

Cobalt-mediated oligomerization reactions of amino-substituted acetylene derivatives

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Received 23 November 2004; revised 2 March 2005; accepted 2 March 2005

Available online 26 May 2005

Dedicated to Professor Peter I. Paetzold on the occasion of his 70th birthday

Abstract

Reactions of the aminoacetylenes $\text{Et}_2\text{N}-\text{C}\equiv\text{C}-\text{R}$ ($\text{R} = \text{SiMe}_3, \text{SPh}, \text{PPh}_2$; **1a–c**) with $(\eta^5\text{-pentamethylcyclopentadienyl})\text{bis}(\text{ethene})\text{cobalt}$ yield the corresponding $(\eta^5\text{-pentamethylcyclopentadienyl})(\eta^4\text{-cyclobutadiene})\text{cobalt}$ complexes **2a–c**. Treatment of 1-phenylthio-2-diethylaminoacetylene **1b** with three equivalents of $\text{CpCo}(\text{CO})_2$ leads to the 1,3-dicobalta-bicyclobutane derivative **3'b**. The analogous compound **3'd** and the trinuclear cobalt complex **4'd** are obtained from the reaction of bis(diethylamino)acetylene (**1d**) with $(\eta^5\text{-cyclopentadienyl})\text{bis}(\text{ethene})\text{cobalt}$. Treatment of **1d** with excess $\text{Co}_2(\text{CO})_8$ yielded unexpectedly a mixture of di- and tetranuclear cobalt-carbene complexes **7** and **8**, most likely formed through interaction of oxygen. A designed route to **7** and **8** is found by reacting the tetraethyloxamide **6** with $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$, respectively. The catalytic cyclotrimerization reaction of the aminothioacetylene derivative **1b** with $[\text{CpCo}(\text{CO})_2]$ or $[\text{Co}_2(\text{CO})_8]$ leads to tris(phenylthio)-tris(diethylamino)benzene derivative **9**. The new compounds have been characterized by NMR spectroscopy, mass spectrometry as well as by X-ray structure analyses for **3'd**, **7** and **8**. The molecular structure of **3'd** in the crystal reveals the presence of a bicyclobutane framework with a Co–Co distance (2.36 Å) lying between a single and a double bond, whereas the former CC triple bond is completely ruptured (2.13 Å). The Co–C(carbene) distances in **7** and **8** are 1.93 and 1.95 Å, respectively.

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Keywords: Aminoacetylenes; Benzene derivatives; Cobalt-carbene complexes; (Cyclobutadiene)cobalt complexes; Dinuclear cobalt complexes

1. Introduction

Over the last few decades, transition metal-mediated cyclooligomerization of alkynes is a general and powerful method for constructing a vast range of cyclization products [1]. It is astounding that among the many reported reactions in this context [2], very few works have so far been done with boryl- [3] and aminoalkynes [4]. Due to the possibility of interaction of the empty orbital at the boron atom with the π system of the triple bond in borylacetylenes and the lone electron pair of the nitrogen

atom of the amino group with the adjacent sp carbon atom in aminoalkynes, one can expect a variety of interesting products from the reactions of transition metal complexes with these heteroatom-substituted acetylenes. Very recently, we have reported cobalt-mediated cycloaddition reactions of borylacetylenes [5]. The reactions of borylacetylenes with the cobalt complexes $\text{CpCo}(\text{CO})_2$ and $\text{Co}_2(\text{CO})_8$ did not give any carbene, carbyne or multinuclear cobalt complexes [3,5]. On the other hand, King et al. [6] studied thermal reactions of $\text{C}_5\text{H}_5\text{M}(\text{CO})_2$ ($\text{M} = \text{Co}, \text{Rh}$) with the mono- and diaminoacetylenes **1a** and **1d** ($\text{Et}_2\text{N}-\text{C}\equiv\text{C}-\text{R}$, $\text{R} = \text{SiMe}_3, \text{NEt}_2$), in which trimetallic complexes $(\text{C}_5\text{H}_5)_3\text{M}_3\text{C}_2(\text{NEt}_2)(\text{SiMe}_3)$ and $(\text{C}_5\text{H}_5)_3\text{M}_3\text{C}_2(\text{NEt}_2)$ were obtained by complete rupture

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of the carbon–carbon triple bond of the diaminoacetylene to form trigonal-bipyramidal clusters with carbon atoms at the apical and transition metals at the equatorial vertices. It has also been found that a carbon–carbon double bond in bis(1,3-dimethylimidazolidin)-2-ylidene is cleaved by $\text{CpCo}(\text{CO})_2$ to form the corresponding mononuclear cobalt-carbene complex [7]. The insertion of 1-dialkylaminoacetylenes into the metal–carbene bond has been studied by Dötz et al. [8], who noticed that nitrogen atoms flanking carbon–carbon multiple bonds cause an increase of their susceptibility to cleavage by the transition metal complexes. This unique nitrogen atom effect in amino-substituted acetylenes encouraged us to perform further studies. Here, we report reactions of the diethylaminoacetylenes **1a–d** with cobalt complexes.

2. Results and discussion

2.1. (η^4 -Cyclobutadiene)cobalt complexes **2a–c**

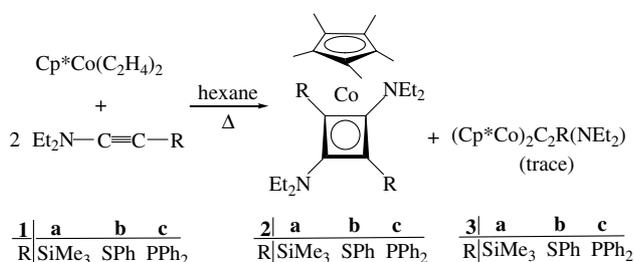
In 1965, Pettit and coworkers [9] reported the first generation of the tricarbonyl(η^4 -cyclobutadiene)iron complex. Among the various synthetic methods, the reactions of alkynes with transition metal complexes in particular have been studied extensively during the past four decades. In an analogous manner, reactions of diethylaminoacetylenes **1a–c** with (η^5 -pentamethylcyclopentadienyl)bis(ethene)cobalt in a 2:1 ratio gave the corresponding (η^5 -pentamethylcyclopentadienyl)(η^4 -cyclobutadiene)cobalt complexes **2a–c** in good yield (Scheme 1) [10]. However, the analogous complex $\text{CpCoC}_4(\text{NEt}_2)_4$ (**2'd**, prime indicates C_5H_5 ligand versa C_5Me_5 in **2**) (Scheme 3) was not obtained from the reaction of $\text{CpCo}(\text{C}_2\text{H}_4)_2$ with the electron-rich $(\text{Et}_2\text{N})_2\text{C}_2$ (**1d**) [11]. In addition to **2a–c**, trace amounts of dicobalt complexes **3a–c** were detected in the mass spectra.

The liquid cobalt complexes **2a–c** were purified by column chromatography and characterized by ^1H , ^{13}C , ^{29}Si , ^{31}P NMR spectroscopy as well as by mass spectrometry. In the ^1H NMR spectrum of **2a**, a singlet ($\delta = 0.15$ ppm) for SiMe_3 , a triplet and a quartet ($\delta = 1.21$ and 2.93 ppm) for the ethyl group and a singlet

($\delta = 2.12$ ppm) for C_5Me_5 are found. The ^{29}Si NMR spectrum of **2a** features a signal at $\delta = -16.2$ ppm. The NMR spectroscopic data of **2a** as well as of **2b** and **2c** (see below) do not allow to distinguish between the two possible geometrical isomers (*cis*- and *trans*-), formed by head-to-head and head-to-tail dimerization of **1a–c**, respectively. This problem was addressed by analyzing the major peaks in terms of the degradation of the cyclobutadiene ring in the mass spectra. In general, three different acetylenes are released from the *cis*-isomer, whereas only one acetylene is detected in the case of the *trans*-isomer [12]. The mass spectrum of **2a** shows that only one acetylene is released from the molecular ion, which confirms the identity of the *trans*-isomer. The ^1H NMR spectrum of **2b** exhibits a triplet ($\delta = 1.24$ ppm), a quartet ($\delta = 3.06$ ppm) and a multiplet for C_6H_5 in addition to a singlet ($\delta = 2.11$ ppm) for the pentamethylcyclopentadienyl ligand. In the ^{13}C NMR spectrum of **2b**, two signals ($\delta = 70.82$ and 89.82 ppm) for the two quaternary carbon atoms of the C_4 ring and a signal ($\delta = 84.82$ ppm) for the C_5Me_5 ligand are detected. In the mass spectrum, the molecular ion peak appears with the correct isotopic pattern. The ^1H NMR spectrum of **2c** features a triplet ($\delta = 1.27$ ppm), a quartet ($\delta = 3.05$ ppm) and two multiplets ($\delta = 7.29$ and 7.62 ppm) for PPh_2 in addition to a singlet ($\delta = 1.97$ ppm) for the pentamethylcyclopentadienyl ligand. In the ^{13}C NMR spectrum of **2c**, two signals ($\delta = 68.95$ and 94.69 ppm) for the two quaternary carbon atoms of the C_4 ring and a signal ($\delta = 87.65$ ppm) for the C_5Me_5 ligand are detected. The ^{31}P NMR spectrum of the cobalt complex **2c** shows a singlet at $\delta = -13.5$ ppm. EI-MS data confirm the identity of compound **2c** through the appearance of the molecular ion peak with the expected isotopic pattern. In both cases, no evidence for the presence of the *cis*-isomers was found by MS.

2.2. Synthesis of di- and trinuclear cobalt complexes **3'b**, **3'd** and **4'd**

As mentioned in Section 1, King et al. [6] have noticed that treatment of the aminoacetylene derivatives **1a** and **1d** with $\text{CpCo}(\text{CO})_2$ at high temperature (130–140 °C) led to the trimetallic clusters $(\text{CpCo})_3\text{C}_2(\text{SiMe}_3)(\text{NEt}_2)$ (**4'a**) and $(\text{CpCo})_3\text{C}_2(\text{NEt}_2)_2$ (**4'd**), respectively. However, the reaction of the diethylaminoacetylene derivative **1b** with $\text{CpCo}(\text{CO})_2$ in a 1:3 ratio at 115 °C did not give the trimetallic cluster **4'b**, but the dinuclear species **3'b** was obtained in 41% yield (Scheme 2) [10]. Compound **3'b**, a brown oil, was characterized by ^1H , ^{13}C NMR spectroscopy as well as by mass spectrometry. The ^1H NMR spectrum of **3'b** shows a triplet ($\delta = 1.21$ ppm) and a quartet ($\delta = 3.03$ ppm) in addition to the Cp resonance ($\delta = 5.03$ ppm). In the ^{13}C NMR spectrum, two signals are found at $\delta = 12.19$ and 47.32 ppm for ethyl



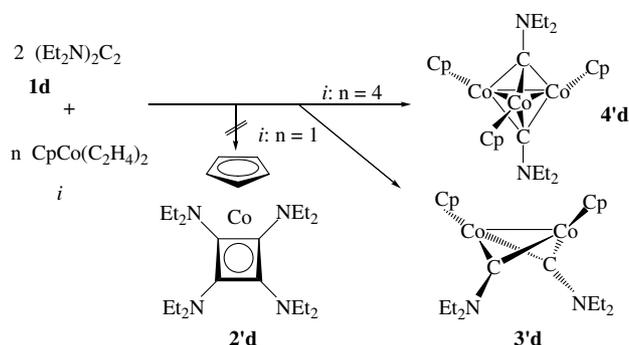
Scheme 1.

group along with the signal for the Cp resonance ($\delta = 86.42$ ppm). The ^{13}C resonances of the two different quaternary carbon atoms of the C–NEt₂ and C–SPh groups could not be resolved, possibly owing to broadening through coupling with the quadrupolar cobalt atoms. The formation of the dicobalt complex **3'b** was supported by EI-MS through the appearance of the molecular ion peaks with the expected isotopic pattern. Although the spectroscopic data clearly indicate the presence of a dinuclear cobalt complex, it was not possible to deduce the connectivity in **3'b** with respect to cobalt–cobalt and carbon–carbon bonding (see Scheme 2).

As shown in Scheme 3, the reaction of bis(diethylamino)acetylene **1d** with CpCo(C₂H₄)₂ in a 2:1 ratio did not give rise to the (η^4 -cyclobutadiene)cobalt complex (**2'd**), but formation of the dinuclear cobalt complex **3'd** in good yield occurred by the complete breaking of the carbon–carbon triple bond in **1d** [11]. The black crystals were characterized by ¹H NMR spectroscopy, mass spectrometry and an X-ray structure analysis. The ¹H NMR spectrum of **3'd** shows a triplet ($\delta = 0.93$ ppm) and a quartet ($\delta = 3.52$ ppm) in addition to one singlet ($\delta = 4.90$ ppm) for C₅H₅ (ratio 6:4:5).

When the reagents were reacted in a 1:2 ratio at room temperature, the known [6a] green cluster **4'd** was obtained (17% yield, characterized by EI-MS). Obviously, the formation of the trigonal-bipyramid cluster **4'd** occurred by insertion of a CpCo complex fragment into **3'd**, which causes the 1,3-dicobalta-bicyclo[1,1,0]butane to transform into the trimetallic *closo*-cluster **4'd** having $2n + 2 = 12$ SE. EI-MS data confirm the identity of complex **4'd** through the appearance of the molecular ion peak with the expected isotopic pattern.

The structure of **3'd** has been determined by performing a single crystal X-ray diffraction analysis, which reveals a bicyclobutane C₂Co₂-framework. Fig. 1 exhibits a Co–Co bond and two bridging carbon atoms; each cobalt atom carries a η^5 -bonded Cp ligand and each carbon atom (C1, C1A) bears a diethylamino group. Complex **3'd** possesses a C₂ axis passing through the middle of Co–Co bond and C1–C1A vector. The bonding parameters of **3'd** show that the Co1–C1 and Co1–C1A are rather short (1.82–1.83 Å) in comparison to other cobalt–carbenes (1.88–2.10 Å) [13]. The almost equal bond distances between cobalt (Co1 and Co1A) and the C_{carbyne} atoms (C1 and C1A) suggest partial double bond character due to electron delocalization be-



Scheme 3.

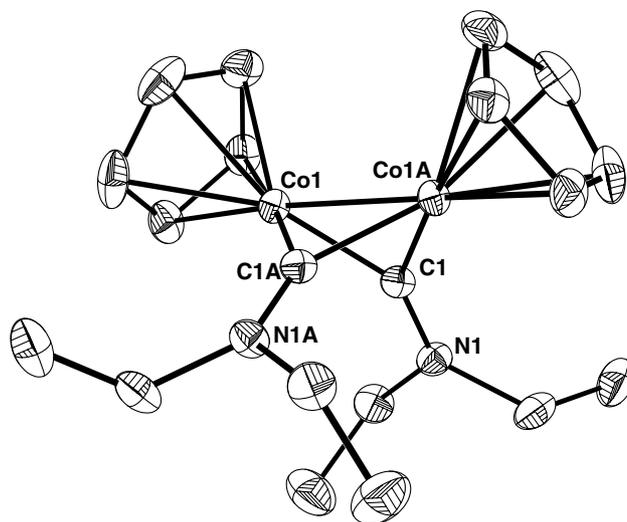
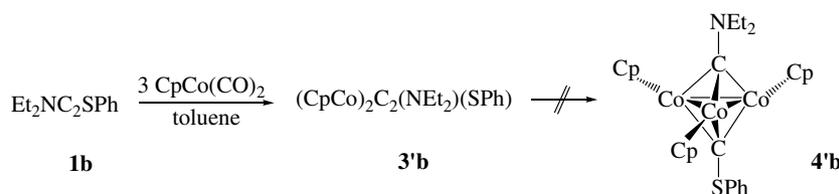
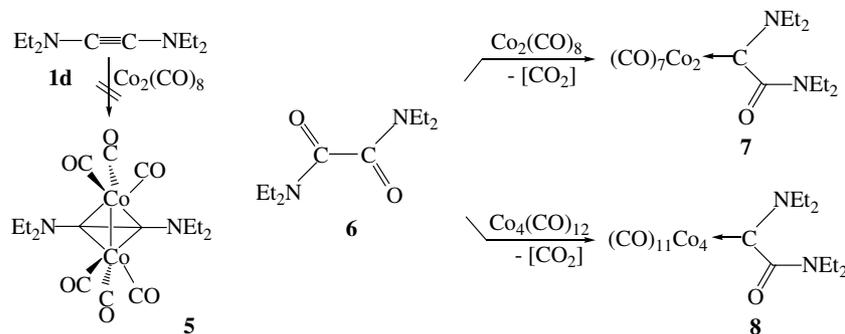


Fig. 1. Molecular structure of **3'd** in the solid state. Selected bond lengths (Å) and bond angles [°]: Co1–Co1A, 2.366(1); Co1–C1, 1.830(3); Co1–C1A, 1.821(3); C1–C1A, 2.131; C1–N1, 1.312(4) and C1–Co1–Co1A, 49.5(1); C1A–Co1–Co1A, 49.8(1); C1–Co1–C1A, 71.4(2); Co1–C1–Co1A, 80.8(1); Co1–C1–N1, 139.0(2); Co1A–C1–N1, 139.7(2).

tween cobalt atoms, C1 and C1A. The solid state structure implies that the cobalt–cobalt bond is shorter than the Co–Co single bond (2.48 Å) [14] and longer than Co=Co bond (2.18 Å) [15]. Formation of organometallic complexes by breaking of a carbon–carbon triple bond is also known for alkynes without amino substituents, as Vollhardt and coworkers [15,16], Yamazaki et al. [17], and Butenschön and coworkers [18] have reported examples of similar metalcarbyne complexes.



Scheme 2.



2.3. Di- and tetranuclear cobalt-carbene complexes 7 and 8

An attempt to prepare the (acetylene)hexacarbonyldicobalt cluster **5** from the reaction of bis(diethylamino)acetylene (**1d**) with excess $\text{Co}_2(\text{CO})_8$ was not successful, but the di- and tetranuclear cobalt-carbene complexes **7** and **8** were obtained in low yield after the reaction mixture had been stored for a long time at room temperature [11]. To clarify their formation, the novel Fischer-carbene complexes were obtained by a designed route: treatment of the oxamide **6** [19] with $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$, respectively, gave the expected carbene complexes in moderate yields (Scheme 4) [10].

This indicates that in the former attempt the diaminoacetylene **1d** most likely was first oxidized to $[\text{Et}_2\text{N}-\text{C}(\text{O})_2]$ (**6**) or to $[\text{Et}_2\text{N}-\text{C}(\text{O})-\text{C}(\text{NEt}_2)_2]$, which on further reaction with an excess of dicobaltoctacarbonyl led to the cobalt-carbene complexes, characterized by ^1H , ^{13}C NMR spectroscopy, IR spectroscopy and mass spectrometry. From the integration of the ^1H NMR peaks of **7** and **8**, it is clear, the signals for the three different ethyl groups in amide and amino are not overlapping with each other. However, correlation spectroscopic measurements (H,H-COSY, HMQC, HMBC) were carried out as suggested by a referee, which reconfirmed our interpretation. Due to fast exchange of carbonyl groups [20] and the quadrupole moment of cobalt atoms [6b,21], only one small broad signal is detected in the ^{13}C NMR spectrum of compound **7**. The IR-spectrum of **8** shows bands at $\tilde{\nu} = 1974, 1996, 2009, 2016$ and 2065 cm^{-1} for terminal CO ligands and a weak band is observed at $\tilde{\nu} = 1846\text{ cm}^{-1}$ for bridging CO group. The band for the CO group of the carbene ligand is found at $\tilde{\nu} = 1652\text{ cm}^{-1}$.

The cobalt complexes **7** and **8** were characterized by performing a single crystal X-ray structure analysis (Figs. 2, 3). Dark red crystals of **7** were grown from a solution in hexane. The molecular structure of **7** shows the $\text{Co}_2(\text{CO})_7$ framework; the Co1 and Co2 each atom is surrounded by three terminal CO ligands with stag-

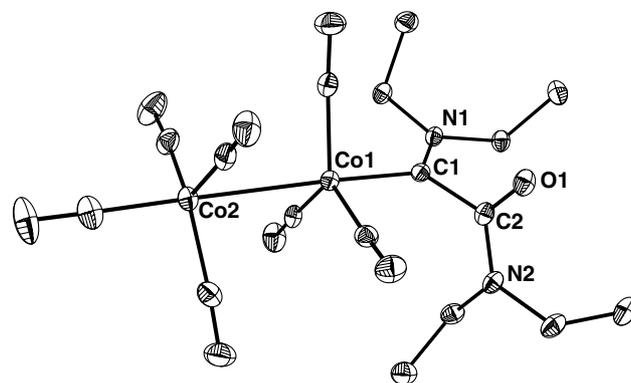


Fig. 2. Molecular structure of **7** in the solid state. Selected bond lengths (Å) and bond angles (°): C1–Co1, 1.930(2); C1–N1, 1.303(2); C1–C2, 1.514(2); C2–N2, 1.342(2); Co1–Co2, 2.715(1) and Co1–C1–N1, 129.5(1); Co1–C1–C2, 114.4(1); N1–C1–C2, 116.1(1); C1–Co1–Co2, 173.67(4).

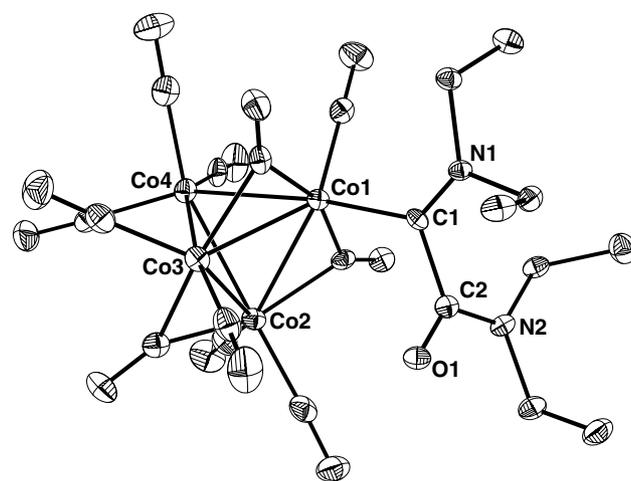


Fig. 3. Molecular structure of **8** in the solid state. Selected bond lengths (Å) and bond angles (°): C1–Co1, 1.955(3); C1–N1, 1.305(4); C1–C2, 1.509(4); C2–N2, 1.353(4); Co1–Co2, 2.495(1); Co1–Co3, 2.473(1); Co2–Co3, 2.436(1); Co1–Co4, 2.544(1); Co2–Co4, 2.522(1); Co3–Co4, 2.506(1) and Co1–C1–N1, 130.0(2); Co1–C1–C2, 115.9(2); N1–C1–C2, 113.16(3); C1–Co1–Co2, 114.7(1); C1–Co1–Co3, 110.9(1); C1–Co1–Co4, 170.7(1).

gered conformation and Co2 atom bears an additional terminal CO group, which lies in line with the metal–metal bond axis. The solid state structure of **7** indicates an almost linear C1–Co1–Co2 moiety with a considerably longer Co–Co bond distance (2.715 Å) than that in Co₂(CO)₈ (2.58 Å).

Black crystals of **8** were obtained from a solution in hexane, which crystallized with a hexane molecule in a special position (inversion center). The four cobalt atoms form a tetrahedral cluster with Co–Co distances of 2.436 to 2.544 Å. The arrangement of three μ₂-bridging CO and nine terminal ligands is identical with that in Co₄(CO)₁₂, in which one CO is replaced by the carbene ligand. The bonding in the carbene ligands in **7** and **8** is very similar [Co1–C1: 1.930 vs. 1.955 Å, C1–N1: 1.303 vs. 1.305 Å; **3'd**: 1.312 Å]. The planes C1–Co1–N1–C2 and C2–C1–O1–N2 are almost perpendicular (88.7° vs. 85.1°).

2.4. [2 + 2 + 2]-Catalytic cyclotrimerization reaction

In refluxing toluene, only the aminothioacetylene derivative **1b** formed the light yellow tris(phenylthio)-tris(diethylamino)benzene derivative **9** (70% yield) in the presence of a catalytic amount of [CpCo(CO)₂] or [Co₂(CO)₈] (Scheme 5) [10]. The oily **9**, well soluble in common organic solvents, was purified by column chromatography and characterized by ¹H and ¹³C NMR spectroscopy as well as by mass spectrometry.

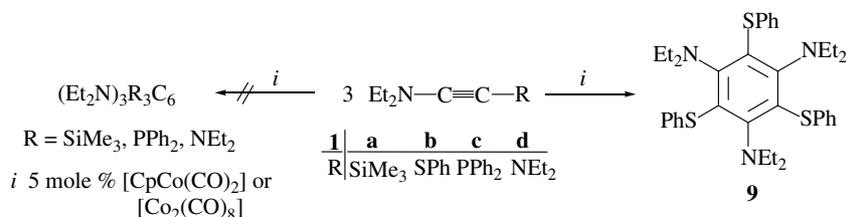
The ¹H NMR spectrum of **9** exhibits a triplet (δ = 1.34 ppm) and a quartet (δ = 3.17 ppm) in addition to the multiplets in the region δ = 7.14 – 7.51 ppm. In the ¹³C NMR spectrum, two signals (δ = 121.3 and 132.5 ppm) are assigned to the *ipso*-carbon atoms of the symmetrical central benzene ring. No ¹³C signals for unsymmetric central aromatic ring were found. Compound **9** was identified by mass spectrum through the appearance of the molecular ion peak with the expected isotopic pattern. Attempts to obtain the corresponding benzene derivatives from the reactions of aminoalkynes **1a**, **1c** and **1d** [11] with catalytic amounts of [CpCo(CO)₂] or [Co₂(CO)₈] were not successful, which may be explained on steric grounds.

3. Conclusion

Reactions of diethylamino-substituted acetylenes with Cp*Co(C₂H₄)₂, CpCo(C₂H₄)₂ and Co₂(CO)₈ have been studied. The reactions of aminoalkyne derivatives **1a–d** with bis(ethene)cobalt complexes discovered during this work indicate two different modes of interactions: (1) cyclization reactions to form mononuclear (η⁴-cyclobutadiene)cobalt complexes **2a–c** which involve the interactions of the (C₅Me₅)Co fragment with the carbon–carbon triple bond of the aminoacetylenes; (2) complete cleavage of the carbon–carbon triple bond to give the di- and trinuclear (C₅H₅)Co complexes **3'd** and **4'd** containing the diethylaminocarbyne units. The di- and tetranuclear cobalt-carbene complexes **7** and **8** are obtained from the reactions of tetraethyloxamide **6** with dicobaltoctacarbonyl and tetracobaltdodecacarbonyl, respectively. The tris(phenylthio)-tris(diethylamino)benzene derivative **9** is formed from the catalytic [2 + 2 + 2]-cyclotrimerization reaction of the aminoacetylene **1b** with [CpCo(CO)₂] or [Co₂(CO)₈].

4. Experimental

General. All reactions were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried with the appropriate drying agents and distilled under nitrogen atmosphere. Glasswares were dried with heat-gun under high vacuum. Column chromatography: silica gel 60 (Machery-Nagel). ¹H, ¹³C and ³¹P NMR: Bruker AC 200 spectrometer; ¹H and ¹³C spectra were referenced to (CH₃)₄Si and ³¹P spectra to H₃PO₄. IR: Bruker Vector 22 FT-IR. Mass spectra were obtained on Finnigan MAT 8230 plus spectrometers using the EI and FAB techniques. Tetraethyloxamide (**6**) [19], 1-trimethylsilyl-2-diethylaminoacetylene (**1a**) [22], 1-phenylthio-2-diethylaminoacetylene (**1b**) [23], 1-diphenylphosphino-2-diethylaminoacetylene (**1c**) [24], bis(diethylamino)acetylene (**1d**) [25], (cyclopentadienyl)-bis(ethene)cobalt [26] and (pentamethylcyclopentadienyl)-bis(ethene)cobalt [27] were prepared according to the literature procedures. Dicobaltoctacarbonyl and tetracobaltdodecacarbonyl were purchased from Strem.



Scheme 5.

[Et₂N–C(O)–C(NEt₂)₂] [11] not previously reported in the literature was prepared by the air oxidation of two equivalents of bis(diethylamino)acetylene. The compound was characterized only by EI-MS (*m/z* = 368).

4.1. (η^5 -Pentamethylcyclopentadienyl)-[η^4 -bis(trimethylsilyl)-bis(diethylamino)cyclobutadiene]cobalt(I) (**2a**), (η^5 -pentamethylcyclopentadienyl)-[η^4 -bis(phenylthio)-bis(diethylamino)-cyclobutadiene]cobalt(I) (**2b**), (η^5 -pentamethylcyclopentadienyl)-[η^4 -bis(diphenylphosphino)-bis(diethylamino)cyclobutadiene]cobalt(I) (**2c**)

The corresponding aminoacetylene (**1a**: 0.41 g, **1b**: 0.50 g, **1c**: 0.68 g; 2.43 mmole) and (pentamethylcyclopentadienyl)bis(ethene)cobalt (0.30 g; 1.21 mmole) were heated at 70 °C in hexane for 2 d. After cooling, the dark solution was filtered and solvent was removed by HV. The crude product was purified by column chromatography (SiO₂; hexane:toluene 1:1).

2a: 0.40 g (62%) yellow oil. ¹H NMR (200.1 MHz, CDCl₃): δ = 0.15 [s, 18H, SiMe₃], 1.21 [t, ³*J*(H,H) = 7.2 Hz, 12H; CH₂CH₃], 2.12 [s, 15H, Cp*-CH₃], 2.93 [q, ³*J*(H,H) = 7.1 Hz, 8H; CH₂CH₃] ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 0.95 (SiMe₃), 11.29 (Cp*-CH₃), 12.69 (CH₂CH₃), 47.70 (CH₂CH₃), 64.23, 91.58 (C_{ring}), 89.98 (Cp*C) ppm. ²⁹Si NMR (39.7 MHz, CDCl₃): δ = -16.2 ppm. MS (70 eV, EI): *m/z* (%) = 532 (65) [M⁺], 470 (70) [M⁺ - NEt₂], 363 [M⁺ - Me₃SiC₂NEt₂], 194 (35) [Cp*Co⁺]. MS (70 eV, HR-EI): *m/z* (%) = 532.3099 (50.0) [M⁺; ¹²C₂₈¹H₅₃⁵⁹Co¹⁴N₂²⁸Si₂: 532.3079]; Δ mmu = 2.0.

2b: 0.51 g (69%) brown oil. ¹H NMR (200.1 MHz, CDCl₃): δ = 1.24 [t, ³*J*(H,H) = 7.2 Hz, 12H; CH₂CH₃], 2.11 [s, 15H, Cp*-CH₃], 3.06 [q, ³*J*(H,H) = 7.1 Hz, 8H; CH₂CH₃], 7.15–7.41 (m, 10H, C₆H₅) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 11.18 (Cp*-CH₃), 13.18 (CH₂CH₃), 48.31 (CH₂CH₃), 70.82, 89.82 (C_{4ring}), 84.82 (Cp*C), 124.7, 125.4, 128.8, 138.3 (phenylthio) ppm. MS (70 eV, EI): *m/z* (%) = 604 (65) [M⁺], 496 (20) [M⁺ - SPh], 399 (2) [M⁺ - PhSC₂NEt₂], 194 (35) [Cp*Co⁺]. MS (70 eV, HR-EI): *m/z* (%) = 604.2371 (82.5) [M⁺; ¹²C₃₄¹H₄₅⁵⁹Co¹⁴N₂³²S₂: 604.2356]; Δ mmu = 1.5.

2c: 0.59 g (65%) yellow oil. ¹H NMR (200.1 MHz, CDCl₃): δ = 1.27 [t, ³*J*(H,H) = 7.2 Hz, 12H; CH₂CH₃], 1.97 [s, 15H, Cp*-CH₃], 3.05 [q, ³*J*(H,H) = 7.2 Hz, 8H; CH₂CH₃], 7.29, 7.62 (m, 20H, C₆H₅) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 10.94 (Cp*-CH₃), 13.16 (CH₂CH₃), 48.06 (CH₂CH₃), 68.95, 94.69 (C_{4ring}), 87.65 (Cp*C), 128.3, 131.9, 132.3, 139.4 (diphenylphosphino) ppm. ³¹P NMR (80.9 MHz, CDCl₃): δ = -13.5. MS (FAB+): 756 (10) [M⁺], 563 (80) [M⁺ - Cp* + 1], 475 (5) [M⁺ - Ph₂PC₂NEt₂]. MS (70 eV, HR-FAB): *m/z* (%) = 756.3195 (12.0) [M⁺; ¹²C₄₆¹H₅₅⁵⁹Co¹⁴N₂³¹P₂: 756.3172]; Δ mmu = 2.3.

4.2. Dinuclear cobalt complex 3'b

To a stirred solution of (cyclopentadienyl)dicarbonylcobalt (1.18 g, 6.6 mmole) in 40 ml of toluene, 1-phenylthio-2-diethylaminoacetylene (**1b**) (450 mg, 2.2 mmole) was added slowly at 0 °C. The reaction mixture was heated at 115 °C for 3 d. After filtration, the solvent was removed by HV and the black residue was subjected to column chromatography (SiO₂; hexane:toluene 1:2).

3'b: 0.41 g (41%) brown oil. ¹H NMR (200.1 MHz, CDCl₃): δ = 1.21 [t, ³*J*(H,H) = 7.2 Hz, 6H; CH₂CH₃], 3.03 [q, ³*J*(H,H) = 7.1 Hz, 4H; CH₂CH₃], 5.03 (s, 10H, Cp-H), 7.08–7.41 (m, 5H, C₆H₅) ppm. ¹³C NMR (50.3 MHz, CDCl₃): δ = 12.19 (CH₂CH₃), 47.32 (CH₂CH₃), 86.42 (CpC), 124.5, 125.4, 129.0, 138.9 (phenylthio) ppm. MS (70 eV, EI): *m/z* (%) = 454 (65) [M⁺ + 1]. MS (70 eV, HR-EI): *m/z* (%) = 454.0425 (30) [M⁺ + 1; ¹²C₂₂¹H₂₆⁵⁹Co₂¹⁴N³²S: 454.0449]; Δ mmu = -2.4.

4.3. Dinuclear cobalt complex 3'd

To a stirred solution of (cyclopentadienyl)-bis(ethene)cobalt (400 mg, 2.2 mmole) in 10 ml of pentane, the bis(diethylamino)acetylene (**1d**) (750 mg, 4.5 mmole) was added slowly at -70 °C. After stirring overnight at room temperature, the green solution was filtered, leaving black needles in the frit. The solvent of the filtrate was removed and the black residue was washed several times with toluene and THF. Solvents were evaporated by HV leaving a black residue. The mass spectra of the black needles and the black residue were identical.

3'd: 300 mg (65%). ¹H NMR (200.1 MHz, C₆D₆): δ = 0.93 [t, ³*J*(H,H) = 7.1 Hz, 12H; CH₂CH₃], 3.52 [q, ³*J*(H,H) = 7.1 Hz, 8H; CH₂CH₃], 4.90 (s, 10H, C₅H₅) ppm. MS (70 eV, EI): *m/z* (%) = 416 (70) [M⁺], 387 (25) [M⁺ - Et], 330 (36) [M⁺ - NEt₂CH₂], 292 (5) [M⁺ - CpCo], 124 (20) [CpCo], 28 (46) [C₂H₄].

4.4. Di- and tetranuclear cobalt-carbene complexes 7 and 8

4.4.1. Procedure A

To a solution of 1.03 g of dicobaltoctacarbonyl (3.01 mmole) in hexane, bis(diethylamino)acetylene **1d** was added slowly at -30 °C. After warming up to room temperature, the reaction mixture was stirred for 3 d and filtered. The solvent was evaporated by HV and the residue purified by column chromatography (Al₂O₃, hexane). After long time storage in hexane at room temperature, a mixture of deep-red (**7**) and black crystals (**8**) was obtained (total yield 30 mg).

4.4.2. Procedure B

To a solution of tetraethyloxamide **6** (0.11 g, 0.55 mmole) in 20 ml of hexane, cobaltcarbonyl complex (dicobaltoctacarbonyl: 0.19 g; tetracobaltdodecacar-

bonyl: 0.31 g; 0.55 mmole) was added slowly at $-30\text{ }^{\circ}\text{C}$. The reaction mixture was allowed to stir for 3 d at room temperature. The dark solution was filtered and purified by column chromatography on aluminiumoxide (5% water) with hexane as elute. The purified hexane solution was concentrated and a solid residue was obtained.

7: 101 mg (37%) red solid, m.p. $92\text{--}93\text{ }^{\circ}\text{C}$, ^1H NMR (200.1 MHz, CDCl_3): $\delta = 0.92$ [t, $^3J(\text{H,H}) = 7.1$ Hz, 6H; NCH_2CH_3], 1.06 [t, $^3J(\text{H,H}) = 7.0$ Hz, 3H; $\text{C}(\text{O})\text{NCH}_2\text{CH}_3$], 1.14 [t, $^3J(\text{H,H}) = 7.0$ Hz, 3H; $\text{C}(\text{O})\text{NCH}_2\text{CH}_3$], 2.41 [q, $^3J(\text{H,H}) = 7.2$ Hz, 4H; NCH_2CH_3], 3.03 [q, $^3J(\text{H,H}) = 7.1$ Hz, 2H; $\text{C}(\text{O})\text{NCH}_2\text{CH}_3$], 3.15 [q, $^3J(\text{H,H}) = 7.1$ Hz, 2H; $\text{C}(\text{O})\text{NCH}_2\text{CH}_3$] ppm. ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 11.43$ (NCH_2CH_3), 12.44, 13.85 ($\text{C}(\text{O})\text{NCH}_2\text{CH}_3$), 38.16, 42.17 ($\text{C}(\text{O})\text{NCH}_2\text{CH}_3$), 46.13 (NCH_2CH_3), 164.6 ($\text{C}(\text{O})\text{NEt}_2$), 200.2 (CO). IR (hexane): $\tilde{\nu}$ [cm^{-1}] = 1651(s), 1992(w), 2026(s), 2058(vs). MS (70 eV, EI): m/z (%) = 470 (5) [$\text{M}^+ - \text{CO}$], 398 (8) [$\text{M}^+ - \text{NEt}_2 - \text{CO}$], 370 (85) [$\text{M}^+ - \text{NEt}_2 - 2\text{CO}$], 342 (20) [$\text{M}^+ - \text{NEt}_2 - 3\text{CO}$], 314 (10) [$\text{M}^+ - \text{NEt}_2 - 4\text{CO}$], 286 (80) [$\text{M}^+ - \text{NEt}_2 - 5\text{CO}$], 258 (50) [$\text{M}^+ - \text{NEt}_2 - 6\text{CO}$]. MS (70 eV, HR-EI): m/z (%) = 469.9956 (6.0) [$\text{M}^+ - \text{CO}$; $^{12}\text{C}_{16}^{1}\text{H}_{20}^{59}\text{Co}_2^{14}\text{N}_2^{16}\text{O}_7$: 469.9934]; $\Delta\text{mmu} = 2.2$.

8: 164 mg (41%) black solid, m.p. $111\text{--}113\text{ }^{\circ}\text{C}$, ^1H NMR (200.1 MHz, CDCl_3): $\delta = 0.85$ [t, $^3J(\text{H,H}) = 7.2$ Hz, 6H; NCH_2CH_3], 1.00 [t, $^3J(\text{H,H}) = 7.1$ Hz, 3H; $\text{C}(\text{O})\text{NCH}_2\text{CH}_3$], 1.03 [t, $^3J(\text{H,H}) = 7.1$ Hz, 3H;

$\text{C}(\text{O})\text{NCH}_2\text{CH}_3$], 2.35 [q, $^3J(\text{H,H}) = 7.1$ Hz, 4H; NCH_2CH_3], 3.09 [q, $^3J(\text{H,H}) = 7.1$ Hz, 2H; $\text{C}(\text{O})\text{NCH}_2\text{CH}_3$], 3.25 [q, $^3J(\text{H,H}) = 7.1$ Hz, 2H; $\text{C}(\text{O})\text{NCH}_2\text{CH}_3$] ppm. ^{13}C NMR (50.3 MHz, CDCl_3): $\delta = 11.03$ (NCH_2CH_3), 12.04, 13.45 ($\text{C}(\text{O})\text{NCH}_2\text{CH}_3$), 37.76, 41.77 ($\text{C}(\text{O})\text{NCH}_2\text{CH}_3$), 45.73 (NCH_2CH_3), 164.2 ($\text{C}(\text{O})\text{NEt}_2$), 200.9 (CO). IR (hexane): $\tilde{\nu}$ [cm^{-1}] = 1652(vs), 1846(w), 1974(s), 1996(m), 2009(s), 2016(s), 2065(s). FAB-MS: m/z (%) = 729 (11) [$\text{M}^+ + 1$], 672 (18) [$\text{M}^+ - 2\text{CO}$], 644 (100) [$\text{M}^+ - 3\text{CO}$], 616 (51) [$\text{M}^+ - 4\text{CO}$], 588 (80) [$\text{M}^+ - 5\text{CO}$], 560 (52) [$\text{M}^+ - 6\text{CO}$], 532 (11) [$\text{M}^+ - 7\text{CO}$], 504 (29) [$\text{M}^+ - 8\text{CO}$]. MS (70 eV, HR-FAB): m/z (%) = 728.8454 (55.0) [$\text{M}^+ + 1$; $^{12}\text{C}_{21}^{1}\text{H}_{21}^{59}\text{Co}_4^{14}\text{N}_2^{16}\text{O}_{12}$: 728.8424]; $\Delta\text{mmu} = 3.0$.

4.5. Tris(phenylthio)-tris(diethylamino)benzene derivative **9**

A mixture of 1-phenylthio-2-diethylaminoacetylene (**1b**) (0.70 g, 3.41 mmole) and 5 mole% of $[\text{CpCo}(\text{CO})_2]$ (0.03 g) or $[\text{Co}_2(\text{CO})_8]$ (0.06 g) in 20 ml of toluene was refluxed for 2 d. After cooling, the solvent was removed to dryness and the product was isolated by column chromatography (SiO_2 ; hexane).

9: 0.49 g (70%) light yellow oil. ^1H NMR (200.1 MHz, CDCl_3): $\delta = 1.34$ [t, $^3J(\text{H,H}) = 7.0$ Hz, 18H; CH_2CH_3], 3.17 [q, $^3J(\text{H,H}) = 7.1$ Hz, 8H; CH_2CH_3], 7.41–7.51 (m, 15H, C_6H_5) ppm. ^{13}C NMR (50.3 MHz,

Table 1
Crystal data and structure refinement for **3'd**, **7** and **8**

	3'd	7	8
Empirical formula	$\text{C}_{20}\text{H}_{30}\text{Co}_2\text{N}_2$	$\text{C}_{17}\text{H}_{20}\text{Co}_2\text{N}_2\text{O}_8$	$\text{C}_{24}\text{H}_{27}\text{Co}_4\text{N}_2\text{O}_{12}$
Formula weight	416.32	498.21	771.20
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	$P4_12_12$	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a (Å)	14.769(7)	10.1981(5)	15.535(4)
b (Å)	14.769(7)	19.7845(10)	10.920(3)
c (Å)	9.169(5)	11.4151(6)	18.597(5)
α (°)	90	90	90
β (°)	90	111.99(1)	99.63(2)
γ (°)	90	90	90
Volume (Å ³)	2000(2)	2135.6(2)	3110.4(13)
Z	4	4	4
Calculated density (g cm^{-3})	1.383	1.550	1.647
μ (mm^{-1})	1.662	1.597	2.156
$F(000)$	872	1016	1556
Crystal size (mm)	$0.60 \times 0.20 \times 0.20$	$0.45 \times 0.28 \times 0.22$	$0.23 \times 0.22 \times 0.06$
Θ_{max} (°)	27.49	28.32	26.39
Index ranges	$-19/19, -13/13, -11/11$	$-13/12, 0/25, 0/15$	$-19/19, 0/13, 0/23$
Reflections collected	2734	14571	34415
Independent reflections	2304(0.016)	5135(0.026)	6370(0.099)
Parameters	115	342	487
Goodness-of-fit on F^2	0.965	0.982	0.947
$R1[I > 2\sigma I]$	0.0321	0.0263	0.0344
wR_2 (All reflections)	0.0700	0.0670	0.0783
T (K)	203(2)	153(2)	153(2)
Residual electron density ($\text{e}/\text{Å}^3$)	0.223/–0.301	0.517/–0.217	0.827/–0.663

CDCl₃): δ = 12.40 (CH₂CH₃), 47.51 (CH₂CH₃), 121.3, 132.5 (central ring), 124.9, 125.6, 128.9, 138.5 (phenylthio) ppm. MS (70 eV, EI): m/z (%) = 615 (50) [M⁺], 506 (80) [M⁺ - SPh]. MS (70 eV, HR-EI): m/z (%) = 615.2763 (50) [M⁺; ¹²C₃₆¹H₄₅¹⁴N₃³²S₃: 615.2776]; Ammu = -1.3.

5. Crystal structure determinations of 3'd, 7 and 8

Crystal data and details of the structure determinations are listed in Table 1. Reflections were collected for 3'd with a Siemens-Stoe AED2 diffractometer, for 7 and 8 with a Bruker-AXS SMART 1000 diffractometer (Mo K α radiation, λ = 0.71073 Å, graphite monochromator, ω -scan). Empirical absorption corrections were applied. The structures were solved by direct methods and refined by least square methods based on F^2 with all measured reflections (SHELXTL 5.1) [28]. All non-hydrogen atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-256504 (3'd), CCDC-256505 (7), CCDC-256506 (8). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 1223/336033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 623) and the Fonds der Chemischen Industrie.

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