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Reactions of Carbon Electrophiles with Cobalt-Coordinated Enynes: Scope and Limitations

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

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Abstract—The kinetics of the reactions of the dicobalt-coordinated enynes **2a–d** with the benzhydryl cations **3a–c,f** have been studied photometrically. The reactions follow second-order kinetics and indicate that $Co_2(CO)_6$-coordination increases the nucleophilic reactivity of enynes by a factor of $> 10^6$. The exchange of one CO ligand by PPh_3 (**2a→2d**), however, has only little effect on the reactivity of the enyne moiety. The second-order rate constants match the linear free energy relationship $\lg k_{20°C} = s(E+N)$ and allow to determine the nucleophilicity parameters N and s for **2a–d**. It is shown that at −70°C, electrophiles with $E>0$ are able to react with the enyne complexes **2a**, **2c**, and **2d** whereas electrophilic reagents with $E>-2$ are suitable for reactions with **2b**.

Introduction

Consecutive additions of electrophiles and nucleophiles to cobalt-coordinated enynes provide a regio- and stereoselective access to a variety of carbon-frameworks (Scheme 1).[1]

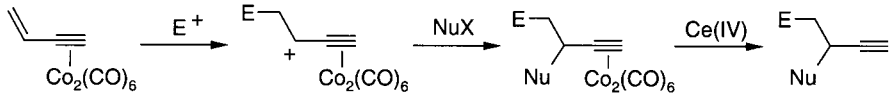
For a consideration of this reaction sequence in retrosynthetic approaches, it is necessary to know which types of electrophiles are able to attack at cobalt enyne complexes and which types of nucleophiles undergo reactions with cobalt-coordinated propargyl cations. The latter question, i.e. the scope of the Nicholas reaction[2] has recently been answered:[3] Dicobalthexacarbonyl-coordinated propargyl cations with primary or secondary propargyl carbons are fairly strong electrophiles with electrophilicity parameters $E=-1$ to -2,[4] almost independent of the substitutents at the propargyl fragment. As a consequence, these propargyl cation complexes react with nucleophiles characterized by $N>-3$, i.e. with electron-rich arenes (e.g. anisole,[5] furans,[6] and indoles[7]) or alkenes (e.g. monoalkylated ethylenes[5] or enamines[8]). Structurally analogous propargyl cation complexes, in which one of the six carbonyl ligands at cobalt is replaced by triphenylphosphine are considerably less electrophilic and react only with strong nucleophiles as silyl enol ethers, allylstannanes, or enamines.[3] Since kinetic data on electrophilic additions to enyne complexes have not yet been determined, we set out to explore the scope of the first step of the reaction sequence depicted in Scheme 1.

Our analysis is based on Eq. (1), which has been shown[4] to yield the rate constants for the reactions of carbocations and related electrophiles with non-charged nucleophiles within an accuracy of factor 10 to 100. This precision is sufficient for semiquantitative predictions of rate constants since the E-, N-, and s-values presently known cover a reactivity range of more than thirty orders of magnitude.

$$\lg k(20°C) = s(E + N) \quad (1)$$

Where E=electrophilicity parameter, N=nucleophilicity parameter and s=nucleophile-specific slope parameter (typically $0.6<s<1.2$).

We have now studied the kinetics of the reactions of the benzhydryl cations **3** with the enyne complexes **2a–2d** in order to determine the nucleophilicity parameters N (and s) of the latter, which are needed to define electrophiles that are able to attack at the enyne complexes **2**.



Scheme 1.

Keywords: carbenium ions; cobalt and compounds; enynes; kinetics; linear free energy relations.

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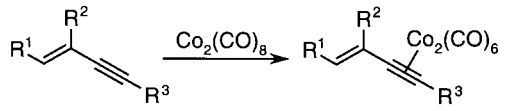


R^1	R^2	R^3		
H	H	$SiMe_3$	**1a**	**2a** (90 %)
H	Ph	$SiMe_3$	**1b**	**2b** (81 %)
$-(CH_2)_4-$		H	**1c**	**2c** (83 %)

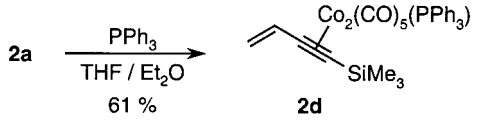
Scheme 2.

Results

Synthesis of the cobalt enyne complexes 2

The red oily dicobalthexacarbonyl complexes **2a–c** were obtained by stirring the enynes **1a–c** with 1.00–1.05 equiv. of $Co_2(CO)_8$ in dichloromethane at ambient temperature, as described for the complexation of propargyl alcohols by Nicholas[9] (Scheme 2).

Treatment of **2a** with one equivalent of triphenylphosphine at 35–50°C in ether/tetrahydrofuran resulted in replacement of one carbonyl ligand by triphenylphosphine to give the crystalline complex **2d** which was analyzed by X-ray crystallography.



As previously reported for an analogous $Co_2(CO)_5(PPh_3)$-complex of a propargyl alcohol,[10] this complex can be considered as a dicobaltatetrahedrane (Fig. 1). While the cobalt–carbon bond lengths in the dimetallatetrahedrane range from 1.97–2.03 Å, the Co–Co distance is 2.48 Å, and the CC-triple bond has been elongated to 1.31 Å, comparable to a CC-double bond. The C(6)–C(7)–C(8) angle (143°) and the C(7)–C(6)–Si angle (144°) also show that the sp-character of carbons 6 and 7 has been abandoned.

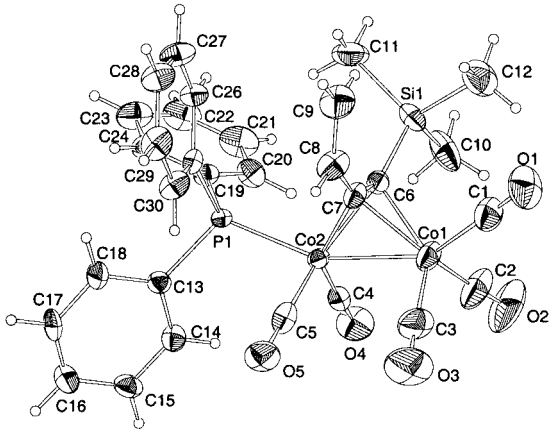


Figure 1. ORTEP plot of the cobalt-complexed enyne **2d**. Selected bond lengths [Å] and bond angles [°]: Co(1)–C(6) 2.031, Co(1)–C(7) 1.982, Co(2)–C(6) 1.982, Co(2)–C(7) 1.970, C(6)–C(7) 1.313, C(8)–C(9) 1.320, C(6)–C(7)–C(8) 143.4, C(7)–C(8)–C(9) 121.9.

The bond length C(8)–C(9) (1.32 Å) and the angle C(7)–C(8)–C(9) (122°) indicate that the vinyl group has not been affected by the complexation.

Reactions of the cobalt enyne complexes 2 with the benzhydryl cations 3

The chlorotitanates of the benzhydryl cations **3a–c** which were obtained from the corresponding benzhydryl chlorides and 2–3 equiv. of titanium tetrachloride react with the enyne complex **2a** to give the propargyl cation complexes **4a–c**, which were not isolated but intercepted with (2-methylallyl)trimethylsilane and then treated with CAN [$=Ce(NH_4)_2(NO_3)_6$] to give the decomplexed products **5a–c** in fair yield (Scheme 3).

Compound **5c** was obtained in 70% yield when the reaction sequence described in the bottom line of Scheme 3 was carried out with **2d** instead of **2a**. Since the intermediate $Co_2(CO)_5(PPh_3)$-coordinated propargyl cation obtained in this way is considerably less electrophilic than **4c**,[3] the reaction with (2-methylallyl)trimethylsilane had to be performed at room temperature.

We have not been able to observe similar reaction sequences with **2b**. The propargyl cation complexes obtained from **2b** and **3b**, **3d**, or **3e** did not react with (2-methylallyl)-trimethylsilane (48 h, −78°C).[11] Therefore, the reaction mixtures obtained from **2b** and **3b**,**d**,**e** were worked up with water to give the $Co_2(CO)_6$-complexes of **6b**,**d**,**e**, two of which were oxidized with CAN to give the metal-free enynes **6b** and **6e** (Scheme 4).

The $Co_2(CO)_6$-complex of **6d** was formed as a 4:1 mixture of two stereoisomers. It can be assumed that the major isomer is the one with the phenyl and the benzhydryl group being *cis* to each other, since the purified enynes **6b** and **6e** consisted only of this isomer, as unequivocally proven by the X-ray analysis of **6e** (Fig. 2).

In analogy to the examples described in Scheme 4, the reaction of **3b** with **2c** gave a tertiary propargyl cation complex which could not be intercepted by (2-methylallyl)-trimethylsilane or tributylsilane (hydride transfer). Workup

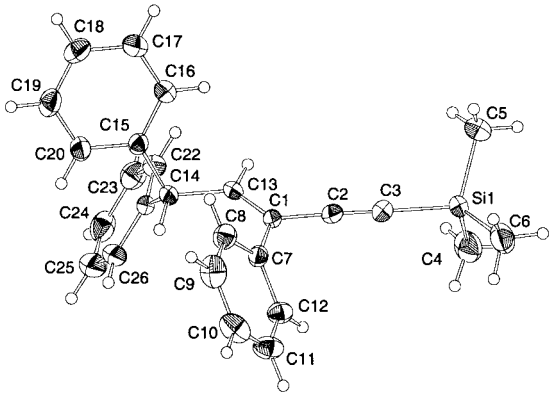
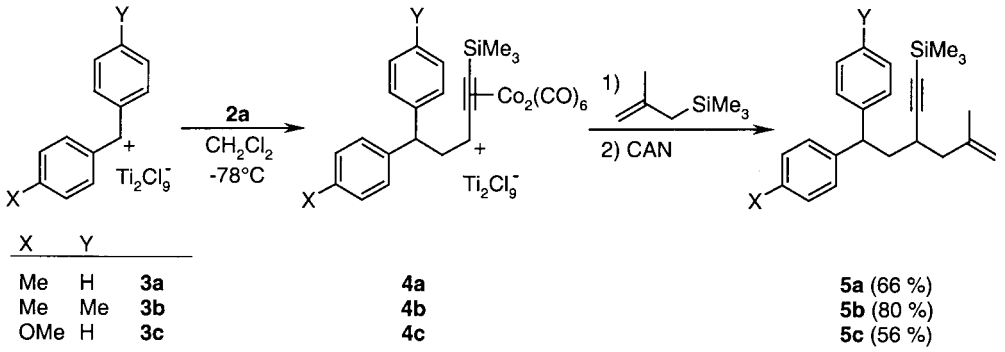
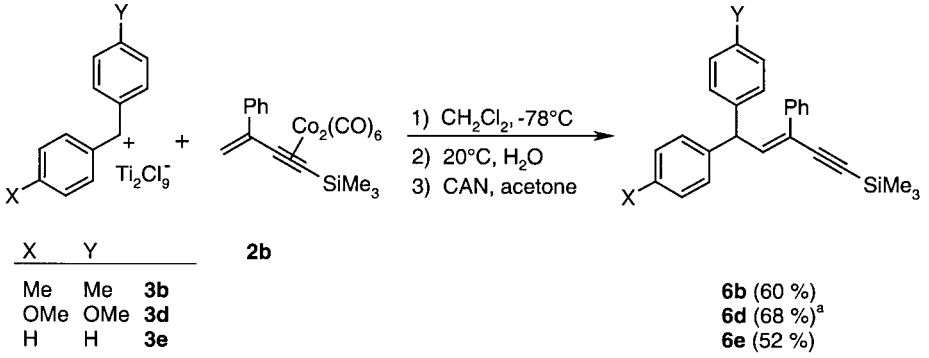


Figure 2. ORTEP plot of the enyne **6e**. Selected bond lengths [Å] and bond angles [°]: C(2)–C(3) 1.197, C(1)–C(13) 1.331 C(13)–C(14) 1.507, C(1)–C(2)–C(3) 178.3, C(2)–C(3)–Si(1) 178.0, C(2)–C(1)–C(13) 119.8, C(1)–C(13)–C(14) 128.5.



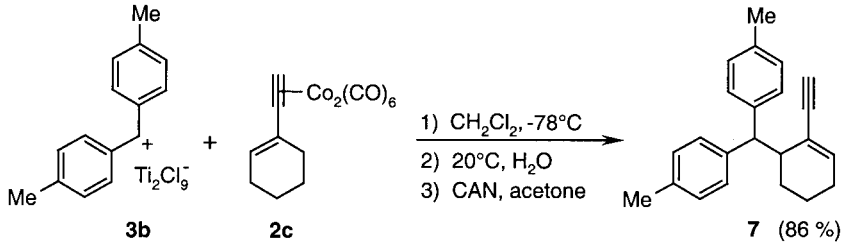
Scheme 3.



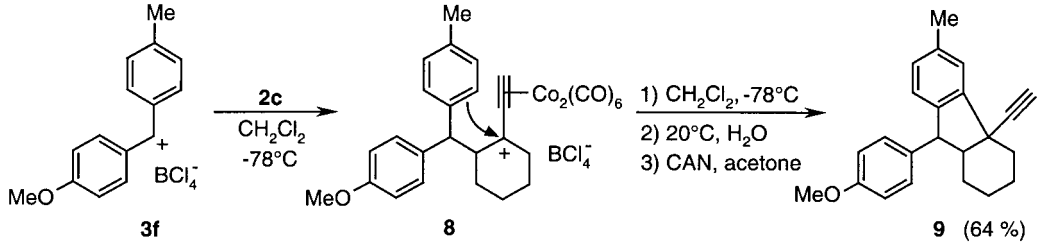
Scheme 4. [a]Yield of the $Co_2(CO)_6$-complex of **6d**.

of the reaction mixture with water and CAN as shown in Scheme 5 gave the benzhydrylated enyne **7** in good yield.

The reaction of **2c** with the benzhydryl tetrachloroborate **3f**−BCl_4^- did not give an analogous enyne by deprotonation of the intermediate **8**. A single diastereomer of the hexahydrofluorene derivative **9** was isolated instead (Scheme 6), which could be rationalized by intramolecular electrophilic substitution of the *p*-methyl substituted phenyl ring in **8**. The preferential attack at the methyl substituted phenyl ring rather than at the methoxy substituted ring is in accord with the relative magnitude of the Hammett substituent constants for methyl (σ_m=−0.06) and methoxy (σ_m=0.10).[12] It is not clear, however, why different types of products are obtained in the reactions described in Schemes 5 and 6. Since **2c** yields a complex mixture of



Scheme 5.



Scheme 6.

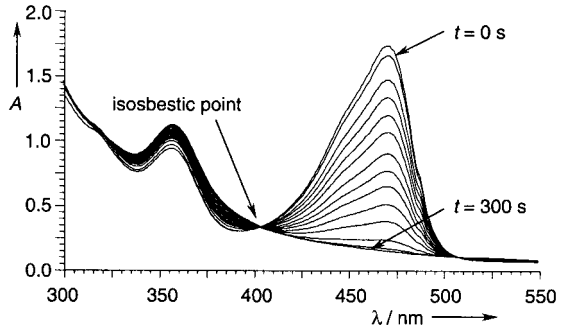


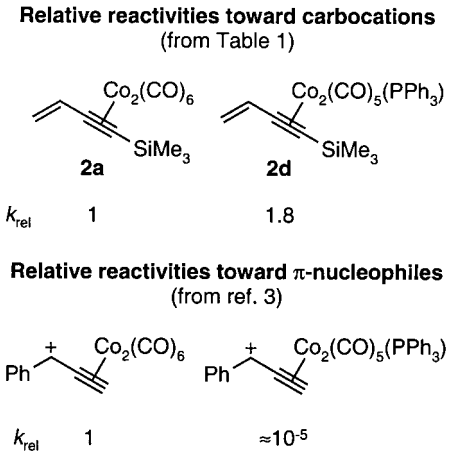
Figure 3. UV–Vis spectra during the reaction of the $Co_2(CO)_6$-enyne complex **2b** with the benzhydryl cation **3c** (in CH_2Cl_2 at −60.8°C).

products with **3f**−$Ti_2Cl_9^-$ under the same conditions, the presence of BCl_4^- seems to be important for the formation of **9**.

Kinetics

The rates of the reactions of the benzhydryl cations **3a**, **3b**, **3c**, and **3f** with the enyne complexes **2a–d** were followed by UV–Vis spectroscopy. Since the propargyl cation complexes (e.g. **4**) formed in these reactions absorb only weakly at $\lambda > 400$ nm (Fig. 3), the decay of the benzhydryl cation absorbances at $\lambda = 460–490$ nm[13] can be evaluated as described in Ref. 14. Nucleophile concentrations considerably higher than the benzhydryl cation concentrations were usually employed ($[\mathbf{2}]_0 \gg [\mathbf{3}]_0$), resulting in pseudo-first order kinetics with an exponential decay of the benzhydryl cation concentration. The independence of the reaction rates of the nature of the counterions is demonstrated by the fact that rate constants measured with **3c**−$Ti_2Cl_9^-$ and **3c**−BCl_4^- match the same Eyring plot, as examined for the reactions with the enynes **2b** and **2d** (Tables 5 and 7, see Experimental).

The rate constants obtained for the reactions with the *p*-methoxybenzhydrylium ion **3c** (Table 1) show that the phenyl-substituted enyne complex **2b** is 10^2 times more reactive than the complexes **2a**, **2c**, and **2d**. The closely similar reactivities of the $Co_2(CO)_6$ complex **2a** and the $Co_2(CO)_5(PPh_3)$ complex **2d** are particularly striking, since the replacement of a carbonyl ligand by PPh_3 was found to reduce the electrophilicity of the corresponding propargyl cation complexes by five orders of magnitude (Scheme 7).[3] One has to conclude that the stabilization of the propargyl cation complexes produced by these electrophilic additions is hardly noticed in the corresponding transition states.



Scheme 7.

In order to determine the nucleophilicity parameters of the enyne complexes, the rate constants of the reactions of **2a** and **2c** with benzhydryl cations were plotted against the electrophilicity parameters[4] of these carbenium ions. Fig. 4 shows linear correlations with slopes close to 1 as previously found for the corresponding additions of benzhydryl cations to olefins. The slightly higher slope for **2c** compared with **2a** has precedence in additions to other π-systems: Alkyl groups at the position of electrophilic attack at alkenes[15] or allylsilanes[16] give rise to increased slopes of the corresponding plots of lg *k* vs. *E*; a satisfactory explanation for this phenomenon has not been given.

With the assumption $s = 1$, *N*-values can also be estimated for the enyne complexes **2b** and **2d**, which have only been investigated with respect to one electrophile (Table 1). The nucleophilicity parameters *N* can now be used to compare the complexes **2a–d** with other nucleophiles.

Fig. 5 shows that the nucleophilicities of **2a**, **2c**, and **2d** are comparable to 1,3-butadiene. Only **2b**, the most reactive enyne complex investigated, arrives at the nucleophilic reactivity of isobutylene. Comparison of 1-hexene with **2a** or **2d** reveals that the dicobaltatetrahedrane substituent activates the double bond slightly more than alkyl. On the other hand, comparison of 1-methylcyclohexene with **2c** and of α-methylstyrene with **2b** shows that in more highly substituted systems the dicobaltatetrahedrane substituent activates even less than a methyl group.

In view of the high stabilities of the dicobalt-coordinated propargyl cations, which are produced in the electrophilic

Table 1. Rate constants (20°C) and Eyring activation parameters for the reactions of the cobalt-enyne complexes **2a–d** with the benzhydryl cations **3a–f** (in CH_2Cl_2)

Enyne complex	Benzhydryl cation	k_2/L mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
2a	**3a**	1778	22.3±0.7	−106.7±3.3
	3b	159	32.5±1.3	−91.8±5.3
	3c	8.95	–	–
2b	**3c**	1256	17.8±0.9	−124.8±4.0
2c	**3b**	2647	23.6±1.3	−98.6±5.8
	3c	38.1	23.0±0.8	−136.0±3.3
	3f	17.0	31.8±1.3	−112.7±4.8
2d	**3c**	16.5	39.6±1.4	−86.6±5.2

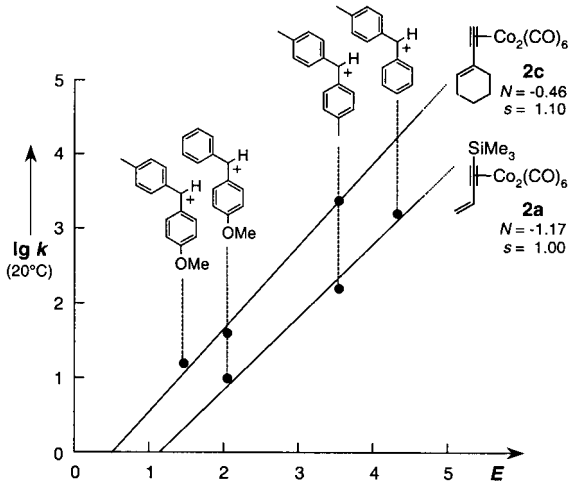


Figure 4. Determination of the nucleophilicities of the $Co_2(CO)_6$-coordinated enynes **2a** and **2c**.

additions to the enynes **2a**–**d**, the observed nucleophilicities of these complexes are unexpectedly small. Since dicobalt coordinated propargylium triflates and tetrafluoroborates in contrast to the corresponding *tert*-alkyl, *sec*-alkyl and monoalkyl allyl salts are stable at room temperature, we had intuitively anticipated **2a**–**d** to be considerably more nucleophilic than isobutylene, 1-alkenes, or 1,3-butadiene. This presumption was supported by the previously reported relationship between the nucleophilicities of ordinary alkenes and the stabilization of the resulting carbocations.[17] Since cobalt-coordinated propargylium ions are better stabilized than tertiary alkyl cations, as shown by the pK_{R^+} values[18,19] and the electrophilicity parameters[3] E (Table 2), the enyne complexes **2a**–**2d** had originally been extrapolated to be considerably more nucleophilic than isobutylene. The reason for the failure of this relationship is presently unknown.

In order to determine the influence of the $Co_2(CO)_6$ coordination on the nucleophilicity of enynes, we tried to determine the rate of reaction of the free enyne **1a** with **3b**. However, when **1a** and bis(*p*-tolyl)methyl chloride were treated with BCl_3 at −30°C, no reaction was observed after 3 weeks, and **1a** could be recovered almost quantitatively. Since bis(*p*-tolyl)methyl chloride was predominantly ionized under these conditions, this observation corresponds to $k_2(-30°C) < 10^{-5}$ L mol^{-1} s^{-1} for the reaction of **3b** with **1a**, which has to be compared with $k_2(-30°C) = 10$ L mol^{-1} s^{-1} for the reaction of **3b** with **2a**. Metal-coordination thus enhances the enyne's reactivity by more than a factor of 10^6.

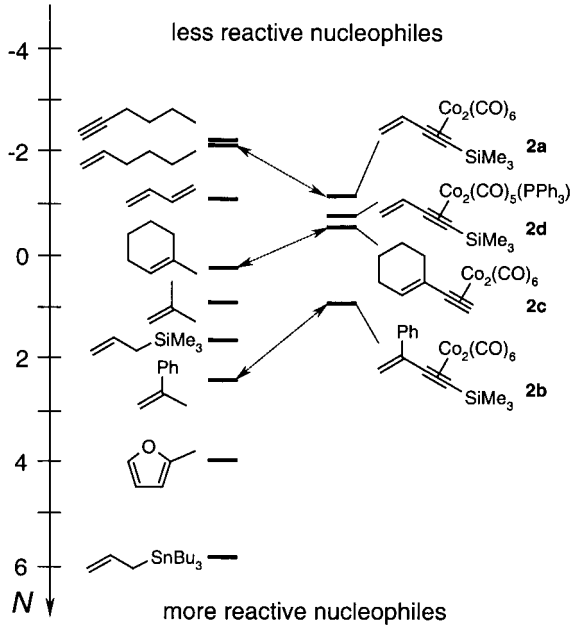


Figure 5. Comparison of the nucleophilicities of cobalt-enyne-complexes with those of other π-nucleophiles.

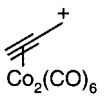
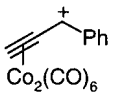
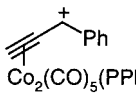
Conclusion

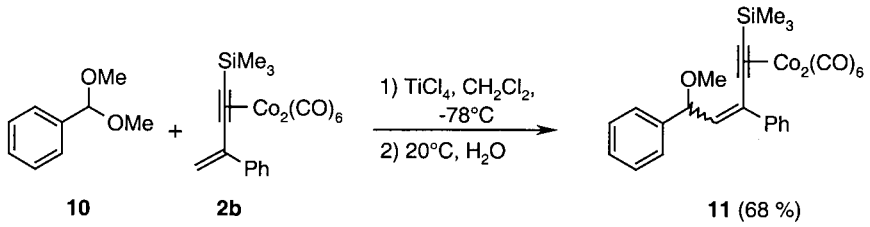
Based on the rule of thumb that at 20°C reactions of cationic electrophiles with uncharged nucleophiles can be expected if $N+E>-5$,[4] one can derive that electrophiles with $E>-4$ will be potential reaction partners for the enyne complexes **2a**, **2c**, and **2d**. One has to consider, however, that only those cobalt propargyl cation complexes which do not possess β-hydrogens can be handled without decomposition at room temperature. Other types have to be kept below −30°C.[21] For that reason, it is important to know the electrophiles which will react with **2a–2d** at low temperatures.

Let us assume that second-order rate constants $k_2 > 10^{-5}$ L mol^{-1} s^{-1} are sufficient for synthetically useful reactions. With an approximated entropy of activation of −100 J mol^{-1} K^{-1} (Table 1), a rate constant of 10^{-5} L mol^{-1} s^{-1} at −70°C corresponds to 10^{-1} L mol^{-1} s^{-1} at 20°C. As a consequence of Eq. (1) the enyne complexes **2a**, **2c**, and **2d** can be expected to react with electrophiles of $E>0$ at −70°C, while **2b** should react with electrophiles of $E>-2$.

In accord with this conclusion, **2a** and **3d**−$Ti_2Cl_9^-$ (E=0)

Table 2. Comparison of the stabilization of cobalt coordinated propargylium cations and tertiary alkyl cations

Carbocations				
Lewis acidity parameter pK_{R^+}	−6.8 (Ref. 18a) −5.5 (Ref. 18b)	–	–	−14.7 (Ref. 19)
Electrophilicity parameter E	−1.22 (Ref. 3)	−1.34 (Ref. 3)	−6.71 (Ref. 3)	≈8.5 (Ref. 20)



10 2b 11 (68 %)

Scheme 8.

did not react within 12 h at −78°C, and **2a** was recollected in almost quantitative yield. In contrast, **2b** reacted with **3d**−$Ti_2Cl_9^-$ under these conditions (Scheme 4). Early experiments (when the nucleophilicities of the complexes **2** were overestimated) showed that **2c** did not react with the bis(*p*-dimethylamino)benzhydryl cation (E=−7.45).

In accord with E=3.26 for $Ph(OMe)CH^+$,[22] benzaldehyde dimethyl acetal (**10**) was found to react with **2b** at −78°C in the presence of titanium tetrachloride to yield **11** as a mixture of diastereoisomers (Scheme 8).

Previously, only very strong electrophiles as the *tert*-butyl cation (E≈8.5)[20] or acylium ions (E>3)[23] have been reported[1] to react with cobalt enyne complexes. It has now been shown that the enyne complexes **2**, though being relatively weak nucleophiles, are able to react with a much wider variety of electrophiles which can be identified by our electrophilicity scales.[4]

Experimental

General methods and materials

All reactions with moisture- or oxygen-sensitive reagents were run in an atmosphere of dry argon or dry nitrogen in carefully dried glassware. Dichloromethane was freshly distilled from CaH_2 prior to use, other solvents were dried according to Ref. 24. Benzhydryl chlorides[25] **3**-Cl and (2-methylallyl)trimethylsilane[16] were obtained according to literature procedures. Dicobalt octacarbonyl was purchased from Acros.

^1H and ^{13}C NMR spectra were recorded with a Bruker WM 300 or with a Bruker ARX 300 spectrometer. ^1H NMR chemical shifts (300 MHz) refer to $CDCl_3$ (δ_H 7.24), d_6-acetone (δ_H 2.04), and CD_2Cl_2 (δ_H 5.32). ^{13}C NMR spectra (75.5 MHz) were calibrated to $CDCl_3$ (δ_C 77.0), d_6-acetone (δ_C 29.8), and CD_2Cl_2 (δ_C 53.5). DEPT-135 experiments were used to obtain information about the multiplicity of ^{13}C resonances. $^1H,^1H$- and $^1H,^{13}C$-COSY experiments were performed on a Varian VXR 400 (400 MHz) spectrometer. Mass spectra were obtained with a Finnigan MAT 95Q, and IR spectra were collected with Perkin–Elmer 1750 and Perkin–Elmer Spectrum 1000 spectrometers.

The UV/Vis photometers used for kinetic experiments were Schölly KGS III with band-pass filters by Corion and J&M Tidas DAD 2062 with probes by Hellma.

Preparation of the enynes

1-(Trimethylsilyl)but-3-en-1-yne (1a). In analogy to a procedure described by Hopf,[26] DBU (14 g, 92 mmol) was added dropwise to a solution of 4-(trimethylsilyl)but-3-yn-1-yl tosylate (29 g, 98 mmol) in DMSO (120 ml) at 0°C. After stirring for 12 h at ambient temperature, water (20 ml) was added, and the solution was extracted with diethyl ether (3×10 ml). The combined extracts were dried with $MgSO_4$. Kugelrohr distillation (40°C, 0.15 mbar) afforded 5.3 g (46%) of **1a**. −^1H NMR (300 MHz, $CDCl_3$) δ 5.78 (dd, 1H, J=17.6, 10.8 Hz, 3-H); 5.64 (dd, 1H, J=17.6, 2.6 Hz, 4-H); 5.45 (dd, 1H, J=10.8, 2.6 Hz, 4-H), 0.16 (s, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 127.8 (t, C-4); 117.2 (d, C-3); 103.7, 94.9 (2 s, C-1 and C-2); −0.2 (q, $SiMe_3$).

3-Phenyl-1-(trimethylsilyl)but-3-en-1-yne (1b).[27] Toluenesulfonic acid (30 mg, 0.17 mmol) and 2-phenyl-4-(trimethylsilyl)but-3-yn-2-ol (2.2 g, 10 mmol) were dissolved in toluene (20 ml) and refluxed for 1 h. The solvent was evaporated in vacuo, and the residue was distilled with a Kugelrohr apparatus (50°C, 1.5×10^{-3} mbar) to give 1.2 g (60%) of **1b**. −^1H NMR (300 MHz, $CDCl_3$) δ 7.75–7.72 (m, 2H, Ph); 7.46–7.38 (m, 3H, Ph); 6.01, 5.79 (2 s, 2×1H, 4-H), 0.35 (s, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.9, 130.6 (2 s, Ph and C-3); 128.33, 128.29, 126.0 (3 d, Ph); 121.4 (t, C-4); 104.1, 95.9 (2 s, C-1 and C-2); −0.1 (q, $SiMe_3$).

Preparation of enyne complexes 2a–d

(1-(Trimethylsilyl)but-3-en-1-yne)dicobalt hexacarbonyl (2a). $Co_2(CO)_8$ (2.89 g, 8.45 mmol) was added in portions to a solution of **1a** (991 mg, 7.98 mmol) in CH_2Cl_2 (50 ml). After stirring for 5 h, the solvent was evaporated to yield 2.94 g (90%) of **2a** as a red oil.—MS (70 eV) m/z (%): 410 (M^+, <1), 382 (21), 354 (25), 326 (24), 298 (35), 270 (89), 242 (37), 226 (13), 124 (20), 109 (100). IR (KBr, cm^{-1}): 2962, 2089, 2049, 2020, 1626, 1553, 1407, 1250, 964, 911, 841, 519, 498. ^1H NMR (300 MHz, d_6-acetone) δ 7.02 (dd, 1H, J=16.0, 10.2 Hz, 3-H); 5.64 (d, 1H, J=17.0 Hz, 4-H); 5.51 (d, 1H, J=9.6 Hz, 4-H); 0.35 (s, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, d_6-acetone) δ 200.6 (s, CO); 134.9 (d, C-3); 120.1 (t, C-4); 0.5 (q, $SiMe_3$); due to slow relaxation, the signals of C-1 and C-2 were not detected. HRMS ($C_{13}H_{12}Co_2O_6Si$): Calcd 409.9067; Found 409.9100.

(3-Phenyl-1-(trimethylsilyl)but-3-en-1-yne)dicobalt hexacarbonyl (2b). Enyne **1b** (2.0 g, 10 mmol) was dissolved in CH_2Cl_2 (50 ml), and $Co_2(CO)_8$ (3.4 g, 9.9 mmol) was added in portions. The solution was stirred for 5 h and the

solvent was evaporated to yield 3.9 g (81%) of **2b** as a red oil.—MS (70 eV) *m/z* (%): 486 (M^+, <1), 458 (10), 402 (33), 374 (17), 346 (76), 318 (41), 200 (34), 185 (100). IR (KBr, cm^{-1}): 2088, 2048, 2017, 1566, 1493, 1444, 1409, 1354, 1250, 839, 772, 700. ^{1}H NMR (300 MHz, d_6-acetone) δ 7.41 (m_c, 5H, Ph); 5.81, 5.58 (2 br s, 2×1H, 4-H); 0.32 (s, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, d_6-acetone) δ 200.3 (s, CO); 148.2, 142.7 (2 s, Ph and C-3); 128.5, 128.3, 127.8 (3 d, Ph); 119.8 (t, C-4); 107.4, 82.2 (2 s, C-1 and C-2); 0.5 (q, $SiMe_3$).

(1-Ethinylcyclohexene)dicobalt hexacarbonyl (2c). Enyne **1c** (750 mg, 7.1 mmol), prepared from 1-ethinyl-1-cyclohexanol and $POCl_3$,[28] was dissolved in CH_2Cl_2 (50 ml), and $Co_2(CO)_8$ (2.42 g, 7.08 mmol) was added in portions. Stirring for 5 h and evaporation of the solvent gave 2.31 g (83%) of **2c**[29] as a red oil.—^{1}H NMR (300 MHz, $CDCl_3$) δ 6.61 (s, 1H, ≡CH); 6.30 (m_c, 1H, =CH); 2.32, 2.12, 1.74, 1.64 (4 m_c, 4×2H, 4×CH_2). ^{13}C NMR (75.5 MHz, d_6-acetone) δ 201.5 (s, CO); 133.3 (s, C-1); 130.4 (d, C-2); 72.9 (d, –C≡*C*H); 30.0, 25.4, 22.2, 21.2 (4 t, 4×CH_2); due to slow relaxation, the signal of *C*≡CH was not detected.

(1-(Trimethylsilyl)but-3-en-1-yne)dicobalt pentacarbonyl triphenylphosphine (2d). In analogy to a literature procedure,[10] **2d** was prepared by ligand exchange from **2a**. A solution of **2a** (1.00 g, 2.44 mmol) was dissolved in Et_2O/THF (v/v 1/2, 22 ml) and heated at 35°C in a three-neck flask with dropping funnel and reflux condenser. A solution of PPh_3 (640 mg, 2.44 mmol) in Et_2O/THF (v/v 1/2, 10 ml) was added dropwise, and the mixture was heated at 50°C for 4 h. After evaporation of the solvent, the residue was recrystallized from a pentane/Et_2O mixture (v/v 1/8) to yield 0.96 g (61%) of **2d** as red crystals.—Decomp. >110°C. MS (70 eV) *m/z* (%): 642 (M^+, <1), 588 (6), 560 (7), 532 (41), 504 (100), 321 (39), 302 (27). IR (KBr, cm^{-1}): 2962, 2055, 2008, 1998, 1986, 1955, 1609, 1556, 1481, 1435, 1249, 1092, 970, 905, 842, 694, 512. ^{1}H NMR (300 MHz, d_6-acetone) δ 7.50 (m_c, 15H, PPh_3); 6.32 (dd, 1H, *J*=16.7, 10.2 Hz, 3-H); 5.26 (d, 1H, *J*=16.7 Hz, 4-H); 5.06 (d, 1H, *J*=10.2 Hz, 4-H); 0.16 (s, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, d_6-acetone) δ 202.0 (s, CO); 135.9 (s, Ph) 135.6 (d, C-3 or Ph), 135.5 (s, Ph); 134.1, 134.0, 131.4, 131.3, 129.5, 129.4 (6 d, C-3 or Ph); 118.5 (t, C-4); 1.6 (q, $SiMe_3$); due to slow relaxation, the signals of C-1 and C-2 were not detected. Anal. ($C_{30}H_{27}Co_2O_5PSi$): Calcd C, 55.91; H, 4.22. Found C, 55.85; H, 4.19.

Reactions of the complexes 2a and 2d with the benzhydryl salts 3$^-$$Ti_2Cl_9^-$ and (2-methylallyl)-trimethylsilane (general procedure 1)

In a 100 ml flask, triply evacuated, heated and flushed with argon, the benzhydryl chlorides **3**-Cl were dissolved in CH_2Cl_2 (50 ml) and cooled to −78°C. After addition of $TiCl_4$ (2–3 equiv.) and 5 min stirring, a CH_2Cl_2 solution of the enyne complex (1 equiv.) was slowly added through a dropping funnel. The mixture was stirred for 48 h at −78°C, (2-methylallyl)trimethylsilane (2 equiv.) was added, and stirring was continued for 12 h. The mixture was then warmed at ambient temperature and stirred with a 1:1 mixture of Et_2O and aqueous $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3×20 ml). After drying the combined organic phases ($MgSO_4$), the solvent was evaporated in vacuo. The residue was dissolved in acetone (20 ml) and cooled at −30°C. Cerium ammonium nitrate (CAN, 5 equiv.) was added and after 5 min combined with a water/Et_2O mixture (v/v 1/1, 50 ml).[29] The organic layer was separated, and the aqueous layer was extracted with Et_2O (3×10 ml). After drying the extracts ($MgSO_4$), the solvent was evaporated in vacuo, and the products were isolated as described individually.

5-Methyl-3-(2-(*p*-methylphenyl)-2-phenylethyl)-1-(trimethylsilyl)hex-5-en-1-yne (5a). Benzhydryl chloride **3a**-Cl (0.21 g, 0.97 mmol), $TiCl_4$ (0.46 g, 2.4 mmol), **2a** (0.41 g, 1.0 mmol), (2-methylallyl)trimethylsilane (0.26 g, 2.0 mmol) and CAN (2.74 g, 5.00 mmol) were employed for the operations described in the General Procedure 1. The resulting brownish oil was purified by column chromatography (silica gel, cyclohexane/Et_2O 9/1) to give 0.23 g (66%) **5a** (as a 1:1-mixture of diastereomers).—MS (70 eV) *m/z* (%): 360 (M^+, 6), 305 (12), 194 (100), 181 (93), 179 (40), 166 (38), 165 (30), 73 (Me_3Si^+, 65). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.08 (m, 9H, arom. H); 4.78, 4.71 (2 br s, 2×1H, 6-H); 4.33–4.28 (m, 1H, –C*H*Ar_2); 2.32/2.31 (s, 3H, Me); 2.27–1.95 (m, 5H, 3-H, 4-H and 3-CH_2); 1.62/1.60 (s, 3H, 5-Me); 0.20 (s, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 145.6, 143.9, 142.7, 142.4, 140.6, 135.8, 135.5 (7 s, arom. C and C-5); 129.2, 129.1, 128.5, 128.4, 128.1, 128.0, 127.7, 127.6, 126.2, 126.0 (10 d, arom. C); 112.7 (t, C-6); 110.1, 86.4 (2 s, C-1 and C-2); 48.4 (d, -*C*HAr_2); 43.6, 40.23, 40.17 (3 t, C-4 and 3-CH_2); 29.0 (d, C-3); 22.19, 22.15, 20.99, 20.93 (4 d, Me); 0.2 (q, $SiMe_3$). HRMS ($C_{25}H_{32}Si$): Calcd 360.2273; Found 360.2277.

3-(2,2-Bis(*p*-methylphenyl)ethyl)-5-methyl-1-(trimethylsilyl)hex-5-en-1-yne (5b). Benzhydryl chloride **3b**-Cl (0.26 g, 1.1 mmol), $TiCl_4$ (0.47 g, 2.5 mmol), **2a** (0.50 g, 1.2 mmol), (2-methylallyl)trimethylsilane (0.27 g, 2.1 mmol) and CAN (3.4 g, 6.2 mmol) were employed for the operations described in the General Procedure 1. The resulting yellowish oil was purified by column chromatography (silica gel, cyclohexane/Et_2O 9/1) to give 0.33 g (80%) **5b**.—MS (70 eV) *m/z* (%): 374 (M^+, 3), 319 (8), 317 (5), 208 (71), 195 (100), 165 (23), 73 (Me_3Si^+, 30). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15–7.05 (m, 8H, arom. H); 4.76, 4.70 (2 br s, 2×1H, 6-H); 4.26 (m_c, 1H, –C*H*Ar_2); 2.35–2.15 (m, 4H, 3-H, 4-H, 3-CH_2); 2.29, 2.27 (2 s, 6H, Me); 2.02–1.87 (m, 1H, 3-CH_2); 1.60 (s, 3H, 5-Me); 0.18 (s, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 142.7, 142.6 (2 s, 2×arom. C); 140.8 (s, C-5); 135.6, 135.4 (2 s, 2×arom. C); 129.1, 128.9, 128.0, 127.5 (4 d, 4×arom. C), 112.7 (t, C-6), 110.2, 86.1 (2 s, C-1 and C-2); 47.9 (d, -*C*HAr_2); 43.6, 40.3 (2 t, C-4 and 3-CH_2); 29.0 (d, C-3); 22.2 (q, 5-Me); 21.0, 20.9 (2q, ArMe); 0.24 (q, $SiMe_3$); signal assignments are based on ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY experiments. HRMS ($C_{26}H_{34}Si$): Calcd 374.2430; Found 374.2391.

3-(2-(*p*-Methoxyphenyl)-2-phenylethyl)-5-methyl-1-(trimethylsilyl)hex-5-en-1-yne (5c). Method A: Benzhydryl chloride **3c**-Cl (0.23 g, 0.99 mmol), $TiCl_4$ (0.46 g, 2.4 mmol), **2a** (0.41 g, 1.0 mmol), (2-methylallyl)trimethylsilane (0.26 g, 2.0 mmol) and CAN (2.75 g, 5.02 mmol)

were employed for the operations described in the General Procedure 1. The resulting yellowish oil was purified by column chromatography (silica gel, cyclohexane/Et_2O 9/1) to give 0.21 g (56%) **5c** (as a 1:1-mixture of diastereomers).

Method B: Benzhydryl chloride **3c**-Cl (0.16 g, 0.69 mmol), $TiCl_4$ (0.26 g, 1.4 mmol), **2d** (0.45 g, 0.70 mmol), (2-methylallyl)trimethylsilane (0.18 g, 1.4 mmol) and CAN (1.88 g, 3.43 mmol) were employed for the operations described in the General Procedure 1, however after the addition of (2-methylallyl)trimethylsilane, stirring was continued for 72 h at ambient temperature. The resulting yellowish oil was purified by column chromatography (silica gel, *n*-hexane/Et_2O 1/1) to give 182 mg (70%) **5c** (as a 1:1-mixture of diastereomers).—MS (70 eV) *m/z* (%): 376 (M^+, 5), 321 (12), 319 (7), 210 (95), 197 (100), 165 (15), 73 (Me_3Si^+,25). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–6.96 (m, 7H, arom. H); 6.82–6.77 (m, 2H, arom. H); 4.75, 4.68 (2 br s, 2×1H, 6-H); 4.30–4.23 (m, 1H, –C*H*Ar_2); 3.70/3.69 (s, 3H, OMe); 2.30–1.90 (m, 5H, 3-H, 4-H, and 3-CH_2); 1.57/1.56 (s, 3H, 5-Me); 0.17 (s, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 157.9, 144.1, 142.8, 137.5 (4 s, C-5 and arom. C); 129.1, 128.6, 128.5, 128.4, 128.1, 127.6, 126.2, 126.0, 113.9, 113.8 (10 d, arom. C); 112.7 (t, C-6); 110.1, 86.3 (2 s, C-1 and C-2); 55.22, 55.19 (2 q, OMe); 47.9 (d, -*C*HAr_2); 43.6, 40.4 (2 t, C-4 and 3-CH_2); 29.0 (d, C-3); 22.2 (q, 5-Me); 0.26 (q, $SiMe_3$). HRMS ($C_{25}H_{32}OSi$): Calcd 376.2222; Found 376.2221.

Reactions of the $Co_2(CO)_6$-complexes 2b and 2c with benzhydryl salts (general procedure 2)

In a Schlenk flask, triply evacuated, heated and flushed with Ar, the benzhydryl chlorides **3**-Cl were dissolved in CH_2Cl_2 (30 ml) and cooled to -78°C. After addition of $TiCl_4$ (2–3 equiv.) and 5 min stirring, a CH_2Cl_2 solution of the enyne complex (1 equiv.) was slowly added through a dropping funnel. The mixture was stirred at −78°C for 48 h, and was then allowed to warm at ambient temperature and hydrolyzed with a 1:1 mixture of Et_2O and aq. $NaHCO_3$. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3×20 ml). After drying the combined organic phases ($MgSO_4$) and evaporating the solvent in vacuo, the products were isolated as described individually.

5,5-Bis(*p*-methylphenyl)-3-phenyl-1-(trimethylsilyl)pent-3-en-1-yne (6b). Benzhydryl chloride **3b**-Cl (0.12 g, 0.52 mmol), $TiCl_4$ (0.20 g, 1.1 mmol), and **2b** (0.25 g, 0.51 mmol) were employed for the operations described in the General Procedure 2. The residue was dissolved in acetone (20 ml) and cooled to −30°C. Then CAN (1.43 g, 2.61 mmol) was added, and after 5 min stirring a mixture of water/Et_2O (v/v 1/1) was added. The organic layer was separated, and the aqueous phase was extracted with Et_2O (3×10 ml). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The resulting brownish oil was purified by column chromatography (silica gel, cyclohexane/Et_2O 9/1) to give 0.12 g (60%) **6b**.—MS (70 eV) *m/z* (%): 394 (M^+, 100), 321 (82), 305 (24), 229 (27), 73 (58). IR (KBr, cm^{-1}): 3021, 2960, 2922, 2138, 1629, 1508, 1441, 1250, 1067, 868, 858, 842, 761, 700. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.26 (m, 5H, Ph); 7.07, 6.99 (2 d, 2×4H, J_{AB}=8.0 Hz, arom. H); 6.58 (d, 1H, *J*=10.9 Hz, 5-H); 4.85 (d, 1H, *J*=10.9 Hz, 4-H); 2.29 (s, 6H, 2×Me); 0.15 (s, 9H, $SiMe_3$). HRMS ($C_{28}H_{30}Si$): Calcd 394.2117; Found 394.2123.

(5,5-Bis(*p*-methoxyphenyl)-3-phenyl-1-(trimethylsilyl)-pent-3-en-1-yne)dicobalt hexacarbonyl (6d-$Co_2(CO)_6$). Benzhydryl chloride **3d**-Cl (0.26 g, 0.99 mmol), $TiCl_4$ (0.38 g, 2.0 mmol), and **2b** (0.50 g, 1.0 mmol) were employed for the operations described in the General Procedure 2. The remaining red oil was purified by column chromatography (silica gel, cyclohexane/Et_2O 9/1) to give 0.48 g (68%) **6d-$Co_2(CO)_6$** (as a 4:1-mixture of stereoisomers).—IR (KBr, cm^{-1}): 3032, 3001, 2957, 2836, 2086, 2047, 2016, 1609, 1583, 1511, 1464, 1443, 1302, 1249, 1176, 1037, 842. ^{1}H NMR (300 MHz, d_6-acetone) δ 7.46–7.20 (m, 5H, arom. H); 7.09–7.01, 6.88–6.83 (2 m, 2×4H, arom. H); 6.77 (d, 1H, *J*=10.7 Hz, major compd); 6.67 (d, 1H, *J*=10.9 Hz, minor compd); 4.86 (d, 1H, *J*=10.7 Hz, 5-H minor compd); 4.52 (d, 1H, *J*=10.4 Hz, 5-H major compd); 3.74 (s, 6H, OMe); 0.23 (s, 9H, $SiMe_3$ major compd); 0.16 (s, 9H, $SiMe_3$ minor compd). ^{13}C NMR (75.5 MHz, d_6-acetone), major compd: δ 201.6 (s, CO); 159.3, 159.2, 141.2, 138.9 (4 s); 138.7 (d, C-4); 136.7 (s); 129.8, 129.7, 129.5, 129.4, 129.3, 129.2, 128.7, 114.7 (6 d); 55.4 (q, OMe); 49.9 (d, C-5); 0.6 (q, $SiMe_3$); additional signals of the minor compd: 159.3 (s); 142.9 (d, C-4); 130.0, 129.1, 128.8, 114.9 (4 d); 55.5 (q, OMe); 49.6 (d, C-5); 0.0 (q, $SiMe_3$); signal assignments are based on ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY experiments; due to slow relaxation, the signals of C-1 and C-2 were not detected.

3,5,5-Triphenyl-1-(trimethylsilyl)pent-3-en-1-yne (6e). Benzhydryl chloride **3e**-Cl (0.20 g, 0.99 mmol), $TiCl_4$ (0.39 g, 2.1 mmol), and **2b** (0.49 g, 1.0 mmol) were employed for the operations described in the General Procedure 2. The residue was dissolved in acetone (20 ml) and cooled to −30°C. Then CAN (2.75 g, 5.02 mmol) was added, and after 5 min stirring a mixture of water/Et_2O (v/v 1/1) was added. The organic layer was separated, and the aqueous phase was extracted with Et_2O (3×10 ml). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The residue was recrystallized to yield 0.19 g (52%) **6e** as colorless crystals.—Mp 156–157°C (hexane). MS (70 eV) *m/z* (%): 366 (M^+, 24), 289 (28), 167 (50), 154 (100), 136 (85), 107 (34), 89 (49), 77 (57), 73 (Me_3Si^+, 43). IR (KBr, cm^{-1}): 3081, 3059, 3023, 2960, 2898, 2140, 1596, 1491, 1450, 1367, 1251, 1084, 1060, 1026, 900, 866, 842, 776, 766, 752, 741. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.02 (m, 15H, Ph); 6.55 (d, 1H, *J*=10.9 Hz, 4-H); 4.85 (d, 1H, *J*=10.8 Hz, 5-H); 0.09 (s, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 143.6 (s, Ph); 141.1 (d, C-4); 136.9 (s, Ph); 128.63, 128.60, 128.4, 128.3, 127.8, 126.6 (6 d, Ph); 123.9 (s, C-3); 106.5, 93.2 (2 s, C-1 and C-2); 50.2 (d, C-5); 0.0 (q, $SiMe_3$).

6-(Bis(*p*-methylphenyl)methyl)-1-ethinyl-cyclohexene (7). Benzhydryl chloride **3b**-Cl (248 mg, 1.08 mmol), $TiCl_4$ (0.32 g, 1.7 mmol), and **2c** (0.50 g, 1.3 mmol) were employed for the operations described in the General Procedure 2. The residue was dissolved in acetone (20 ml) and cooled to −30°C. Then CAN (2.7 g, 4.9 mmol) was added, and after 5 min stirring a mixture of water/Et_2O (v/v 1/1) was added. The organic layer was separated, and the

Table 3. Crystallographic data and parameters of the crystal structure determinations

Compound	**2d**	**6e**
Empirical formula	$C_{30}H_{27}Co_2O_5PSi$	$C_{26}H_{26}Si$
Fw	644.44	366.56
Crystal size (mm)	0.53×0.30×0.20	0.57×0.57×0.17
Crystal system	monoclinic	monoclinic
Space group	*P*21	$P2_1/n$
a (Å)	8.840(2)	10.729(2)
b (Å)	16.154(3)	6.286(2)
c (Å)	11.038(2)	32.650(10)
β (°)	98.57(2)	94.68(2)
V (Å^3)	1558.6(5)	2194.7(10)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.373	1.109
μ (mm^{-1})	1.189	0.114
F(000)	600	784
Temperature (K)	293(2)	293(2)
θ range (degrees)	2.25–22.98	2.78–22.55
Index ranges	$0\le h\le 9$	$0\le h\le 11$
	$-17\le k\le 17$	$-6\le k\le 0$
	$-12\le l\le 11$	$-35\le l\le 35$
No. of reflns measd	4045	3068
No. of indep reflns with $I>2\sigma(I)$	3492	2888
No. of parameters	366	247
*R*1 (obs. data)	0.0458	0.0755
*wR*2 (obs. data)	0.1394	0.1710
*R*1 (all data)	0.0501	0.1318
*wR*2 (all data)	0.1440	0.2026
GooF on F^2	1.148	1.086
Resid. Electron density (eÅ^{-3})	+1.212/−0.365	+0.264/−0.278

aqueous phase was extracted with Et_2O (3×10 ml). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The residue was recrystallized to yield 0.28 g (86%) **7** as a yellow powder.—Mp 112–113°C (Et_2O). MS (70 eV) *m*/*z* (%): 300 (M^+, <1), 195 (100), 165 (8). ^{1}H NMR (300 MHz, d_6-acetone) δ 7.27–7.17, 7.09–7.03 (2 m, 2×4H, arom. H); 6.19 (m_c, 1H, 2-H); 4.42 (d, 1H, *J*=7.2 Hz, –C*H*Ar$_2$); 3.12–3.05 (m, 1H, 6-H); 3.01 (s, 1H, –C≡CH); 2.27 (s, 6H, Me); 2.08–2.01 (m, 2H, covered by solvent signal); 1.70–1.54 (2m, 2×2H, 2×CH_2). ^{13}C NMR (75.5 MHz, d_6-acetone) δ 142.1, 141.2 (2 s, arom. C); 138.7 (d, C-2); 136.0, 135.9 (2 s, arom. C); 129.7, 129.6, 129.5, 129.3 (4 d, arom. C); 125.0 (s, C-1); 85.6 (s, -*C*≡CH); 77.8 (d, –C≡*C*H); 54.1 (d, -*C*HAr$_2$); 41.6 (d, C-6); 26.1, 25.8 (2 t, 2×CH_2); 20.9 (q, Me); 19.1 (t, CH_2). HRMS ($C_{23}H_{24}$): Calcd 300.1878; Found 300.1875.

4a-Ethinyl-9-(*p*-methoxyphenyl)-6-methyl-2,3,4,4a,9,9a-hexahydro-1*H*-fluorene (9). Benzhydryl chloride **3f**-Cl (1.05 g, 4.26 mmol), BCl_3 (1.11 g, 9.47 mmol), and **2c** (2.00 g, 5.10 mmol) were employed for the operations described in the General Procedure 2. The residue was dissolved in acetone (20 ml) and cooled to −30°C. Then CAN (7.0 g, 13 mmol) was added, and after 5 min stirring a mixture of water/Et_2O (v/v 1/1) was added. The organic layer was separated, and the aqueous phase was extracted with Et_2O (3×10 ml). The combined organic phases were dried ($MgSO_4$), and the solvent was evaporated in vacuo. The remaining yellow oil was purified by column chromatography (silica gel, n-hexane/Et_2O 1/1) to give 0.86 g (64%) **9**.—MS (70 eV) *m*/*z* (%): 316 (M^+, 100), 301 (12), 273 (15), 259 (45), 184 (19). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (br s, 1H, 5-H); 7.12–7.08 (m, 2H, anisyl-H); 6.96 (br d, 1H, *J*=7.6 Hz, 7-H); 6.86–6.83 (m, 2H, anisyl-H); 6.76 (d, 1H, *J*=7.7 Hz, 8-H); 4.05 (d, 1H, *J*=11.6 Hz, 9-H); 3.79 (s, 3H, OMe); 2.47 (dd with fine coupling, 1H, *J*=11.4 Hz, 4.7 Hz, 9a-H); 2.36 (s, 3H, Me); 1.93–1.33 (m, 8H, 4×CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 158.4, 149.4, 141.4, 136.8, 134.7 (5 s, arom. C); 129.9 (d, anisyl-C); 128.0 (d, C-7); 125.2 (d, C-8); 123.0 (d, C-5); 113.8 (d, anisyl-C); 88.9 (s, –*C*≡CH); 69.2 (d, –C≡*C*H); 56.7 (d, C-9a); 55.2 (q, OMe); 49.5 (d, C-9); 44.4 (s, C-4a); 36.3 (t, CH_2); 22.5 (t, CH_2); 22.0 (t, CH_2); 21.3 (q, Me); 20.9 (t, CH_2); signal assignments are based on ^{1}H,^{1}H- and ^{1}H,^{13}C-COSY experiments. HRMS ($C_{23}H_{24}O$): Calcd 316.1827; Found 316.1831.

(5-Methoxy-3,5-diphenyl-1-(trimethylsilyl)pent-3-en-1-yne)dicobalt hexacarbonyl (11). Acetal **10** (0.28 g, 1.8 mmol), $TiCl_4$ (0.35 g, 1.8 mmol), **2b** (0.49 g, 1.0 mmol) were employed for the operations described in the General Procedure 2. The remaining red oil was purified by column chromatography (silica gel, cyclohexane/Et_2O 30/1) to give 0.41 g (68%) **11** as a mixture of diastereomers.—MS (70 eV) *m*/*z* (%): 606 (M^+, <1), 578 (3), 522 (8), 494 (21), 438 (32), 392 (12), 334 (21), 320 (77), 290 (100), 217 (43), 216 (45), 215 (49), 121 (94), 105 (33), 73 (59). IR (KBr, cm^{-1}): 3030, 2928, 2821, 2088, 2049, 2018, 1629, 1561, 1448, 1249, 1084, 839, 700, 516. ^{1}H NMR (300 MHz, d_6-acetone) δ 7.56–7.15 (m, 10H, 2×Ph); 6.36 (m_c, 1H, 4-H); 4.58 (m_c, 1H, 5-H); 3.25 (s, 3H, OMe); 0.22 (q, 9H, $SiMe_3$). ^{13}C NMR (75.5 MHz, d_6-acetone), major compd: δ 200.8 (s, CO); 142.3, 142.0, 140.9 (3 s, arom. C and C-3); 136.1 (d, C-4); 129.5, 129.4, 129.2, 128.8, 128.4, 127.3 (6 d, arom. C); 80.9 (d, C-5); 56.2 (q, OMe); 0.6 (q, $SiMe_3$); due to slow relaxation, the signals of C-1 and C-2 were not detected; additional signals of the minor compd: 143.0; 142.5 (2 s); 129.4, 129.3, 128.4, 128.1, 127.5, 127.2 (6 d); 82.4 (d, C-5); 57.1 (q, OMe); 0.3 (q, $SiMe_3$).

X-Ray crystallography

Data for the crystal structure determinations were collected on a Nonius ENRAF-CAD4 diffractometer. The SHELXS86 software was used to determine the structures, and the refinement was performed using the SHELXS93 software. The results of the crystal structure determinations and the crystallographic data of **2d** and **6e** are summarized in Table 3.[30]

Kinetics

Solutions of the benzhydryl cations **3** were obtained by slow addition of the corresponding chlorides **3**-Cl to a solution of the Lewis acid ($TiCl_4$ or BCl_3) in dichloromethane. The consumption of the cations **3** after the addition of the cobalt enyne complexes **2** was followed photometrically in the range of λ=460–490 nm by using fiber optics and the workstation described in Ref. 14. Calibration curves, i.e. the correlation between absorbance and the concentration of the benzhydryl cations **3**, were obtained by adding the chlorides **3**-Cl to a solution of excess $TiCl_4$ or BCl_3 in dichloromethane and determination of the absorbance after ionization of each portion. Because the absorbance at the monitored wavelenghts did not disappear completely,

Table 4. Kinetics of the reactions of the $Co_2(CO)_6$-enyne-complex **2a** with the benzhydryl cations **3a–c** (in CH_2Cl_2)

Electrophile	T/°C	c_o(**3**)/mol L^{-1}	c_o(**2a**)/mol L^{-1}	$c_o(TiCl_4)$/mol L^{-1}	Conversion/%	k/L mol^{-1} s^{-1}
3a	−25.8	1.42×10^{-5}	3.22×10^{-4}	5.88×10^{-3}	60	263
	−46.7	2.15×10^{-5}	6.52×10^{-4}	5.96×10^{-3}	93	99.1
	−53.6	2.06×10^{-5}	1.25×10^{-3}	5.69×10^{-3}	69	64.7
	−61.2	2.35×10^{-5}	1.42×10^{-3}	6.51×10^{-3}	90	39.9
	−71.5	3.28×10^{-5}	1.16×10^{-3}	5.28×10^{-3}	86	18.4
3b	0.3	1.68×10^{-5}	7.77×10^{-4}	6.52×10^{-3}	60	64.2
	−5.1	3.25×10^{-5}	1.51×10^{-3}	6.33×10^{-3}	89	38.9
	−10.0	3.58×10^{-5}	1.66×10^{-3}	6.97×10^{-3}	79	29.0
	−18.6	3.81×10^{-5}	8.82×10^{-4}	7.40×10^{-3}	79	17.2
	−29.7	4.24×10^{-5}	2.62×10^{-3}	5.50×10^{-3}	63	9.98
	−50.8	5.83×10^{-5}	3.60×10^{-3}	7.56×10^{-3}	62	1.69
3c	20.0	2.84×10^{-5}	1.29×10^{-3}	5.89×10^{-3}	68	9.41
	20.2	3.02×10^{-5}	6.87×10^{-4}	6.28×10^{-3}	55	8.48

Table 5. Kinetics of the reactions of the $Co_2(CO)_6$-enyne-complex **2b** with the benzhydryl cation **3c** (in CH_2Cl_2)

T/°C	c_o(**3c**)/mol L^{-1}	c_o(**2b**)/mol L^{-1}	$c_o(TiCl_4)$ /mol L^{-1}	Conversion/%	k/L mol^{-1} s^{-1}
−4.5	1.94×10^{-5}	2.82×10^{-4}	1.32×10^{-2}	30	634
−14.7	2.01×10^{-5}	2.90×10^{-4}	1.39×10^{-2}	75	361
−25.6	2.11×10^{-5}	3.06×10^{-4}	3.59×10^{-3}	83	270
−37.1	1.70×10^{-5}	4.94×10^{-4}	7.88×10^{-3} [a]	93	186
−38.5	1.65×10^{-5}	1.60×10^{-4}	1.50×10^{-2}	85	173
−49.5	2.22×10^{-5}	4.85×10^{-4}	3.87×10^{-2} [a]	86	106
−60.8	2.01×10^{-5}	3.66×10^{-4}	6.87×10^{-3}	89	52.1

[a] BCl_3 was employed instead of $TiCl_4$.

Table 6. Kinetics of the reactions of the $Co_2(CO)_6$-enyne-complex **2c** with the benzhydryl cations **3b**, **3c** and **3f** (in CH_2Cl_2)

Electrophile	T/°C	c_o(**3**)/mol L^{-1}	c_o(**2c**)/mol L^{-1}	$c_o(TiCl_4)$/mol L^{-1}	Conversion/%	k/L mol^{-1} s^{-1}
3b	−20.6	7.30×10^{-6}	3.03×10^{-4}	5.68×10^{-3}	80	463
	−33.4	1.35×10^{-5}	5.60×10^{-4}	5.24×10^{-3}	78	281
	−50.6	3.45×10^{-5}	7.16×10^{-4}	6.72×10^{-3}	89	81.0
	−58.6	2.72×10^{-5}	1.13×10^{-3}	5.28×10^{-3}	90	56.9
	−65.2	3.04×10^{-5}	6.31×10^{-4}	5.92×10^{-3}	84	36.9
3c	21.5	1.76×10^{-5}	1.27×10^{-3}	5.97×10^{-3}	86	45.8
	12.1	4.31×10^{-5}	1.56×10^{-3}	7.32×10^{-3}	92	28.4
	−0.3	4.67×10^{-5}	8.44×10^{-4}	7.92×10^{-3}	75	17.3
	−7.0	3.62×10^{-5}	1.67×10^{-3}	5.98×10^{-3}	71	11.0
	−18.4	3.28×10^{-5}	1.51×10^{-3}	5.42×10^{-3}	80	7.60
	−20.6	4.03×10^{-5}	1.46×10^{-3}	6.58×10^{-3}	89	7.99
	−30.0	4.65×10^{-5}	1.43×10^{-3}	5.13×10^{-3}	95	4.18
	−46.7	2.93×10^{-5}	1.35×10^{-3}	4.97×10^{-3}	81	2.21
	−65.5	2.99×10^{-5}	1.38×10^{-3}	5.08×10^{-3}	87	0.522
3f	25.0	2.62×10^{-5}	1.41×10^{-3}	5.29×10^{-3}	63	24.3
	12.1	3.71×10^{-5}	9.36×10^{-4}	5.00×10^{-3}	73	10.7
	3.2	2.40×10^{-5}	1.29×10^{-3}	4.85×10^{-3}	62	6.73
	−0.5	4.39×10^{-5}	1.11×10^{-3}	5.92×10^{-3}	85	5.57
	−6.5	3.75×10^{-5}	1.35×10^{-3}	5.06×10^{-3}	91	4.47
	−17.5	6.00×10^{-5}	1.62×10^{-3}	6.07×10^{-3}	92	2.18
	−22.3	5.23×10^{-5}	1.41×10^{-3}	5.29×10^{-3}	90	1.71

Table 7. Kinetics of the reactions of the $Co_2(CO)_5(PPh_3)$-enyne-complex **2d** with the benzhydryl cation **3c** (in CH_2Cl_2)

T/°C	c_o(**3c**)/mol L^{-1}	c_o(**2d**)/mol L^{-1}	$c_o(TiCl_4)$ /mol L^{-1}	Conversion/%	k/L mol^{-1} s^{-1}
20.0	1.98×10^{-5}	1.93×10^{-4}	3.46×10^{-2} [a]	33	17.6
11.5	2.52×10^{-5}	1.94×10^{-4}	3.41×10^{-3}	78	10.1
10.6	2.53×10^{-5}	1.97×10^{-4}	6.91×10^{-3}	86	9.40
1.3	2.34×10^{-5}	1.82×10^{-4}	1.31×10^{-2} [a]	82	4.63
−12.3	2.13×10^{-5}	2.07×10^{-4}	7.28×10^{-3}	84	1.85
−21.4	2.13×10^{-5}	2.07×10^{-4}	7.40×10^{-3} [a]	81	1.08

[a] BCl_3 was employed instead of $TiCl_4$.

the rate constants k_{obs} were obtained from $k_{obs}t = \ln(A_t - A_{end}) — \ln(A_0 - A_{end})$.

The initial concentrations of the reactants and the second-order rate constants k_2 from kinetic measurements at different temperatures are displayed in Tables 4–7.

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30. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-142331 for **2d** and no. CCDC-142332 for **6e**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).