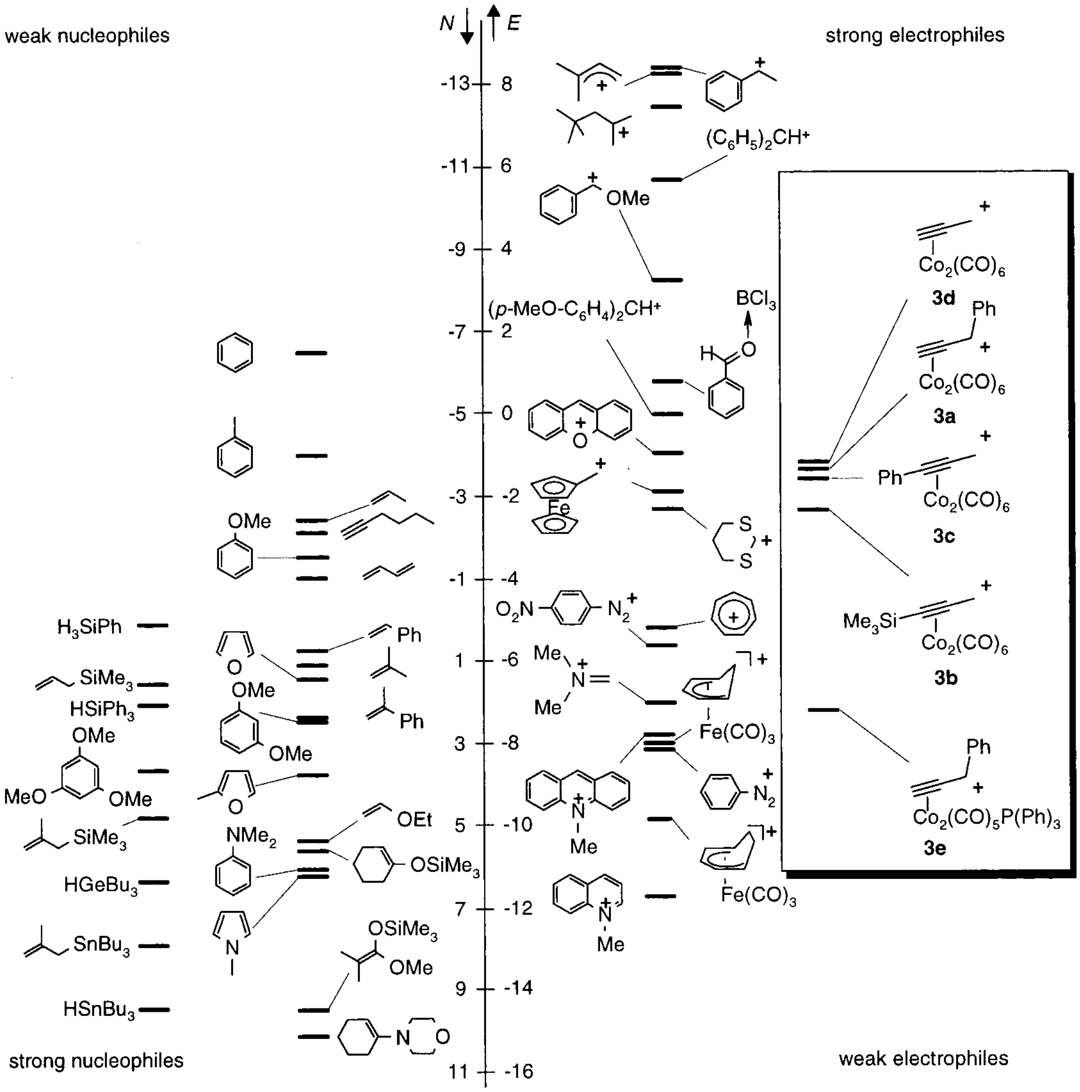
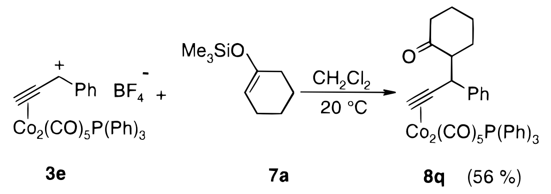
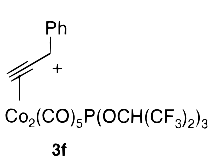


Figure 4. Comparison of the reactivities of the dicobalt-coordinated propargyl cations **3a**−**e** and other electrophiles and analysis of their synthetic potential.

Scheme 6



might be superior to employing the less readily available tris(hexafluoroisopropyl) phosphite complex **3f**[29] .



3f

Though the linear free enthalpy relationship (1) is not precisely followed by the reactions of the cobalt-coordinated propargylium ions **3a**−**e** with the nucleophiles **5**−**7**, it has been shown that the kinetic data reported in this work provide a useful framework for defining scope and limitations of the Nicholas reaction.

Experimental Section

General Procedures. All reactions were run in an atmosphere of dry argon or dry nitrogen because of the air sensitivity of the cobalt compounds **2**, **4**, and **8** and the air and moisture sensitivity of cationic compounds **3a**,**b** and **3d**,**e**. ^1H NMR chemical shifts (300 MHz) refer to *d*-chloroform (δ_H 7.24), d_6-acetone (δ_H 2.04), and d_2-dichloromethane (δ_H 5.32). ^{13}C NMR spectra (75 MHz) were calibrated to *d*-chloroform (δ_C 77.0), d_6-acetone (δ_C 29.8), and d_2-dichloromethane (δ_C 53.5). DEPT-135 experiments were used to obtain information about the multiplicity of ^{13}C resonances. Dichloromethane was freshly distilled from CaH_2 prior to use. Diethyl ether and hexane were dried over and distilled from sodium/benzophenone. The UV photometers used were Schölly KGS III, with band-pass filters by Corion[15] and J&M Tidas DAD 2062. Conductivity measurements were performed with the conductimeter CD 180 (Tacussel) using platinum electrodes. Prop-2-yn-1-ol **(1d)** and 1-phenylprop-2-yn-1-ol **(1a)** are commercially available from Fluka. The 3-(trimethylsilyl)prop-2-yn-1-ol **(1b)** was prepared from **1d** by a previously reported method.[30] (41%, ref.[30] 50%). Reaction of phenylacetylene (Fluka) with EtMgBr and subsequent treatment with paraformaldehyde[31] gave 33% of 3-phenyl-prop-2-yn-1-ol **(1c)** (ref 31, 21%). Complex **2d** was prepared[32] from **1d** and

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(29) Caffyn, A. J. M.; Nicholas, K. M. *J. Am. Chem. Soc.* **1993**, *115*, 6438−6439.

(30) Ahmed, M.; Barley, G. C.; Hearn, M. T. W.; Jones, E. R. H.; Thaller, V.; Yates, J. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1981−1987.

(31) Guest, H. H. *J. Am. Chem. Soc.* **1925**, *47*, 860−863.

(32) Gruselle, M.; Philomin, V.; Chaminant, F.; Jaouen, G. *J. Organomet. Chem.* **1990**, *99*, 317−326.

$Co_2(CO)_8$. A modified procedure[33] has been used for the syntheses of **2a**−**c**. Details are given in the Supporting Information. Treatment of the cobalt complex **2a** with triphenylphosphane gave complex **2e**[34] (75%, ref 34, 93%). The cobalt carbonyl coordinated propargyl cations **3a**,**b**,**e** were prepared by the reaction of the complexes **2a**,**b**,**e** with tetrafluoroboric acid−diethyl ether complex following the previously reported procedure.[13] Details are given in the Supporting Information. For the synthesis of **3d**−**BF$_4$** a slightly different procedure[32] was employed. Complex **8l** was prepared according to a published procedure[28] (94%, ref 28, 83%). Oxidative decomplexation of the cobalt complexes **8b** and **8p** was carried out with ceric ammonium nitrate in dry acetone.[33]

Typical Procedure for the Reaction of Cobalt Carbonyl Coordinated Propargyl Cations 3−BF$_4$ with the Nucleophiles 5−7.[33] (Prop-2-ynylbenzene)dicobalt Hexacarbonyl (8a). The complex **3a**−**BF$_4$** (1.42 g, 2.91 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to −20 °C, and dimethylphenylsilane **5a** (0.59 g, 4.33 mmol) was added. The mixture was stirred for 4 h, and then the solvent was evaporated in vacuo. After treatment with diethyl ether, traces of a black residue were separated by filtration. Removal of the solvent under reduced pressure gave complex **8a** (0.64 g, 55%): red oil; ^1H NMR (d_6-acetone) δ 4.19 (s, 2 H, 1-H), 6.55 (s, 1 H, 3-H), 7.22−7.38 (m, 5 H, Ph); ^{13}C NMR (d_6-acetone) δ 40.55 (t, C-1), 74.90 (d, C-3), 127.64, 129.30, 129.72 (3 d, Ph), 141.47 (s, Ph), 200.07, 201.34 (2 s, CO); due to slow relaxation, the signal of C-2 was not detected; IR (CH_2Cl_2) 2209, 2053, 2025 cm^{-1}.

(1-(Trimethylsilyl)prop-1-yne)dicobalt Hexacarbonyl (8d). Reaction of **3b**−**BF$_4$** (1.44 g, 2.97 mmol) and dimethylphenylsilane **5a** (0.923 g, 6.77 mmol) in CH_2Cl_2 (40 mL) gave **8d** (0.77 g, 65%): red oil; ^1H NMR[35] (d_6-acetone)[36,37] δ 0.33 (s, 9 H, $SiMe_3$), 2.82 (s, 3 H, 3-H); ^{13}C NMR (d_6-acetone) δ 0.40 (q, $SiMe_3$), 21.23 (q, C-3), 201.70 (s, CO); due to slow relaxation, the signals of C-1 and C-2 were not detected; IR (CH_2Cl_2) 2086, 2046, 2017 cm^{-1}.

(6-(Trimethylsilyl)hex-1-en-5-yne)dicobalt Hexacarbonyl (8e). Treatment of **3b**−**BF$_4$** (0.70 g, 1.5 mmol) with **6a** (0.256 g, 2.24 mmol) in CH_2Cl_2 (50 mL) gave **8e** (0.51 g, 81%): red oil; ^1H NMR ($CDCl_3$) δ 0.82 (s, 9 H, $SiMe_3$), 2.37, 2.98 (2 m$_c$, each 2 H, 3-H, 4-H), 5.05 (d, J_{cis} = 10.4 Hz, 1 H, 1-H), 5.12 (d, J_{trans} = 17.0 Hz, 1 H, 1-H), 5.92 (m$_c$, 1 H, 2-H); ^{13}C NMR ($CDCl_3$) δ 1.02 (q, $SiMe_3$) 34.70, 36.25 (2 t, C-3, C-4), 77.20 (s, C-6), 115.76 (t, C-1), 137.05 (d, C-2), 199.96 (s, CO); due to slow relaxation, the signal of C-5 was not detected.

(2-Methyl-6-(trimethylsilyl)hex-1-en-5-yne)dicobalt Hexacarbonyl (8f). Compound **3b**−**BF$_4$** (0.25 g, 0.52 mmol) was treated with (2-methylallyl)trimethylsilane **6b** (0.19 g, 1.5 mmol) and poly(2,6-di-*tert*-butyl-4-vinylpyridine) (0.30 g, 0.65 mmol) in CH_2Cl_2 (50 mL) to give **8f** (0.20 g, 87%) as a red oil: ^1H NMR (d_6-acetone) δ 0.36 (s, 9 H, $SiMe_3$), 1.82 (s, 3 H, Me), 2.43, 3.18 (2 m$_c$, each 2 H, 3-H, 4-H), 4.83 (m$_c$, 2 H, 1-H); ^{13}C NMR (d_6-acetone) δ 0.00 (q, $SiMe_3$), 21.73 (q, Me), 33.53, 40.31 (2 t, C-3, C-4), 79.16 (s, C-6), 110.40 (t, C-1), 112.60 (s, C-5), 144.39 (s, C-2), 200.68 (s, CO).

(1-Hexen-5-yne)dicobalt Hexacarbonyl (8l) was prepared according to ref 28 from **3d**−**BF$_4$** (0.39 g, 0.97 mmol) and allyltrimethylsilane **6a** (0.25 g, 2.2 mmol) in CH_2Cl_2 (80 mL): 0.33 g, 94% (ref 28, 83%); red oil; ^1H NMR (d_6-acetone) δ 2.44 (m$_c$, 2 H, 3-H), 3.05 (t, J = 7.5 Hz, 2 H, 4-H), 5.06 (d, J_{cis} = 10.2 Hz, 1 H, 1-H), 5.15 (d, J_{trans} = 17.0 Hz, 1 H, 1-H), 5.85−6.10 (m, 1 H, 2-H), 6.47 (s, 1 H, 6-H); ^{13}C NMR (d_6-acetone) δ 34.32, 36.45 (2 t, C-3, C-4), 74.66 (d, C-6), 116.06 (t, C-1), 138.15 (d, C-2), 201.2 (s, CO); due to slow relaxation, the signal of C-5 was not detected.

(2-Methylhex-1-en-5-yne)dicobalt Hexacarbonyl (8m). Reaction of **3d**−**BF$_4$** (0.21 g, 0.51 mmol), (2-methylallyl)trimethylsilane **6b** (0.11 g, 0.86 mmol), and poly(2,6-di-*tert*-butyl-4-vinylpyridine) (0.17 g, 0.38 mmol) in CH_2Cl_2 (60 mL) gave **8m** (0.17 g, 87%): red oil; ^1H NMR (d_6-acetone) δ 1.99 (s, 3 H, Me), 2.60, 3.30 (2 m$_c$, each 2 H, 3-H, 4-H), 5.01 (s, 2 H, 1-H), 6.64 (s, 1 H, 6-H); ^{13}C NMR (d_6-acetone) δ 22.39 (q, Me), 33.15, 40.37 (2 t, C-3, C-4), 74.64 (d, C-6), 98.11 (s, C-5), 111.39 (t, C-1), 145.13 (s, C-2), 201.90 (s, CO); IR (CH_2Cl_2) 2021, 2052, 2089 cm^{-1}.

(Prop-2-ynylbenzene)dicobalt Pentacarbonyl Triphenylphosphane (8n). The complex **3e**−**BF$_4$** (0.39 g, 0.54 mmol) was treated with tributylstannane **5c** (0.24 g, 0.82 mmol) in CH_2Cl_2 (30 mL), and the crude product was purified by flash chromatography (silica gel, diethyl ether/hexane = 1/10) to give **8n** (0.22 g, 64%): red oil; ^1H NMR (d_6-acetone) δ 3.21 (d, ^2J = 15.1 Hz, 1 H, 1-H), 3.56 (d, ^2J = 15.1 Hz, 1 H, 1-H), 5.50 (d, J = 3.5 Hz, 1 H, 3-H), 6.88−6.90, 7.07−7.17 (2 m, 5 H, Ph), 7.54−7.65 (m, 15 H, PPh_3); ^{13}C NMR (d_6-acetone) δ 40.26 (t, C-1), 73.89 (d, C-3), 127.11, 128.93, 129.33, 129.59, 129.73, 131.49, 133.86, 134.00 (8 d, Ph, PPh_3), 135.02, 135.59, 142.27 (3 s, Ph, PPh_3); due to slow relaxation, the signals of C-2 and CO were not detected; IR (CH_2Cl_2) 2060, 2008, 1996, 1956 cm^{-1}.

(2-Methyl-4-phenylhex-1-en-5-yne)dicobalt Pentacarbonyl Triphenylphosphane (8o). Reaction between **3e**−**BF$_4$** (0.77 g, 1.1 mmol) and (2-methylallyl)tributylstannane **6d** (0.75 g, 2.2 mmol) in CH_2Cl_2 (50 mL) gave complex **8o** (0.41 g, 54%) after purification by flash chromatography (silica gel, diethyl ether/hexane = 1/10) as a red oil. The ^1H NMR spectrum showed a 1:0.8 mixture of two diastereomers: ^1H NMR (d_6-acetone) δ 1.30, 1.59 (2 s, each 3 H, Me), 2.27−2.48, 2.78−2.90 (2 m, each 2 H, 3-H), 3.38−3.42, 3.52−3.56 (2 m, each 1 H, 4-H), 4.35, 4.44, 4.47, 4.62 (4 br s, each 1 H, 1-H), 5.25, 5.62 (2 d, J = 5.8 Hz, 3.7 Hz, each 1 H, 6-H), 6.66−6.67, 7.05−7.45, 7.56−7.60 (3 m, 20 H, Ph, PPh_3); ^{13}C NMR (d_6-acetone) δ 22.65, 23.35 (2 q, Me), 43.68, 47.30 (2 t, C-3), 44.35, 46.04 (2 d, C-4), 73.74, 75.22 (2 d, C-6), 102.20, 102.59 (2 s, C-5), 112.87, 113.09 (2 t, C-1), 126.88, 127.26, 128.49, 128.53, 129.41, 129.57, 129.69, 129.81, 131.48, 133.82, 133.87, 133.97, 134.02 (13 d, Ph, PPh_3), 134.98, 135.27, 135.53, 135.82, 143.52, 143.77, 144.38, 144.81 (8 s, Ph, C-2, Ph, PPh_3), 202.90 (s, CO); IR (CH_2Cl_2) 2060, 2005, 1960 cm^{-1}.

[2-(1-Phenylprop-2-ynyl)cyclohexanone]dicobalt Pentacarbonyl Triphenylphosphane (8q). Compound **3e**−**BF$_4$** (0.25 g, 0.35 mmol) was treated with **7a** (0.13 g, 0.77 mmol) at 0 °C for 12 h in CH_2Cl_2 (50 mL) to give complex **8q** (0.14 g, 56%): red oil; ^1H NMR (d_6-acetone) δ 1.34−1.88 (m, 8 H, CH_2 of cyclohexanone), 2.69−2.81 (m, 1 H, 2-H of cyclohexanone), 3.35 (m$_c$, 1 H, 1-H), 5.71 (d, J = 7.0 Hz, 1 H, 3-H), 7.02−7.21 (m, 5 H, Ph), 7.43−7.68 (m, 15 H, PPh_3); ^{13}C NMR (d_6-acetone) δ 23.78, 29.16, 32.84, 42.08 (4 t, CH_2 of cyclohexanone), 45.89 (d, C-1), 57.43 (d, C-2 of cyclohexanone), 75.46 (d, C-3), 126.87, 127.96, 129.23, 129.35, 129.48, 129.54, 131.25, 133.59, 133.74 (9 d, Ph, PPh_3), 134.82, 135.38, 144.59 (s, Ph, PPh_3), 209.53 (CO of cyclohexanone); due to slow relaxation, the signals of C-2 and Co(CO) were not detected; IR (CH_2Cl_2) 2060, 2007, 1964 cm^{-1}.

4-Phenylhex-1-en-5-yne (9b). The complex **3a**−**BF$_4$** (0.81 g, 1.6 mmol) was dissolved in CH_2Cl_2 (30 mL) and cooled to −30 °C. The mixture was treated with **6a** (0.38 g, 3.3 mmol), stirred for 5 h, and warmed to room temperature before the solvent was removed under reduced pressure. The red oil was dissolved in acetone (100 mL) and cooled to −78 °C. Ceric ammonium nitrate (1.34 g, 2.46 mmol) was added, and the mixture was stirred for 4 h until the evolution of CO ceased. The solution was warmed to room temperature, poured into 150 mL of saturated brine solution, and extracted with four 10-mL portions of diethyl ether. The combined ether extracts were dried over $MgSO_4$, and the solvent was evaporated in vacuo to give compound **9b** (0.18 g, 72%): colorless oil; ^1H NMR ($CDCl_3$)[28] δ 2.21 (d, J = 2.11 Hz, 1 H, 6-H), 2.43 (t, J = 7 Hz, 2 H, 3-H), 3.55−3.68 (m, 1 H, 4-H), 4.88−5.09 (m, 2 H, 1-H), 5.76 (m$_c$, 1 H, 2-H), 7.06−7.39 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 37.62 (d, C-4), 42.35 (t, C-3), 71.38 (d, C-6), 85.29 (s, C-5), 117.15 (t, C-1), 126.87, 127.39, 128.45 (3 d, Ph), 135.09 (d, C-2), 140.68 (s, Ph).

Methyl 2,2-dimethyl-3-phenyl-4-pentynoate (9p) was prepared from **3e**−**BF$_4$** (3.52 g, 4.87 mmol) and silylketene acetal **7b** (1.31 g 7.51 mmol) in CH_2Cl_2 (100 mL). Decomplexation with ceric ammonium nitrate (3.0 g, 5.5 mmol) at −78 °C as described for **9b** gave **9p** (0.55 g, 52%): colorless oil; bp 60 °C (2.6×10^{-2} mbar); ^1H NMR (d_6-acetone) δ 1.09, 1.30 (2 s, each 3 H, 2-Me), 2.79 (d, J = 2.6 Hz,

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1 H, 5-H), 3.61 (s, 3 H, OMe), 4.14 (d, $J = 2.6$ Hz, 1 H, 3-H), 7.19−7.35 (m, 5 H, Ph); ^{13}C NMR (d_6-acetone) δ 21.60, 23.70, (2 q, 2-Me), 46.33 (d, C-3), 47.84 (s, C-2), 52.03 (q, OMe), 74.05 (d, C-5), 83.85 (s, C-4), 128.19, 128.72, 130.17 (3 d, Ph), 138.09 (s, Ph), 176.43 (s, CO).

General Procedure for the Reaction of 3c−OTf with the Nucleophiles 6 and 7. The complex **4c** was dissolved in CH_2Cl_2, and 10 equiv of Me_3SiOTf was added. The solution was cooled to −30 °C and treated with 2 equiv of nucleophile. The mixture was stirred at −30 °C for 5 h and was warmed to room temperature. After treatment with $NaHCO_3$, the solution was stirred for further 30 min. Solid $NaHCO_3$ was separated by filtration, and the reaction mixture was washed with water. After removal of the solvent, the residue was dissolved in dry diethyl ether and separated from traces of black precipitate by filtration. The filtrate was dried over $MgSO_4$, and the solvent was evaporated in vacuo to give complex **8**.

(6-Phenylhex-1-en-5-yne)dicobalt Hexacarbonyl (8h). Complex **4c** (0.20 g, 0.43 mmol), Me_3SiOTf (1.23 g, 5.53 mmol), and **6a** (0.95 g, 0.81 mmol) reacted in CH_2Cl_2 (30 mL) to give complex **8h** (0.13 g, 68%): red oil; ^{1}H NMR (CD_2Cl_2) δ 2.54, 3.18 (2 m$_c$, each 2 H, 3-H, 4-H), 5.10 (d, $J_{cis} = 10.2$ Hz, 1 H, 1-H), 5.20 (d, $J_{trans} = 17.1$ Hz, 1 H, 1-H), 5.94−6.08 (m, 1 H, 2-H), 7.30−7.57 (m, 5 H, Ph); ^{13}C NMR (CD_2Cl_2) δ 33.61, 35.75 (2 t, C-3, C-4), 115.47 (t, C-1), 127.82, 128.88, 129.35 (3 d, Ph), 137.40 (d, C-2), 138.25 (s, Ph), 199.58 (s, CO); due to slow relaxation, the signals of C-5 and C-6 were not detected; IR (CH_2Cl_2) 2089, 2052, 2022 cm^{-1}.

(2-Methyl-6-phenyl-hex-1-en-5-yne)dicobalt Hexacarbonyl (8i). Complex **4c** (0.20 g, 0.43 mmol) was treated with the Lewis acid BCl_3 (0.07 g, 0.6 mmol) instead of TMSOTf in CH_2Cl_2 (30 mL). Reaction with **6b** (0.11 g, 0.86 mmol) in the presence of poly(2,6-di-*tert*-butyl-4-vinylpyridine) (25 mg) gave **8i** (0.14 g, 75%): red oil; ^{1}H NMR (d_6-acetone) δ 1.84 (s, 3 H, Me), 2.48−2.52, 3.28−3.33 (2 m, each 2 H, 3-H, 4-H), 4.82, 4.87 (2 s, each 1 H, 1-H), 7.32−7.45, 7.61−7.65 (2 m, 5 H, Ph); ^{13}C NMR (d_6-acetone) δ 22.65 (q, Me), 33.15, 40.39 (2 t, C-3, C-4), 111.24 (t, C-1), 128.82, 129.84, 130.05 (3 d, Ph), 138.8 (s, Ph), 145.34 (s, C-2), 200.78 (s, Co(CO)); due to slow relaxation, the signals of C-5 and C-6 were not detected; IR (CH_2Cl_2) 2090, 2050, 2023 cm^{-1}.

[2-(3-Phenylprop-2-ynyl)cyclohexanone]dicobalt Hexacarbonyl (8j). Complex **4c** (0.25 g, 0.54 mmol), Me_3SiOTf (0.98 g, 4.4 mmol), and **7a** (0.18 g, 1.1 mmol) were combined in CH_2Cl_2 (40 mL) at −50 °C to give complex **8j** (0.22 g, 83%): red oil; ^{1}H NMR (CD_2Cl_2) δ 1.48−2.45 (m, 8 H, CH_2 of cyclohexanone), 2.64 (m$_c$, 1 H, CH of cyclohexanone), 2.81 (dd, $J = 15.9$, 5.7 Hz, 1 H, 1-H), 3.76 (dd, $J = 15.8$, 5.9 Hz, 1 H, 1-H), 7.21−7.30, 7.51−7.64 (2 m, 5 H, Ph); ^{13}C NMR (CD_2Cl_2) δ 25.44, 28.37, 33.34, 35.54, 42.19 (5 t, CH_2 of cyclohexanone, C-1), 53.36 (d, CH of cyclohexanone), 127.76, 129.85, 129.25 (3 d, Ph), 138.27 (s, Ph), 199.83 (s, Co(CO)), 210.92 (s, CO of cyclohexanone); due to slow relaxation, the signals of C-2 and C-3 were not detected; IR (CH_2Cl_2) 2091, 2053, 2025 cm^{-1}.

Kinetic Investigations. The consumption of the cations **3a−e** was determined conductometrically and/or photometrically by using fiber optics and the workstation previously described.[15] Calibration curves, i.e., the correlation between absorbance (or conductance) and the concentration of the propargyl cations **3a−e**, were obtained by determination of the absorbance or conductance after varying amounts of a concentrated CH_2Cl_2 solution of **3a−BF$_4$**, **3b−BF$_4$**, **3d−BF$_4$**, or **3e−BF$_4$** were added to CH_2Cl_2. Calibration curves for the triflates were obtained by adding the acetates **4a−c** to a solution of excess Me_3SiOTf in CH_2Cl_2 and determination of the absorbance after ionization of each portion.[15]

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Supporting Information Available: Experimental procedures for the generation of the propargyl alcohol complexes **2a−d**, propargyl acetate complexes **4a−c**, and cobalt-coordinated propargyl cations **3a**,**b**,**d**,**e** and tables with concentrations and rate constants of the kinetic experiments at variable temperatures (13 pages). See any current masthead page for ordering and Internet access instructions.

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