The Role of [η^2-Bis(*tert*-butylsulfonyl)acetylene](carbonyl)(η^5-cyclopentadienyl)cobalt(I) as an Intermediate in the Alkyne Dimerisation

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Dedicated to Prof. Dr. Günter Helmchen on the occasion of his 65th birthday

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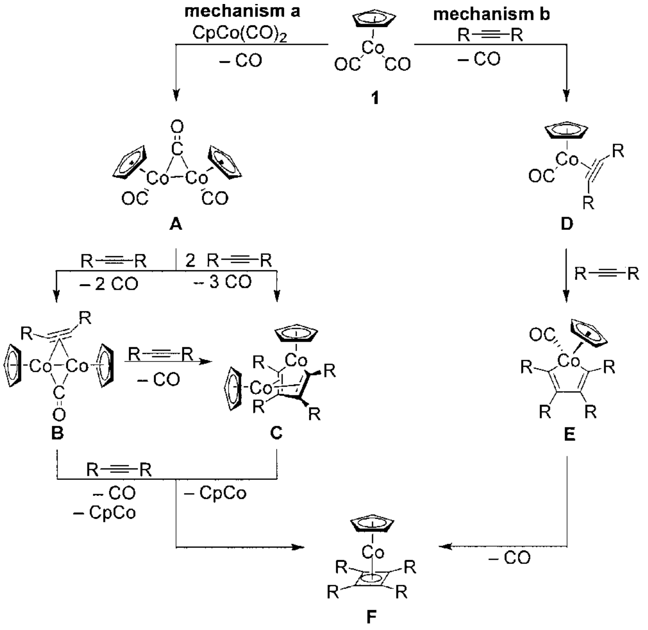
Dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (**1**) reacts with the electron-poor alkyne bis(*tert*-butylsulfonyl)acetylene to give the corresponding cyclobutadiene complex **6**, whereas the reaction of [CpCo(CO)$_2$] with dimethyl acetylenedicarboxylate yields the cyclopentadienone complex **7** under the same conditions. The cyclobutadiene complex **6** could not be obtained by the treatment of [η^2-bis(*tert*-butylsulfonyl)acetylene](carbonyl)(η^5-cyclopentadienyl)cobalt(I) [**3(H)**] with an excess of bis(*tert*-butylsulfonyl)acetylene. The same holds for the treatment of **3(H)** with dimethyl acetylenedicarboxylate and bis(catecholatoboryl)acetylene. With these results we assume that the monoalkyne complex **3(H)** is not an intermediate in the alkyne oligomerisation of electron-poor alkynes, as was shown for electron-rich ones.

Introduction

The CpCo^{I}-mediated dimerisation of alkynes to cyclobutadiene (cbd) complexes is a well-known reaction.[1–4] There are two suggested mechanisms in the literature for the formation of these complexes, one by Brintzinger et al.[5,6] and the other based on work by Bergman, Vollhardt, Yamazaki and others.[6,7] Both mechanisms are shown in Scheme 1.



Scheme 1. Abridged version of mechanisms to rationalize the formation of cyclobutadiene CpCo complexes according to Brintzinger et al. (**a**) and based on the work by Bergman, Vollhardt, Yamazaki and others (**b**).

Brintzinger assumed that the reaction of two equivalents of dicarbonyl(η^5-cyclopentadienyl)cobalt(I) {[CpCo(CO)$_2$], **1**} leads to complex **A**, which can form complexes **B** and **C** by the reaction with alkynes (mechanism **a** in Scheme 1). These intermediates have been isolated and characterised.[6,8] The cyclobutadiene (cbd) complex **F** can arise from both precursors. The second mechanism (**b** in Scheme 1) involves intermediates with only one cobalt nucleus. Complex **1** yields a monoalkyne complex **D** by loss of one CO ligand and subsequent reaction with one equivalent of alkyne. Addition of another alkyne forms the cobaltol species **E**.[9] Dissociation of the second CO unit and subsequent reductive elimination gives the cbd complexes **F**. The second mechanism has also been investigated by theoretical means.[10–12] The first experimental evidence of a monoalkyne species **D** was provided by Brintzinger by means of IR spectroscopy.[5] Later, Krebs et al. were able to isolate the first monoalkyne complex **2** by reaction of 3,3,6,6-tetramethyl-1-thiacycloheptyne[13] with [CpCo(CO)$_2$] (Scheme 2).[14]

The second class of complexes of type **D** were synthesised in our laboratory by the reaction of bis(*tert*-butylsulfonyl)acetylene[15] with [CpRCo(CO)$_2$] derivatives.[16] The

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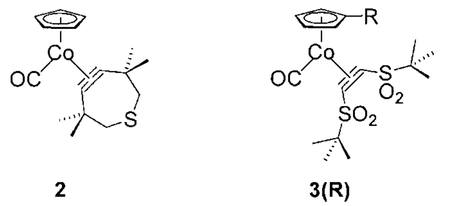
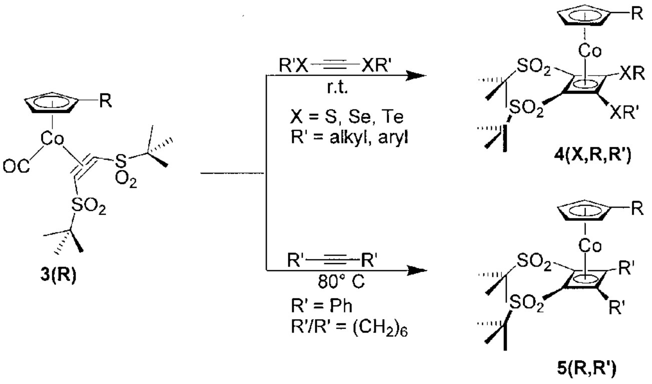


Scheme 2. Isolated monoalkyne Co^I complexes.

obtained complexes **3(R)** (Scheme 2) were treated with different alkynes to yield the corresponding cyclobutadiene complexes, as shown in Scheme 3.[17–19]

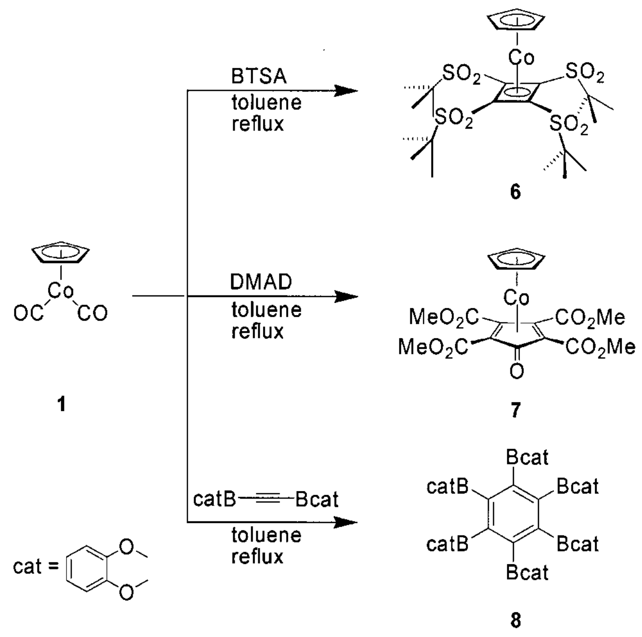


Scheme 3.

We showed that the electrophilic complexes **3(R)** react readily with electron-rich alkynes at room temperature to the corresponding cyclobutadiene complexes **4(X,R,R′)** in good yields. The reaction with alkynes that have no strong donor substituents, for example diphenylacetylene or cyclooctyne, needs higher temperatures to form the complexes **5(R,R′)**. These experiments provide strong evidence that the monoalkyne complexes **3(R)** are intermediates in the cyclobutadiene formation. In this paper we present the reactions of electron-poor alkynes with $[CpCo(CO)_2]$ and **3(H)**.

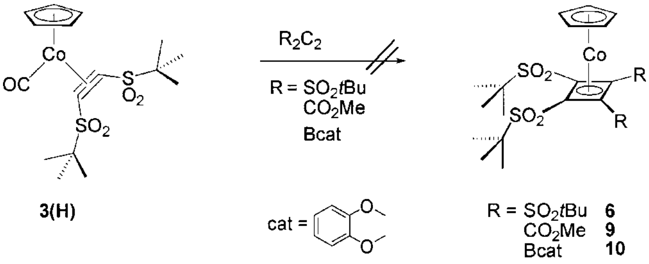
Results and Discussion

As electron-poor alkynes we chose bis(*tert*-butylsulfonyl)acetylene (BTSA) and dimethyl acetylenedicarboxylate (DMAD). They react quite differently towards $[CpCo(CO)_2]$ in refluxing toluene. As shown in Scheme 4, BSTA forms the cbd complex **6** in 19% yield in refluxing toluene, whereas the reaction of **1** with an excess of DMAD gives the cyclopentadienone complex **7** (5% yield). A further electron-poor alkyne derivative, bis(catecholatoboryl)acetylene (BCBA),[20] yielded the hexakis-substituted benzene derivative **8** with **1**.[21]



Scheme 4.

Following our previous studies, we reacted the monoalkyne complex **3(H)** with BTSA, DMAD, and BCBA by heating **3(H)** and the corresponding alkynes in toluene. The anticipated products were not obtained (Scheme 5).



Scheme 5.

These results suggest that the nucleophilic monoalkyne complex **3(H)** is not an intermediate in the alkyne oligomerisation for electron-poor alkynes, as postulated in mechanism **b** (Scheme 1), and it seems more likely that this reaction has dinuclear Co^I intermediates, in analogy to the Brintzinger mechanism (cf. Scheme 1).[5,6]

Structural Investigations

In the case of **6** we were able to obtain single crystals which were investigated by X-ray techniques. Figure 1 shows the molecular structure of **6** (Table 1).

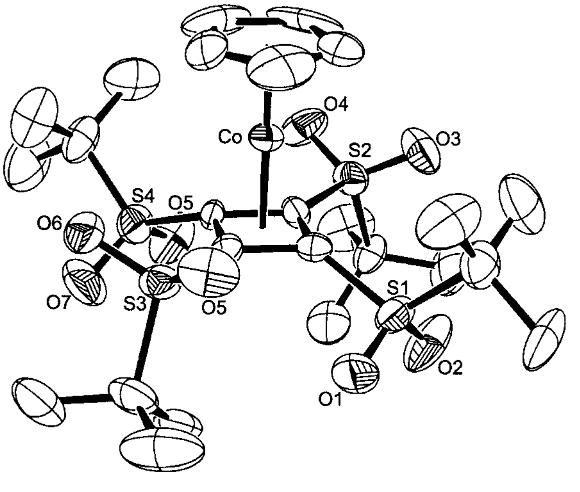


Figure 1. Molecular structure of **6** (ORTEP plot; thermal ellipsoids at 50% probability level; H atoms have been omitted for clarity).

Table 1. Selected bond distances and angles in the molecular structure of **6**.

d(C–C) Cbd [pm]	d(Cp$_{centre}$–Co) [pm]	d(Co$_{centre}$–Cbd) [pm]	α (CpCoCbd) [°]
145	168	169	2.3
147			
145			
147			

Two opposite *tert*-butyl groups point away from the cyclopentadiene ring, whereas the other two groups point towards the Cp ring. This conformation reduces the steric strain and the overall dipole moment of the molecule arising from the sulfonyl groups. The two ring ligands are nearly parallel to each other (2.3° distortion). No bond alternation is found within the cyclobutadiene ring.

Conclusions

The products obtained from the reaction of [CpCo(CO)$_2$] and electron-poor alkynes are highly dependent on the electronic properties of the alkynes. The BTSA monoalkyne complex **3(H)** is not an intermediate in the cyclobutadiene formation with electron-poor alkynes, whereas it is with electron-rich ones.

Experimental Section

Starting Materials: Dicarbonyl(η^5-cyclopentadienyl)cobalt(I),[22] and bis(*tert*-butylsulfonyl)acetylene[11] were prepared according to literature methods. Dimethyl acetylenedicarboxylate (98%) was purchased from ACROS.

General Remarks: All melting points are uncorrected. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. UV absorption data were recorded with a Hewlett–Packard 8452A spectrometer. IR spectra were recorded with a Bruker Vector 22. The NMR spectra were measured with a Bruker Avance 500 spectrometer (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz) using the solvent as internal standard (δ). FAB mass spectra refer to data from a Jeol JMS-700 instrument. *m*-Nitrobenzyl alcohol was used as the matrix for the FAB experiments. All reactions were carried out in dry glassware under argon in dry, oxygen-free solvents.

[η^4-Tetrakis-(*tert*-butylsulfonyl)cyclobutadiene](η^5-cyclopentadienyl)cobalt(I) (6): Dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (200 mg, 1.1 mmol) and bis(*tert*-butylsulfonyl)acetylene (BTSA; 700 mg, 2.6 mmol) were dissolved in toluene (40 mL) and the mixture was stirred for 5 h at 120 °C. The product was purified by column chromatography (SiO$_2$, *n*-hexane/diethyl ether). Yield: 129 mg (19%) of a yellow solid (dec. 167 °C). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.56 (s, 36 H, CH$_3$), 5.73 (s, 5 H, CH) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 25.3 [C(CH$_3$)$_3$], 65.2 [C(CH$_3$)$_3$], 82.2 (Cbd-C), 89.1 (Cp-C) ppm. MS (FAB+): m/z (%) = 679 [M + Na]$^+$, 656 [M$^+$], 583 [M – *t*BuO]$^+$. IR (KBr): $\tilde{\nu}$ = 2978, 2934, 1311, 1189, 1129 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 254 nm (4.36), 304 (4.12), 334 (3.73), 352 (3.65), 388 (3.25). HRMS (FAB+): calcd. for $C_{25}H_{41}CoO_8S_4$ [M$^+$] 656.0989; found 656.1016; calcd. for $C_{25}H_{41}CoNaO_8S_4$ [M$^+$ + Na] 679.0896; found 679.0914. $C_{25}H_{41}CoO_8S_4$: calcd. C 59.77, H 8.13, S 11.00; found, C 59.65, H 8.08, S 10.98.

(η^5-Cyclopentadienyl)[η^4-2,3,4,5-tetrakis(methoxycarbonyl)cyclopentadienone]cobalt(I) (7): Dicarbonyl(η^5-cyclopentadienyl)cobalt(I) (2.0 mg, 11.0 mmol) and dimethyl acetylenedicarboxylate (DMAD; 700 mg, 2.6 mmol) were dissolved in toluene (40 mL) and the mixture was stirred for 5 h at 120 °C. The product was purified by column chromatography (SiO$_2$, *n*-hexane/diethyl ether and diethyl ether/methanol). Yield: 212 mg (5%) of a red solid (m.p. 112 °C). ^{1}H NMR (500 MHz, CH$_3$OD): δ = 3.82 and 3.85 (s, 6 H, CO$_2$CH$_3$), 5.41 (s, 5 H, Cp-CH) ppm. ^{13}C NMR (125 MHz, CH$_3$OD): δ = 53.5 (CO$_2$$CH_3$), 54.2 (CO$_2$$CH_3$), 72.0 (Cpd-C), 84.4 (Cpd-C), 88.2 (Cp-C), 156.1 (Cpd-CO), 165.5 (CO$_2$CH$_3$), 166.2 (CO$_2$CH$_3$) ppm. MS (FAB+): m/z (%) = 459 [M + Na]$^+$, 437 [M + H]$^+$, 436 [M$^+$]. IR (KBr): $\tilde{\nu}$ = 2955, 1733, 1634, 1447, 1234 cm^{-1}. UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 264 nm (4.03), 300 (4.01), 374 (3.49), 430 (2.97). HRMS (FAB+): calcd. for $C_{18}H_{18}CoO_9$ [M + H]$^+$ 437.0282; found 437.0256; calcd. for $C_{18}H_{17}O_9CoNa$ [M + Na]$^+$ 459.0102; found 459.0085.

X-ray Diffraction Analyses: The reflections of **6** were collected with a Syntex R3 diffractometer (Mo-K_α radiation, graphite monochromator). Intensities were corrected for Lorentz and polarisation effects, and an empirical absorption correction (psi-scans) was applied. The structure was solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were calculated according to stereochemical aspects. Structure solution and refinement were carried out with the SHELXTL-PLUS (5.10) software package.[23] ORTEP drawings were obtained using the ORTEP-3 program for Microsoft Windows® by Farrugia.[24] Table 2 contains the crystallographic data and details of the data collection and refinement procedure.

CCDC-269077 (for **6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 2. Structural data of **6**.

	6
Empirical formula	$C_{25}H_{41}CoO_8S_4$
Formula weight	656.792
Crystal system	monoclinic
Space group	$P2_1/n$
Z	4
a [Å]	11.261(9)
b [Å]	19.086(11)
c [Å]	14.223(7)
β [°]	91.21(5)
V [Å^3]	3056(3)
$D_{\text{calcd.}}$ [g cm^{-3}]	1.43
μ [mm^{-1}]	0.878
Crystal shape	cube
Crystal size [mm^3]	$0.40 \times 0.40 \times 0.30$
Temperature [K]	293
Θ [°]	1.8 to 24.1
Index ranges	$0 \le h \le 12$ $0 \le k \le 21$ $-16 \le l \le 16$
Reflections collected	4829
Independent reflections	4829
Observed reflections [$I > 2\sigma(I)$]	2861
Max. and min. transmission	1.00, 0.92
Parameters	357
Goodness-of-fit on F^2	1.08
Final R indices [$I > 2\sigma(I)$]	
R_1	0.085
wR_2	0.129
$(\Delta\rho)_{\text{max.}}$ $(\Delta\rho)_{\text{min.}}$ [e Å^{-3}]	0.46, –0.37

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