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Inter- versus Intramolecular Cyclobutadiene Complex Formation in the Reaction of 1,6-Cyclodecadiyne Derivatives with $(\eta^5\text{Me}_5\text{C}_5)\text{Co}(\text{C}_2\text{H}_4)_2$

Rolf Gleiter,*[,†] Roland Merger,[†] Hermann Irngartinger,[†] and Bernhard Nuber[‡]

Organisch and Anorganisch Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg, Germany

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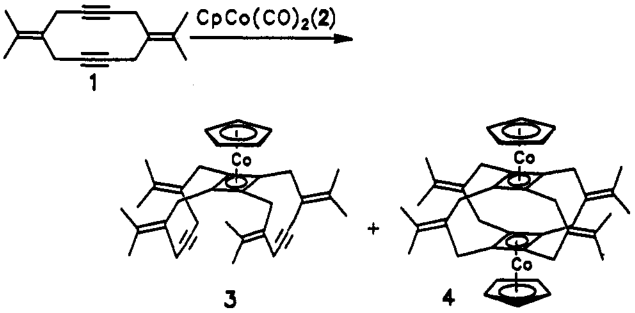
The synthesis of dispiro[2.4.2.4]tetradeca-5,12-diyne (**12**) has been accomplished. X-ray investigations conducted on single crystals of **12** reveal a chair-like 10-membered ring system with a distance of 3.003 Å between the triple bonds. In the case of $\text{Cp*Co(C}_2\text{H}_4)_2$, an intermolecular reaction occurs exclusively, leading to a new superphane of the cyclobutadiene type stabilized by Cp*Co moieties. The distance between the two cyclobutadiene rings is 2.9 Å.

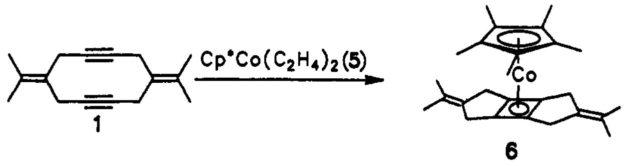
Introduction

Studies by King et al. in the 70's showed that CpCo(CO)_2 reacts with cyclic diacetylenes of ring size C_{12} to C_{14} to yield intramolecular cyclobutadiene derivatives.[1] Our recent studies using medium-sized cyclic diacetylenes (C_{10}, C_{11}) revealed an intermolecular reaction path.[2] As part of these studies we investigated the reaction between 4,9-diisopropylidene-1,6-cyclodecadiyne (**1**) and dicarbonyl(η^5-cyclopentadienyl)cobalt (CpCo(CO)_2) (**2**) in boiling *n*-octane and obtained the intermolecular reaction products **3** and **4**.[3] Different results are obtained, however, when **1** is treated with bis(ethylene)(η^5-pentamethylcyclopentadienyl)cobalt ($\text{Cp*Co(C}_2\text{H}_4)_2$)[4] (**5**) in petroleum ether at 40 °C. In this case, the intramolecular complex **6** is formed in nearly quantitative yield. This difference can be rationalized by invoking several arguments. Since we don't actually know the detailed mechanism, we list two of the possible factors: (a) Formation of a loose coordination with the isopropylidene double bond, a process which seems possible at low temperature. This would favor a "perpendicular approach" of the Co complex. (b) Different substitution mechanism for **2** with tightly bound CO groups as compared to **5** with weakly bound ethylene groups and the electron-rich Cp* ligand. We prefer the first hypothesis because the reaction of 1,6-cyclodecadiyne with **5** at 40 °C gave only minor amounts (1%) of superphane and intramolecular complex.[5] This indicates to us that the double bonds of **1** participate in the reaction with **5**. As a corollary of the first point, we anticipated that sterically demanding groups at the 4 and 9 positions of the 10-membered ring oriented perpendicular to the plane of the triple bonds should instead favor an intermolecular reaction product. These considerations led us to synthesize dispiro[2.4.2.4]tetradeca-5,12-diyne (**12**) and study its reactions with Cp*CoL_2 complexes.

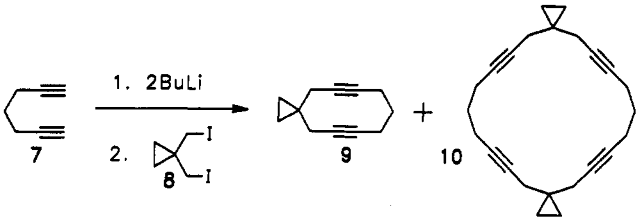
Scheme I



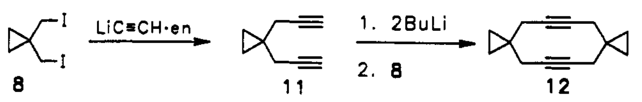
Scheme II



Scheme III



Scheme IV



Synthesis and Properties of Dispiro[2.4.2.4]tetradeca-5,12-diyne (12) and Spiro[2.9]dodeca-5,10-diyne (9)

The synthesis of both spiro systems can be achieved in a straightforward manner as shown in Schemes III and IV. The reaction of the dilithium salt of 1,6-heptadiyne (**7a**) with 1,1-bis(iodomethyl)cyclopropane (**8**)[6] gives spiro[2.9]dodeca-5,10-diyne (**9**) in 22% yield. As a side product we isolated dispiro[2.9.2.9]tetracosa-5,10,17,22-tetrayne

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[†] Organisch Chemisches.

[‡] Anorganisch Chemisches.

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Table I. Averaged Structural Parameters of 12[a]

	distances (Å)	angles (deg)
a	1.515(2)	ab 59.7(3)
b	1.499(5)	bb 60.7(1)
c	1.521(8)	cc 116.5(1)
d	1.473(3)	bc 117.0(3)
e	1.189(8)	cd 112.6(4)
f	3.003(2)	de 171.7(3)

[a] Scatter in parentheses. Standard deviations 0.003–0.004 Å and 0.1–0.2°, respectively. Numbering scheme in Figure 1.

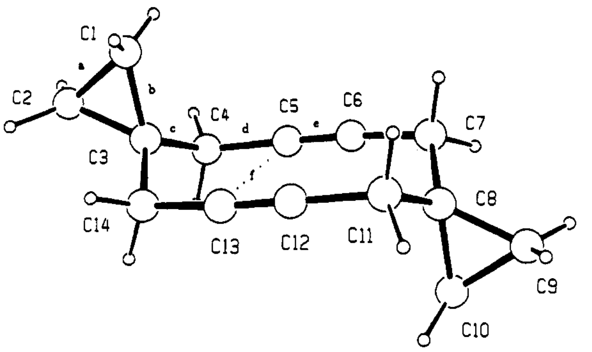
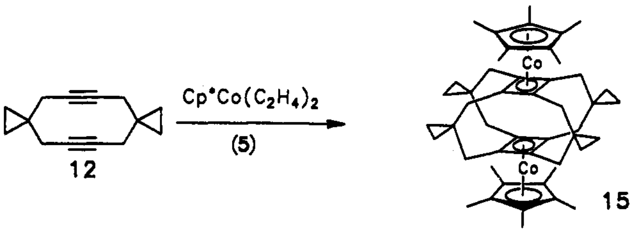


Figure 1. Molecular structure of 12.

Scheme V



(**10**, 3.5%). Similarly, the reaction of 1,1-dipropargylcyclopropane (**11**) (prepared from **8** and lithium acetylide ethylene diamine complex[7]) with **8** yields dispiro[2.4.2.4]-tetradeca-5,12-diyne (**12**) in 12% yield.

It is noteworthy that both strained 10-membered rings are formed in yields above 10%. X-ray investigations conducted on single crystals of **12** reveal a chair conformation in which both triple bonds are arranged parallel to each other and are separated by 3.003 Å. The most relevant bond distances and angles of **12** are given in Table I. The structural parameters of the 10-membered ring are very close to those of 1,6-cyclodecadiyne[8] (Figure 1).

The reaction of **12** with $Cp^*Co(C_2H_4)_2$ at 40 °C gives the superphane **15** (Scheme V) in 10% yield. No intramolecular reaction product could be isolated under these conditions. An X-ray investigation of the superphane **15** reveals two parallel cyclobutadiene units, separated by ca. 2.9 Å. The four bridges adopt a pinwheel conformation (Figure 2) as found in the unsubstituted superphane and in **4**.[2] The two Cp* rings adopt a staggered conformation in the solid state. Selected bond lengths of **15** are listed in Table II. The reaction of **12** with $Cp^*Co(C_2H_4)_2$ is facile (4 h) even at relatively low temperatures as compared to the reaction of **1** with **2** (120 °C, 12 h).

Conclusion

In our work we have shown that 1,1 bis(iodomethyl)-cyclopropane (**8**) is a very good bifunctional component for cyclization reactions. Even strained systems such as 1,6-cyclodecadiyne derivatives can be prepared. This is surprising as one would tend to expect a facile rearrangement.[9] It can therefore be expected that 1,1-bis(iodomethyl)cyclopropane (**8**) can be used for the preparation of a variety of macrocyclic ring systems. This is interesting since the cyclopropane ring is a good precursor for *gem*-dimethyl groups which are quite important for conformational studies.[10]

We have also demonstrated that the course of the reactions of 1,6-cyclodecadiyne systems with $(\eta^5\text{-Me}_5\text{C}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ largely depends on the nature of the substituents at the C-4 and C-9 positions of the ring. Substituents which are capable of coordinating weakly to the cobalt atom can direct the complex fragment to attack the diyne moiety from the "top", thus leading to intramolecular cyclobutadiene formation. However, if the substituents are oriented perpendicular to the plane of the molecule, the "side" attack is sterically favored. Thus, isopropylidene groups at these positions lead to quantitative formation of the intramolecular reaction product, whereas the spirocyclic cyclopropane rings in **12** hinder this reaction pathway leading to the superphane **15**, the product of the side attack, as the only isolable reaction product.

Experimental Section

General. All melting points are uncorrected. The NMR spectra were measured with a Bruker WM 300 spectrometer (^{1}H NMR at 300 MHz and ^{13}C NMR at 75.47 MHz) using $CDCl_3$ as solvent. The mass spectra refer to data from a Vakuum Generators ZAB instrument (EI, 100 eV), while IR spectra were recorded with Perkin-Elmer 580B and Beckmann 4200 instruments.

X-ray Analyses. For the structure analysis, crystals of **12** (colorless needles) from toluene and **15** (yellow prisms) from chloroform were obtained. The data of **12** were collected on a CAD 4 Enraf-Nonius diffractometer using Mo K_α radiation (graphite monochromator, ω–2θ scan), and Lorentz and polarization corrections were applied.[11] The data for **15** were collected on a Siemens-Stoe diffractometer (AED 2) using Mo K_α radiation (graphite monochromator, ω–2θ scan), and Lorentz and polarization corrections were applied. Due to the unfortunate presence of disordered $CHCl_3$ solvent in the crystal, the structural result is not as precise as might be desired. Nevertheless, the bonding parameters of **15** are reasonable within the estimated error limits and clearly define the general structural nature of the molecule in the solid state. The structures of **12** and **15** were solved by direct methods and refined by full-matrix least-squares procedures on F with anisotropic thermal parameters for the carbon and cobalt atoms. The positions of the hydrogen atoms were calculated according to stereochemical requirements and were refined isotropically.[11] For the crystallographic calculations on **12** and **15** the SHELXS-86[12] and the SHELXTL PLUS (Jan 1989)[13] program packages were used, respectively.

$(\eta^5$-Pentamethylcyclopentadienyl)[(1,2:6,7-η)-4,9-diisopropylidenetricyclo[5.3.0.$0^{2,6}$]deca-1^7,2^6-diene]cobalt (6). A mixture of the diyne **1** (212 mg, 1 mmol), bis(ethylene)(η^5-pentamethylcyclopentadiene)cobalt (**5**) (250 mg, 1 mmol) and dry, degassed petroleum ether (20 mL, bp 40–65 °C) was stirred

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[11] The authors have deposited tables of crystallographic refinement parameters, atomic coordinates, and thermal parameters of **12** and **15** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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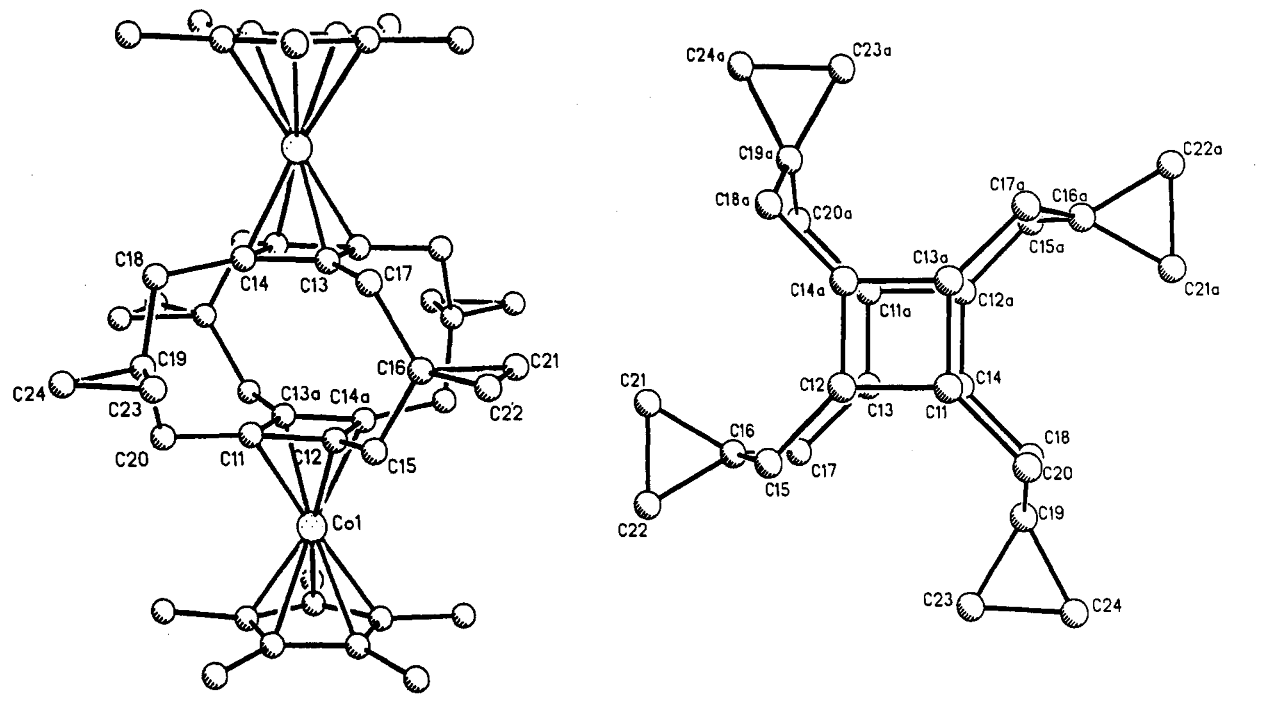

Figure 2. Molecular structure of **15**; side view (left) and top view without the Cp*Co units (right). The hydrogen atoms are omitted.

Table II. Selected Geometrical Parameters of 15[a]

Bond Distances (Å)			
Co1–C11	1.976(4)	C16–C22	1.505(15)
Co1–C12	1.997(13)	C21–C22	1.491(19)
Co1–C13a	1.974(13)	C16–C17	1.481(14)
Co1–C14a	1.976(14)	C14–C18	1.513(19)
C11–C12	1.470(18)	C18–C19	1.522(19)
C12–C14a	1.468(17)	C19–C23	1.495(15)
C11–C13a	1.470(18)	C23–C24	1.502(18)
C13a–C14a	1.451(17)	C19–C24	1.510(20)
C12–C15	1.500(14)	C19–C20	1.537(7)
C15–C16	1.513(20)	C11–C20	1.522(20)
Bond Angles (deg)			
C11–Co1–C14a	62.5(6)	C12–C11–C13a	90.8(11)
C12–Co1–C14a	43.1(5)	C21–C16–C22	59.8(9)
C15–C16–C22	114.1(11)	C15–C16–C17	119.7(10)
C12–C15–C16	114.9(11)	C11–C12–C15	134.9(12)
C11–C12–C14a	88.5(9)		

[a] For the numbering of the atoms, see Figure 2.

at 40 °C under argon for 1 h. After cooling to room temperature, the mixture was filtered through a small amount of Al$_2$O$_3$(3), whereupon the solvent was removed: yield 400 mg (96%); yellow crystals; mp 201 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.62 (d, ^2J = 19 Hz, 4 H) and 2.50 (d, ^2J = 19 Hz, 4 H) (AB-signal); 1.67 (s, 15 H, CpCH$_3$); 1.66 (s, 12 H, (CH$_3$)$_2$C=); ^{13}C NMR (75.46 MHz, CDCl$_3$) δ 138.6(s), 124.1(s), 87.9(s), 75.4(s), 30.0(t), 21.5(q), 8.9-(q); IR (KBr) 2850, 2810, 2770, 2718, 1367 cm^{-1}; MS (EI) M$^+$ = 406. Anal. Calcd for C$_{26}$H$_{35}$Co: C, 76.82; H, 8.68. Found: C, 76.74; H, 8.78.

Spiro[2.9]dodeca-5,10-diyne (9). To a cooled solution (−70 °C) of 1,6-heptadiyne (2.3 g, 25 mmol) in absolute THF (150 mL) was added *n*-butyllithium (31.2 mL, 50 mmol, 1.6 M in hexane) under argon. After the solution was stirred for 10 min, 1,1-bis(iodomethyl)cyclopropane (**8**) (8.05 g, 25 mmol) was added at −70 °C. The mixture was then warmed to +65 °C and stirred for 100 h. After the mixture had been cooled to room temperature, a concentrated solution of NH$_4$Cl in water (50 mL) was added. The layers were separated and the aqueous phase was extracted with CH$_2$Cl$_2$ (3 × 100 mL). The organic phases were dried (MgSO$_4$) and the solvent was removed. The residue was preadsorbed on silica gel and chromatographed (silica gel/CCl$_4$). The fraction with the product exhibiting a R_f value (silica/CCl$_4$) of 0.15 was collected and concentrated. Distillation (Kugelrohr, 150 °C/0.1 torr) yielded 830 mg (21%) of **9** as colorless crystals: mp 130 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.27–2.32 (m, 4 H), 2.1 (s, br, 4 H), 1.66–1.74 (m, 2 H), 0.41 (s, 4 H); ^{13}C NMR (75.46 MHz, CDCl$_3$) δ 83.0 (s), 81.9 (s), 29.0 (t), 19.8 (t), 17.6 (s), 13.3 (t); IR (KBr) 2272, 2214 cm^{-1}. Anal. Calcd for C$_{12}$H$_{14}$ (158.24): C, 91.08; H, 8.92. Found: C, 91.31; H, 8.97.

Dispiro[2.9.2.9]tetracosa-5,10,17,22-tetrayne (10). The remainder from the Kugelrohr distillation of **9** was recrystallized from petroleum ether/ethyl acetate (1:2) to yield 140 mg (3.5%) of **10** as colorless crystals: mp 116 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.33 (tt, ^3J = 6.7 Hz, ^5J = 2.2 Hz, 8 H); 2.28 (t, J = 2.2 Hz, 8 H); 1.66 (quint, J = 6.7 Hz, 4 H); 0.44 (s, 8 H); ^{13}C NMR (75.47 MHz, CDCl$_3$) δ 80.5 (s), 78.7 (s), 27.6 (t), 18.5 (t), 17.7 (t), 11.4 (t); IR (KBr) 2936, 2924, 2910, 1418, 1289, 1012 cm^{-1}; HRMS (EI) calcd for C$_{24}$H$_{28}$ 316.2191, found 316.2152.

1,1-Dipropargylcyclopropane (11). 1,1-Bis(iodomethyl)-cyclopropane (77 g, 0.24 mol) was added to a stirred mixture of lithium acetylide–ethylenediamine complex (50 g (95%), 0.52 mol) and 200 mL of DMSO at 8 °C under argon. After the addition was complete, the mixture was stirred at room temperature for 2 h, whereupon it was poured onto ice. The resulting mixture was extracted with five 100-mL portions of petroleum ether (bp 30–40 °C), and the organic layers were combined, dried over MgSO$_4$, and concentrated. The residue was then distilled under vacuum: yield 8 g (28%), colorless liquid; bp 48 °C/16 torr; ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.37 (d, J = 2.6 Hz, 4 H), 1.98 (t, J = 2.6 Hz, 2 H), 0.54 (s, 4 H); ^{13}C NMR (75.47 MHz, CDCl$_3$) δ 82.6(s), 69.5 (d), 25.8 (t), 17.4 (s), 10.4 (t); IR (neat) 3294, 2112 cm^{-1}; HRMS (EI) calcd. for C$_9$H$_{10}$: 118.0782; found 118.0758.

Dispiro[2.4.2.4]tetradeca-5,12-diyne (12). To a cooled solution (−70 °C) of 1,1-dipropargylcyclopropane (**11**) (2.95 g, 25 mmol) in absolute THF (200 mL) was added *n*-butyllithium (31.2 mL, 50 mmol, 1.6 M in hexane). After completion, 1,1-bis(iodomethyl)cyclopropane (**11**) (8.05 g, 25 mmol) was added at −70 °C whereupon the mixture was refluxed for 120 h. The workup followed the procedure given for **10**. Kugelrohr distillation (160 °C/0.01 torr) and subsequent recrystallization from toluene yielded 552 mg (12%) of **12** as colorless crystals, mp 220 °C dec; ^{1}H NMR (300 MHz), CDCl$_3$) δ 2.15 (s, 8 H), 0.46 (s, 8H); ^{13}C NMR (75.47 MHz, CDCl$_3$) δ 81.7 (s), 25.7 (t), 17.8 (s), 13.3 (t); IR (KBr) 2276, 2211 cm^{-1}. Anal. Calcd for C$_{14}$H$_{16}$ (184.28): C, 91.25; H, 8.75. Found: C, 91.51; H, 8.79.

Superphane 15. A solution of the diyne **12** (147 mg, 0.8 mmol) and bis(ethylene)(η^5-pentamethylcyclopentadiene)cobalt (**5**) (200 mg, 0.8 mmol) in dry, degassed petroleum ether (20 mL, bp 40–65 °C) was stirred at 40 °C under argon for 4 h. After removal of the solvent, the dark residue was chromatographed on Alox-(III) (neutral, 6 g water, 94 g of Al$_2$O$_3$) with petroleum ether (bp

30–40 °C). A yellow zone on the column (R_f: 0.3 on Alox(III)/petroleum ether) was isolated. The removal of the solvent yielded 60 mg (10%) of **15**. Recrystallization from petroleum ether: mp > 250 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.83 (s, 16 H), 1.65 (s, 30 H), 0.31 (s, 16 H); ^{13}C NMR (75.46 MHz, $CDCl_3$) δ 86.8, 73.8, 35.8, 18.9, 15.7, 9.0; HRMS (EI) calcd. for $C_{38}H_{62}Co_2$: 756.3516. Found: 756.3483, m/z (rel inten) 756 (M^+, 100), 562 (M – Cp*Co, 18) 561 (44); IR (KBr) 2900, 1419, 1258, 1005, 938 cm^{-1}.

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