Reactivity of the [η^2-Bis(*tert*-butylsulfonyl)acetylene](carbonyl)(η^5-cyclopentadienyl)cobalt Complex Towards Electron-Rich and -Poor Acetylenes

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

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The electron-rich aminoacetylenes Et_2NC_2R (**2a**–**c**, R = SPh, PPh_2, and Ph, respectively) react smoothly with [η^2-bis(*tert*-butylsulfonyl)acetylene](carbonyl)(η^5-cyclopentadienyl)cobalt (**1**) to form the donor–acceptor stabilized (η^4-cyclobutadiene)cobalt complexes **3a**–**c** in good yields. However, treatment of the electron-poor borylacetylenes **2d**–**f** with the cobalt complex **1** does not lead to the expected (η^4-cyclobutadiene)cobalt complexes. Analogously, the reaction of bis(1-phenylethynyl)sulfide (**2g**) with two equivalents of **1** gives rise to the sulfur-bridged bis[η^4-(cyclobutadiene)cobalt] complex **3g**. The new cobalt complexes were characterized by NMR spectroscopy, mass spectrometry, and by X-ray structure analysis for **3a**, which reveals almost equal C–C bond lengths within the cyclobutadiene ring.

Introduction

Di(carbonyl)(η^5-cyclopentadienyl)cobalt [$CpCo(CO)_2$] is a very convenient and efficient reagent for the di- and trimerization of alkynes.[1] The CpCo-supported oligomerization of unsymmetrical alkynes generally leads to isomers, which is one of the major disadvantages of that reaction. This might be overcome if oligomerization could be carried out in a stepwise fashion. Lee and Brintzinger[2] have been able to demonstrate by means of IR spectroscopy that, on irradiation of [$CpCo(CO)_2$] in the presence of diphenylacetylene, a new complex with only one CO ligand must be present. In order to contribute to the clarification of the mechanism of dimerization and trimerization of alkynes, Krebs et al.[3,4] reported the first generation of a mono(alkyne)cobalt complex by reacting the highly strained alkyne 3,3,6,6-tetramethyl-1-thiacycloheptyne[3] with [$CpCo(CO)_2$]. More recently, Gleiter et al.[5] have synthesized the mono(alkyne)cobalt complex **1** by the replacement of one of the carbonyl groups in di(carbonyl)(η^5-cyclopentadienyl) cobalt with bis(*tert*-butylsulfonyl)acetylene,[6] which was found to be a strong electrophile. In the course of their study, a large number of electron-rich, chalcogen-substituted acetylenes as well as alkyl- and aryl-substituted acetylenes were allowed to react with **1** to form a new class of stable (cyclobutadiene)cobalt complexes.[7] They found that the more electron-rich acetylenes react faster with **1** under mild conditions, whereas carbon-substituted acetylenes require heating to initiate the reactions. We have studied electron-poor borylacetylenes with respect to oligomerization and therefore tested the possibility whether electron-poor acetylenes can react with **1** under drastic conditions. Furthermore, we were interested to find out whether other heteroatom-substituted acetylenes (such as nitrogen and phosphorus) are also able to act in the same way as chalcogen-substituted alkynes. In this paper, we will address the scope and limitations of the replacement of the CO group in **1** by the triple bonds of the electron-rich and -poor acetylenes.

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Results and Discussion

Treatment of Cobalt Complex 1 with Electron-Rich and -Poor Acetylenes

The reactions between the cobalt complex **1** and the electron-rich aminoacetylenes **2a**–**c** were carried out in toluene at room temperature to afford the (η^4-cyclobutadiene)cobalt complexes **3a**–**c**, respectively, in good yields (Scheme 1). On the other hand, reactions of the cobalt complex **1** with the "push-pull" 1-boryl-2-aminoacetylene **2d** as well as electron-poor borylacetylenes **2e** and **2f** in refluxing

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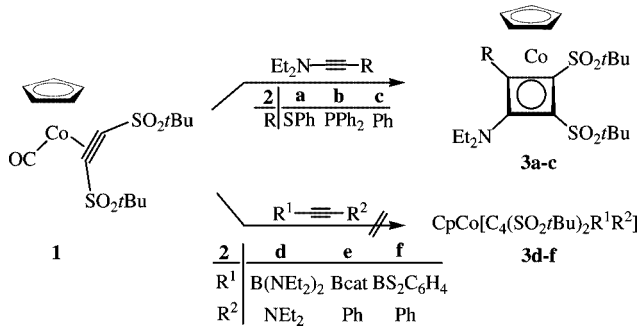
toluene were unsuccessful, and only the starting materials were recovered from the reaction mixtures. This indicates that electron-poor borylacetylenes have no tendency to react with the powerful electrophile **1**, even when applying drastic reaction conditions.



Scheme 1.

The cobalt complexes were isolated by column chromatography on silica gel and characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and by X-ray structure analysis for **3a**. The ^{1}H NMR spectra of **3a**–**c** show two singlets in the region δ = 1.2–1.5 ppm for the *tert*-butyl groups in addition to the Cp resonance (δ = 5.0–5.3 ppm). In general, the characteristic feature of the ^{13}C NMR spectra is the chemical shift of the cyclobutadiene ring atoms, which have values of between δ = 75 and 85 ppm.[7a–7c] However, compounds **3a**,**b** exhibit low-field resonances (δ = 55–75 ppm) for the cyclobutadiene ring atoms. In the ^{13}C NMR spectra of **3a**–**c**, the signals for C_5H_5 (δ = 82–84 ppm) were detected along with the aryl carbon atoms (δ = 125.0–138.9 ppm). EI-MS data confirmed the formation of complexes **3a**–**c** by the appearance of the molecular-ion peaks with the expected isotopic pattern.

The molecular structure of the mononuclear (cyclobutadiene)cobalt complex **3a** is shown in Figure 1. In the solid-state, **3a** crystallizes with toluene. The conformation is highly influenced by the bulky *tert*-butylsulfonyl groups, which point away from the metal center, as does the phenyl group bound to the sulfur atom. This behavior allows an almost parallel orientation of the C_5 and C_4 rings. The space group ($P2_1/c$) of complex **3a** clearly indicates the presence of a racemic mixture.

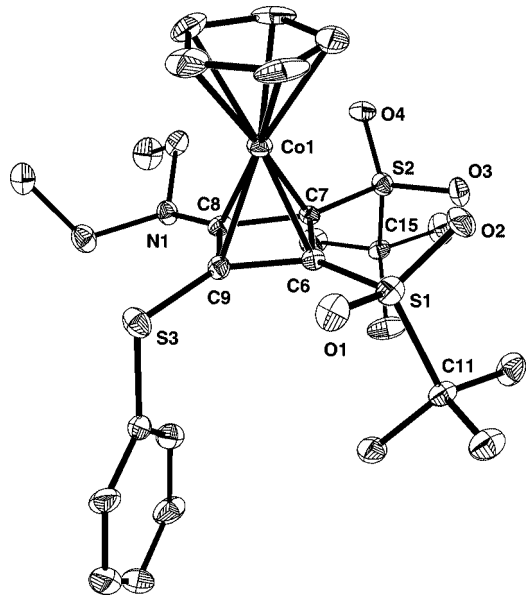
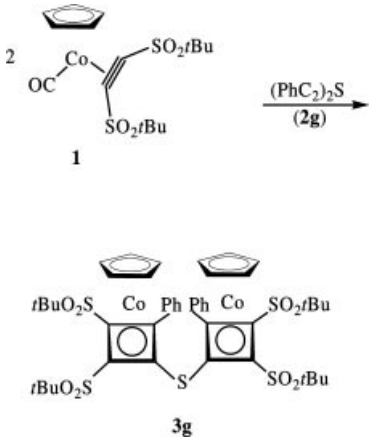


Figure 1. Molecular structure of **3a** in the solid state; hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths [Å] and bond angles [°]: C6–S1 1.769(5), C7–S2 1.755(5), C6–C7 1.494(6), C7–C8 1.484(7), C8–C9 1.459(7), C6–C9 1.476(7), C8–N1 1.360(6), C9–S3 1.741(5); C9–C6–C7 88.8(4), C8–C7–C6 89.8(4), C9–C8–C7 89.9(4), C8–C9–C6 91.5(4).



Scheme 2.

Sulfur-Bridged Dinuclear Cobalt Complex 3g

The sulfur-bridged bis[(η^4-cyclobutadiene)cobalt] complex **3g** was prepared in moderate yield by treating $(PhC_2)_2S$ (**2g**) with two equivalents of **1** (Scheme 2). No evidence for the mononuclear cobalt complex was found.

This reaction reveals an interesting route to a sulfur-bridged bis[(η^4-cyclobutadiene)cobalt] complex, which is important especially because the introduction of a heteroatom between two metal-stabilized cyclobutadiene rings is still difficult. The method used by Wadepohl et al.[8] leads to the mononuclear (η^4-cyclobutadiene)cobalt complex from the reaction of two equivalents of $(Me_3SiC_2)_2S$ with $[CpCo(CO)_2]$.

The brown oil **3g** was purified by column chromatography on silica gel and characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by mass spectrometry. The ^{1}H NMR spectrum of **3g** shows the expected multiplets (δ = 6.9–7.1 ppm) for the aryl hydrogens in addition to two singlets (δ = 1.19 and 1.27 ppm) for the *tert*-butyl groups and the Cp resonance (δ = 5.01 ppm). In the ^{13}C NMR spectrum, the signals (δ = 58.6–75.2 ppm) for the cyclobutadiene ring are found along with the Cp resonance at δ = 83.5 ppm. The molecular-ion peak of **3g** was detected with the correct isotopic distribution in the mass spectrum.

Conclusions

We have shown that the electron-rich aminoacetylenes **2a**–**c** react smoothly (as do the chalcogen-substituted acetylenes) with complex **1** to form CpCo-stabilized η^4-cyclobutadiene complexes **3a**–**c**, respectively However, the CO group in the mono(alkyne)cobalt complex **1** cannot be replaced by the "push-pull" borylacetylene **2d** or by the electron-poor borylacetylenes **2e** and **2f**. This result may be explained by considering the electronic nature of complex **1**. The electron-poor bis(*tert*-butylsulfonyl)acetylene in **1** reduces the back bonding between the Co atom and the CO ligand, which means that CO is easily replaced by the electron-rich acetylenes **2a**–**c**; the electron-poor monoborylacetylenes **2d**–**f** have weaker donor capabilities and thus do not react with **1**. Interestingly, the sulfur-bridged bis[(η^4-cyclobutadiene)cobalt] complex **3g** can be prepared by treating complex **1** with $(PhC_2)_2S$ (**2g**). The cobalt complexes **3a**–**c** and **3g** are stable at room temperature and resistant to light, oxygen, and moisture.

Experimental Section

General: All reactions were performed under nitrogen using standard Schlenk techniques. Solvents were dried with the appropriate drying agents and distilled under nitrogen. Glassware was dried with a heat gun under high vacuum. ^{1}H, ^{11}B, and ^{13}C NMR: Bruker AC 200 spectrometer; ^{1}H and ^{13}C spectra were referenced to $(CH_3)_4Si$. IR spectra were recorded on a Bruker IFS 28 FT spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 plus spectrometer using the EI technique. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. Melting points (uncorrected) were obtained on a Büchi apparatus, using capillaries which were filled under nitrogen and sealed. Complex (**1**),[9] 2-(diethylamino)-1-phenylthioacetylene (**2a**),[10] 2-(diethylamino)-1-(diphenylphosphanyl)acetylene (**2b**),[11] 2-(diethylamino)-1-phenylacetylene (**2c**),[12] 1-(diethylamino)-2-bis(diethylaminoboryl)acetylene,[13] 1-catecholboryl-2-phenylacetylene,[12] 1-dithiocatecholboryl-2-phenylacetylene,[12] and $(PhC_2)_2S$ (**2g**)[14] were prepared according to literature procedures.

General Procedure for the Synthesis of 3a–c and 3g: The mono(alkyne)cobalt complex **1** was dissolved in 30 mL of toluene and the appropriate acetylene was added. The reaction mixture was stirred for 2 d at room temperature. After completion of the reaction, the solvent was removed to dryness and the crude product was purified by column chromatography on silica gel (THF/toluene, 2:1). Cobalt complex **3a** was recrystallized from a solution of toluene at –20 °C.

[η^4-1,2-Bis(*tert*-butylsulfonyl)-4-(diethylamino)-3-phenylthiocyclobutadiene](η^5-cyclopentadienyl)cobalt (3a): Starting material: 0.25 g (1.21 mmol) of **2a**, 0.50 g (1.21 mmol) of **1**. Yield: 0.55 g (0.92 mmol; 76%), orange solid, m.p. 132–133 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.03 (t, 6 H, CH_2CH_3), 1.38, 1.47 [2s, 2×9 H, $C(CH_3)_3$], 3.1, 3.4 (2m, 2×2 H, CH_2CH_3), 5.21 (s, 5 H, Cp), 7.0–7.3 (m, 5 H, SPh) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.05 (CH_2CH_3), 24.32, 24.89 [$C(CH_3)_3$], 42.25 (CH_2CH_3), 61.77, 62.62 [$C(CH_3)_3$], 54.90, 58.34, 65.79, 74.87 (C_{4ring}), 83.24 (Cp-C), 125.1, 125.4, 128.9, 138.9 (SPh) ppm. MS (70 eV, EI): *m*/*z* (%) = 595 (30) [M^+], 475 (20) [$M^+ - SO_2tBu$], 353 (45) [$M^+ - 2SO_2tBu$], 124 (15) [CpCo]. MS (70 eV, HR-EI): *m*/*z* (%) = 595.1277 (95) [M^+; $^{12}C_{27}{}^1H_{38}{}^{14}N^{16}O_4{}^{32}S_3{}^{59}Co$: 595.1295]; Δmmu = –1.8.

[η^4-1,2-Bis(*tert*-butylsulfonyl)-4-diethylamino-3-diphenylphospanylcyclobutadiene](η^5-cyclopentadienyl)cobalt (3b): Starting material: 0.34 g (1.21 mmol) of **2b**, 0.50 g (1.21 mmol) of **1**. Yield: 0.48 g (0.71 mmol; 58%), orange oil. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.85 (t, 6 H, CH_2CH_3), 1.45, 1.49 [2s, 2×9 H, $C(CH_3)_3$], 3.0, 3.3 (2m, 2×2 H, CH_2CH_3), 5.03 (s, 5 H, Cp), 7.2–7.7 (m, 10 H, PPh_2) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.87 (CH_2CH_3), 24.32, 24.89 [$C(CH_3)_3$], 44.02 (CH_2CH_3), 61.77, 62.64 [$C(CH_3)_3$], 65.84, 67.24, 69.79, 72.85 (C_{4ring}), 84.03 (Cp-C), 125.0, 128.1, 129.3, 135.2 (PPh_2) ppm. MS (70 eV, EI): *m*/*z* (%) = 671 (5) [M^+], 550 (60) [$M^+ - SO_2tBu$], 429 (50) [$M^+ - 2SO_2tBu$], 124 (5) [CpCo]. MS (70 eV, HR-EI): *m*/*z* (%) = 671.1688 (51) [M^+; $^{12}C_{33}{}^1H_{43}{}^{14}N^{16}O_4{}^{31}P^{32}S_2{}^{59}Co$: 671.1704]; Δmmu = –1.6.

[η^4-1,2-Bis(*tert*-butylsulfonyl)-4-diethylamino-3-phenylcyclobutadiene](η^5-cyclopentadienyl)cobalt (3c): Starting material: 0.062 g (0.035 mmol) of **2c**, 0.15 g (0.035 mmol) of **1**. Yield: 0.16 g (0.028 mmol; 80%), orange solid, m.p. 127–128 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 0.95 (t, 6 H, CH_2CH_3), 1.18, 1.45 [2s, 2×9 H, $C(CH_3)_3$], 2.9, 3.2 [2m, 2×2 H, CH_2CH_3], 5.35 (s, 5 H, Cp), 7.2, 7.6 (2m, 5 H, Ph) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 11.33 (CH_2CH_3), 24.43, 24.85 [$C(CH_3)_3$], 43.62 (CH_2CH_3), 61.57, 62.17 [$C(CH_3)_3$], 82.70 (Cp-C), 127.5, 128.2, 129.0, 132.48 (Ph) ppm; C_{4ring} not found. MS (70 eV, EI): *m*/*z* (%) = 563 (10) [M^+], 442 (25) [$M^+ - SO_2tBu$]. MS (70 eV, HR-EI): *m*/*z* (%) = 563.1584 (68) [M^+; $^{12}C_{27}{}^1H_{38}{}^{16}O_4{}^{32}S_2{}^{59}Co$: 563.1574]; Δmmu = 1.0. $C_{27}H_{38}CoO_4S_2$ (563.66): calcd. C 57.53, H 6.80, N 2.48; found C 57.65, H 6.88, N 2.54.

Bis[(η^4-cyclobutadiene)]cobalt Complex 3g: Starting material: 0.25 g (1.06 mmol) of $(PhC_2)_2S$ (**2g**), 0.89 g (2.12 mmol) of **1**. Yield: 0.47 g (0.46 mmol; 43%), brown oil. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ = 1.19, 1.27 [2s, 2×18 H, $C(CH_3)_3$], 5.01 (s, 10 H, Cp), 7.0–7.3 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.62, 25.19 [$C(CH_3)_3$], 62.07, 62.92 [$C(CH_3)_3$], 55.20, 58.64, 66.09, 75.17

Table 1. Crystal data and structure refinement for **3a**.

Empirical formula	$C_{27}H_{38}CoNO_4S_3 \cdot C_7H_8$
Formula mass	687.83
Crystal system	monoclinic
Space group	$P2_1/c$
a [Å]	14.7043(8)
b [Å]	8.9725(5)
c [Å]	26.3058(6)
α [°]	90
β [°]	99.080(2)
γ [°]	90
Volume [Å^3]	3427.1(3)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.33
μ [mm^{-1}]	0.72
F(000)	1456
Crystal size [mm]	0.30×0.08×0.04
Θ_{max}(°)	21.5
Index ranges	–15/15, –9/9, –27/27
Reflections collected	20502
Reflections independent (R_{int})	3940 (0.1512)
Reflections observed [$I > 2\sigma(I)$]	2243
Parameters	397
Goodness-of-fit on F^2	0.99
R_1 [$I > 2\sigma(I)$]	0.048
wR_2 [$I > 2\sigma(I)$]	0.071
T [K]	200(2)
Residual electron density [e Å^{-3}]	0.38/–0.35

(C_{4ring}), 83.54 (Cp-C), 125.5, 125.7, 129.3, 135.4 (Ph) ppm. MS (70 eV, EI): *m*/*z* (%) = 1014 (10) [M^+], 941 (15) [$M^+ - t$BuO]. MS (70 eV, HR-EI): *m*/*z* (%) = 1014.1307 (100) [M^+; $^{12}C_{46}{}^{1}H_{56}{}^{16}O_8{}^{32}S_5{}^{59}Co_2$: 1014.1243]; Δmmu = 6.4.

X-ray Crystal Structure Determination of 3a: Crystal data and details of the structure determination are listed in Table 1. Reflections were collected with a Bruker-AXS SMART 1000 diffractometer (Mo-K_α radiation, λ = 0.71073 Å, graphite monochromator, ω-scan). An empirical absorption correction was applied. The structure was solved by direct methods and refined by least-squares methods based on F^2 with all measured reflections (SHELXTL 5.1).[15] All non-hydrogen atoms were refined anisotropically.
CCDC-268675 (for **3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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