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An alternative synthesis of Vollhardt's [1,2-diethynyl-3,4-bis(trimethylsilyl)cyclobutadiene]cyclopentadienylcobalt and selective formation of its dimer

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Abstract

Coupling of bistrimethylsilylpropargylic alcohol over $CpCo(CO)_2$ to give the respective *ortho* and *para* bishydroxymethyl substituted cyclobutadiene complexes is reported. The trimethylsilyl groups have a stereo directing effect furnishing an 8: 1 ratio of *ortho*/*para*. Transformation of the hydroxymethyl groups leads to the formation of the title compound [1,2-diethynyl-3,4-bis(trimethylsilyl)cyclobutadiene]cyclopentadienylcobalt © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkynes; Cobalt; Cyclobutadiene complexes; Hydrogen bonding

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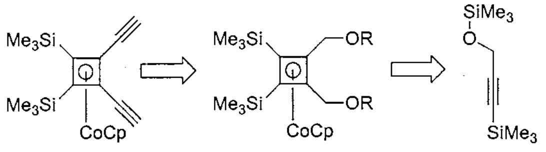
1. Introduction

Multiply ethynylated π-complexes are fascinating and useful building blocks for the synthesis of novel carbon-rich organometallic molecules and materials. These include, but are not restricted to star-shaped arrays [1], organometallic dehydroannulenes [2], rigid linear oligomers and novel liquid-crystalline polymers [1]. The first diethynylated π-complex reported was [1,2-diethynyl-3,4-bis(trimethylsilyl)cyclobutadiene]cyclopentadienylcobalt **1**, prepared by Vollhardt in 1979 through codimerization of 1,6-bis(trimethylsilyl)hexatriyne with bis(trimethylsilyl)acetylene over $CpCo(CO)_2$ [3]. While this reaction works very well for the preparation of small amounts of **1**, attempts to scale up the CpCo coupling reaction was met with limited success only. The yield of **1** is diminished greatly. Its usefulness as starting material [4] however demands larger amounts of **1** to be accessible. We therefore set out to develop a complementary synthetic route to **1**.



1 **2** **3**

Hydroxymethyl groups have been transformed into alkyne functionalities efficiently. Insofar, retrosynthetic analysis suggested to use [1,2-bis(hydroxymethyl)-3,4-bis(trimethylsilyl)cyclobutadiene]cyclopentadienylcobalt **2** as intermediate. Substituted alkynes form CpCo-stabilized cyclobutadienes easily when reacted with $CpCo(CO)_2$ at elevated temperatures. It was expected that **2** and **4** would form by dimerization of **3** over $CpCo(CO)_2$.

2. Results and discussion

Reaction of two equivalents of **3** with $CpCo(CO)_2$ for 4 h in refluxing decane under constant nitrogen purge and subsequent desilylation with potassium carbonate

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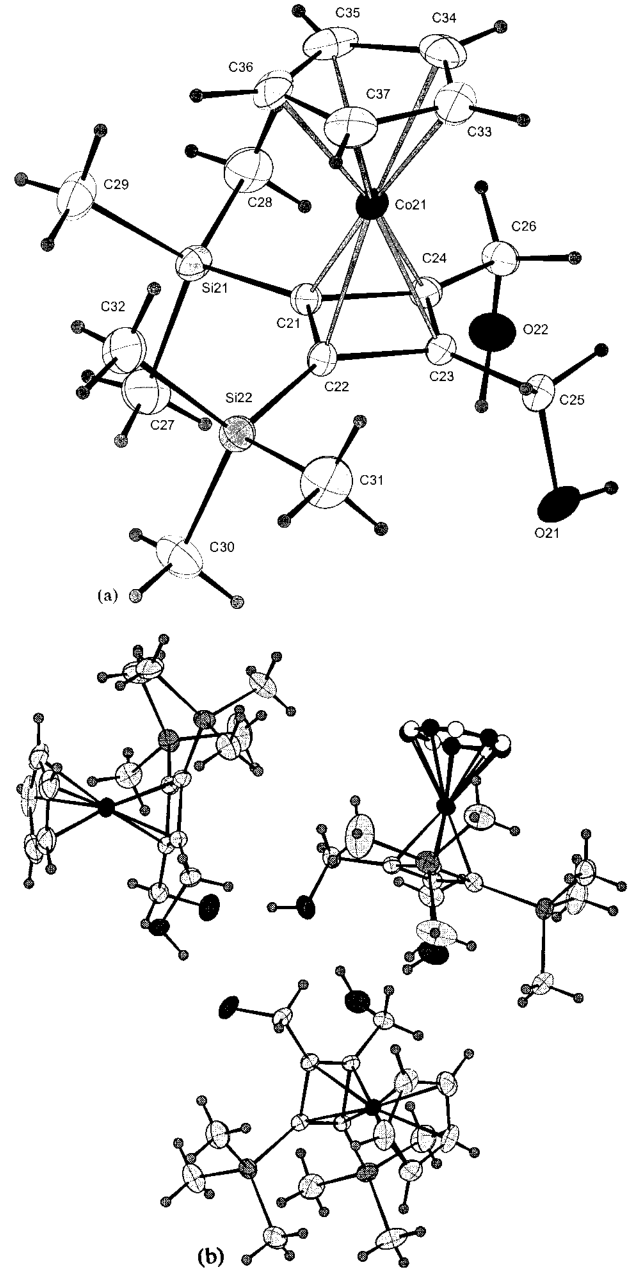


Fig. 1. (a). Molecular structure of **2b**. (b) Packing diagram of **2b**.

furnished two cyclobutadiene complexes, **2b** (60%) and **4b** (8%). The stereochemical course of the dimerization is obscure but can be inferred from the NMR spectra of the products **2b** and **4b**. While **2b** shows a doublet of doublet for the CH_2OH-groups (the protons are diastereotopic) in **4b** due to symmetry only one singulet is observed for the methylenes.

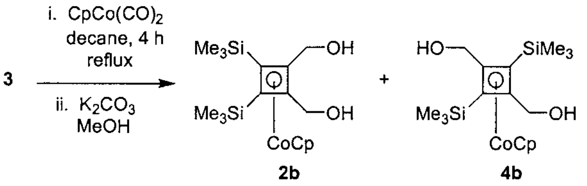
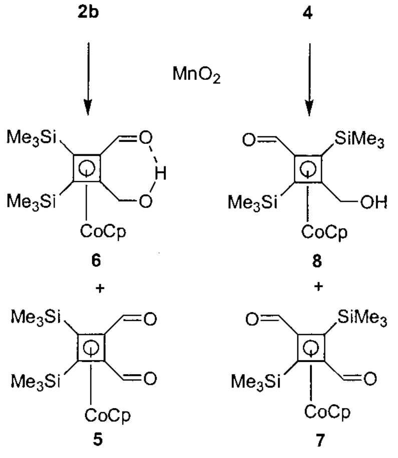


Table 1
Selected bond lengths and angles of **2b**

Atom	Bond length (Å)	Atom	Bond angle (°)
Co(21)–C(33)	2.064(6)	C(21)–Co(21)–C(22)	44.1(2)
Co(21)–C(35)	2.037(6)	C(21)–Co(21)–C(23)	63.2(2)
Co(21)–C(21)	1.979(5)	C(22)–Co(21)–C(23)	43.2(2)
C(21)–C(22)	1.490(7)	C(21)–Co(21)–C(33)	174.0(2)
C(21)–C(24)	1.475(6)	C(22)–Co(21)–C(33)	138.2(3)
C(22)–C(23)	1.466(6)	C(23)–Co(21)–C(33)	114.2(2)
C(23)–C(24)	1.451(7)	C(24)–Co(21)–C(33)	130.5(2)
C(24)–C(26)	1.485(7)		
Si(21)–C(21)	1.851(5)		
O(21)–C(25)	1.431(6)		
O(22)–C(26)	1.442(6)		

To establish the stereochemistry, single crystals of **2b** were grown [5]. Fig. 1(a) shows the ORTEP-plot of the molecular structure. Bond angles and distances (Table 1) are in excellent agreement with literature values [1,2,4]. Fig. 1(b) displays the unusual packing behavior of this amphiphilic compound. Four molecules of **2b** form a hydrogen-bonded, almost micellar tetramer in the solid state, with the lipophilic TMS groups pointing outwards.

The observed stereochemistry, i.e. the predominance of *ortho*-hydroxymethyl substituted **2b** is not completely unprecedented. A similar stereo-directing effect has been found by Brisbois, who noticed that trimethylsilyl-alkyl substituted diynes form *ortho*-substituted cyclobutadienes when reacted with $CpCo(CO)_2$, while ester substituents are strongly *para*-directing [6]. However, 1,4-bis(trimethylsilyl)butadiyne [3] and 1,5-bistrimethylsilyl-(3-thia-1,4-pentadiyne) [7] both furnish cyclobutadiene complexes with an exclusive *para*-substitution pattern. Viewed critically, there is no satisfying explanation for the observed stereochemistry. If instead of trimethylsilyl groups tri*iso*propylsilyl groups are used in **3**, the unreacted alkyne is reisolated, indicating that the *para*-substitution pattern can not be forced upon the system **2b**/**4b** by increasing the steric bulk of the participating alkynes.



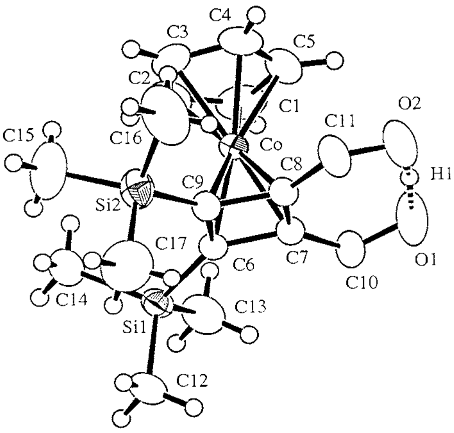
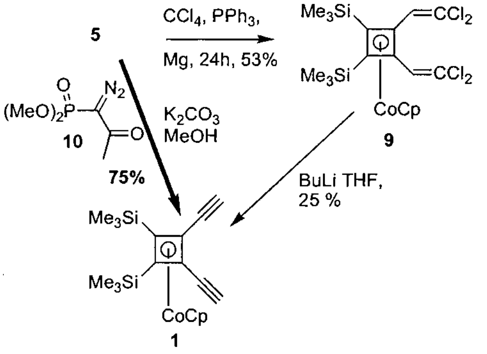


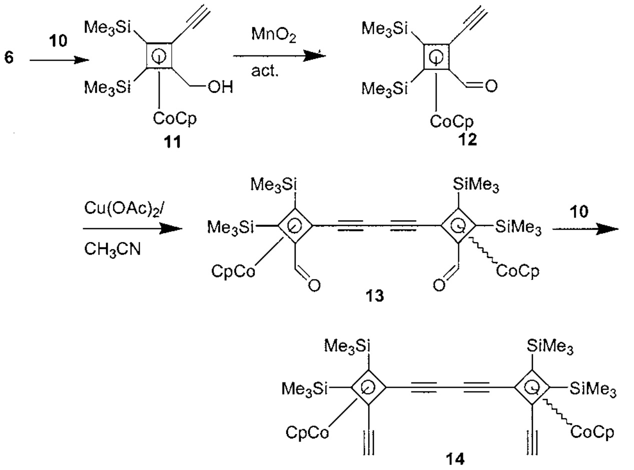
Fig. 2. ORTEP-plot of **6**.

To transform the hydroxymethyl groups of **2b** into the alkyne units of **1**, the stage of **5** had to be traversed. Oxidation of **2b** with MnO_2 led to the isolation of a 58% yield of the monoaldehyde **6** and 18% of the dialdehyde **5**. Longer reflux time in dichloromethane (48 h) made **5** accessible in 39% isolated yield. The *para*-isomer **4b** was oxidized under similar conditions to give **7** in 60% and 13% of the *para*-monoaldehyde **8**. A single crystal structure (Fig. 2) was obtained from a suitable specimen of **6** [8]. In this structure no *inter*molecular hydrogen bonding motif occurs, but strong *intra*molecular hydrogen bonding is visible. The hydroxyl proton is located symmetrically between the aldehyde and the hydroxyl oxygen (Table 2). The structure is disordered, aldehyde and hydroxyl groups cannot be discriminated.



Our first attempt to convert **5** into **1** involved the transformation of the dialdehyde into the tetrachloride **9** in a Corey–Fuchs type reaction [9]. Addition of carbon tetrachloride, triphenylphosphine and magnesium to **5** furnished **9** in 53%. Treatment of **9** with BuLi in THF rendered **1** but only 25%, by far not enough to be of synthetic value.

Treatment of aldehydes with dimethyl-(1-diazo-2-oxopropyl) phosphonate **(10)** in the presence of a base renders the corresponding one-carbon elongated alkynes in high yield. This approach is attractive because it is a one step process [10]. Consequently, reaction of **10** with **5** in the presence of potassium carbonate provides **1** in 75%. Even the unprotected monoaldehyde **6** was transformed into the corresponding monoyne **11** in 63% yield. Surprisingly, the hydroxyl group did not interfere with the alkynylation reaction, so that its protection was unnecessary. The alkyne **11** is stable under ambient conditions and does not display any proclivity for the addition of the hydroxyl group through the alkyne. The monoyne **11** was oxidized with activated manganese dioxide to furnish **12** in 50% yield. Unfortunately we were not able to obtain NMR spectroscopic data of **12**, due to the presence of a paramagnetic impurity. Coupling of **12** under Vögtle conditions [11] gave rise to the formation of a dark garnet-colored material, **13**. This dialdehyde again displayed extremely broad signals in its ^1H- and ^{13}C-NMR spectra rendering its identification difficult. Treatment of **13** however with an excess of the diazophosponate **10** in methanolic potassium carbonate solution gave rise to the formation of a yellow crystalline material which displayed one sharp Cp signal in its ^1H-NMR spectrum and a singlet at 2.78 ppm (ratio 5: 1) attributed to alkyne protons. Diyne **14** had formed in 76% yield. The ^{13}C-NMR spectrum displays a double set of resonances, which indicates that two diastereomers of **14** have formed, as would be expected. The diyne **14** is a valuable starting material for the synthesis of organometallic dehydroannulenes consisting of cyclobutadiene complexes and butadiyne units.



In conclusion we have demonstrated that protected propargylic alcohols undergo dimerization to the corresponding bis(hydroxymethyl) substituted cyclobutadiene complexes **2b** and **4b** in good yields. The *ortho*/*para*-ratio of this reaction is 8:1, favoring the sterically more encumbered *ortho*-isomer **2b**. The major isomer **2b** was converted either into **1** or the diyne **14** by the utilization of a oxidation/alkynylation sequence.

Table 2
Selected bond angles and distances of **6**

Bond lengths involving non-hydrogen atoms (Å)		Bond angles (°)		Bond lengths involving hydrogen atoms (Å)	
CoC(1)	2.049(4)	C(1)–Co–C(2)	40.2(2)	O(1)H(1)	1.36(9)
CoC(6)	1.995(4)	C(1)–Co–C(8)	147.3(2)	O(2)H(1)	1.42(9)
Si(1)C(6)	1.866(4)	Co–C(8)–C(11)	123.8(3)	C(1)H(2)	0.939
O(1)C(10)	1.298(5)	Co–C(9)–Si(2)	127.4(2)		
O(2)C(11)	1.327(5)	C(8)–Co–C(9)	43.5(2)		
C(8)C(11)	1.482(6)	O(2)–C(11)–C(8)	116.7(4)		
		O(1)–C(10)–C(7)	118.2(4)		

3. Experimental

3.1. General procedures

THF was distilled freshly from sodium benzophenone, hexane was distilled over a vigreux column prior to use. All other reagents were of commercial grade and used as obtained. Literature methods were used for the preparation of bis(trimethylsilyl)propargylic alcohol (**3**) and dimethyl-(1-diazo-2-oxopropyl) phosphonate (**10**) [10].

^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ or Benzene-d_6 on a Bruker AM 300 or a Varian Mercury 400 spectrometer. The mass spectra were measured on a VG 70SQ. IR spectra were obtained with a Perkin–Elmer FTIR 1600 on NaCl-plates. X-ray structure analysis of **6** was carried out on a Rigaku AFC6S fully automated four-circle diffractometer using graphite-monochromated Mo-Kα radiation at 20°C, and that of **2b** on a Nonius KCCD diffractometer using Mo-Kα radiation.

3.2. Reaction of bis(trimethylsilyl)propargylic alcohol with $CpCo(CO)_2$

Bis(trimethylsilyl)propargylic alcohol, **3** (15.0 g, 75.0 mmol) and $CpCo(CO)_2$ (6.75 g, 37.5 mmol) were dissolved in 100 ml of *n*-decane and refluxed for 4 h. A constant flow of nitrogen was led through the solution. Following the removal of the solvent by distillation (10^{-1} Torr, 35°C) the residue was redissolved in hexane and doubly chromatographed on Celite/silica gel to furnish **2a** (8.59 g, 60%) and **4a** (1.20 g, 8%) as highly viscous, tan colored oils. **2a**: ^{1}H-NMR ($CDCl_3$) δ 4.76 (s, 5 H, Cp–H), 3.99–4.09 (dd, 4 H, J = 12.12 Hz, CH_2), 0.12 (s, 18 H, OTMS), 0.09 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$): δ 79.1 (5 C, Cp–C), 89.2, 67.1 (4 C, cyclobutadiene–C), 58.8 (4 C, CH_2), 0.86, 0.02 (12 C, TMS–C); IR ν 2956, 2898, 1479, 1247, 842, 807, 752, 689 cm^{-1}; MS (EI) *m*/*z* Calc. for M^+ ($C_{23}H_{45}O_2CoSi_4$) 524.10, Found 524. **4a**: ^{1}H-NMR ($CDCl_3$) δ 4.76 (s, 5 H, Cp–H), 3.92 (s, 4 H, CH_2), 0.14 (s, 18 H, OTMS), 0.06 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$) δ 87.0 (2 C, cyclobutadiene–C), 79.2 (5 C, Cp–C), 60.3 (4C, CH_2), 0.47, −0.46 (12 C, TMS–C); IR ν 2956, 2898, 1457, 1249, 841, 806, 754, 689 cm^{-1}; MS (EI) *m*/*z* Calc. for M^+($C_{23}H_{45}O_2CoSi_4$) 524.10, Found 524.

3.3. General procedure for the deprotection of **2a** and **4a**

In a round bottomed flask, the protected complex **2a**, respectively **4a**, K_2CO_3 and 20 ml of methanol were dissolved at ambient temperature. After stirring for 30 min the solutions were filtered through Celite, dried over $MgSO_4$ and concentrated in vacuo. **2b**: Desilylation was carried out with 8.59 g of **2a** (16.4 mmol) and 50 mg of K_2CO_3 (0.36 mmol). **2b** was obtained as yellow crystals in quantitative yield (6.23 g, 99%). ^{1}H-NMR ($CDCl_3$) δ 4.86 (s, 5 H, Cp–H), 4.01–3.87 (dd, 4 H, *J* = 12.7 Hz, CH_2), 0.13 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$) δ 88.3, 66.9 (4 C, cyclobutadiene–C), 84.1 (5 C, Cp–C), 58.5 (2 C, CH_2), 0.99 (6 C, TMS–C); IR ν 3314, 2954, 2899, 1243, 995, 840, 811, 751, 689 cm^{-1}; m.p. 121°C; MS (EI) *m*/*z* Calc. for M^+ ($C_{17}H_{29}O_2CoSi_2$) 380.10, Found 380; Anal. Calc for $C_{17}H_{29}O_2CoSi_2$: C, 53.68%; H, 7.63%; Found: C, 53.73%; H, 7.64%. **4b**: From 1.20 g **4a** (2.30 mmol) and 50 mg (0.36 mmol) K_2CO_3 0.87 g (99%) of **4b** was obtained as yellow crystals. ^{1}H-NMR ($CDCl_3$): δ 4.88 (s, 5 H, Cp–H), 3.88 (s, 4 H, CH_2), 0.17 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$): δ 88.4, 70.1 (4 C, cyclobutadiene–C), 79.1 (5 C, Cp–C), 60.5 (2 C, CH_2), 0.71 (6 C, TMS–C); IR ν 3250, 2951, 1241, 990, 854, 809, 689 cm^{-1}; m.p. 157 °C; MS (EI) *m*/*z* Calc. for M^+($C_{17}H_{29}O_2CoSi_2$) 380.10, Found 380.

3.4. General procedure for the oxidation of **2b**, **4b** and **12**

Activated MnO_2 (25 g) was added to a solution of the respective alcohols in 250 ml of CH_2Cl_2 and refluxed for 24 h. After cooling, the mixture was filtered over Celite and chromatographed on silica gel using CH_2Cl_2/ethyl ether as eluent. The oxidation of **2b** (3.50 g, 9.20 mmol), followed by chromatography led first to the isolation of the dialdehyde **5** (620 mg, 18%) then to that of the monoaldehyde **6** (1.93 g, 56%). **5**: ^{1}H-

NMR ($CDCl_3$) δ 9.91 (s, 2 H, aldehyde–H), 5.02 (s, 5 H, Cp–H), 0.21 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$) δ 191.8 (2 C, aldehyde–C), 80.2, 81.0 (4 C, cyclobutadiene–C), 80.5 (5 C, Cp–C), 0.94 (6 C, TMS–C); IR ν 2959, 2826, 1652, 1460, 1249, 828, 696 cm^{-1}; m.p. 102 °C; MS (EI) *m*/*z* Calc. for M^+ ($C_{17}H_{25}O_2CoSi_2$) 376.10, Found 376; Anal. Calc. for $C_{17}H_{25}O_2CoSi_2$: C, 54.26%; H, 6.65%; Found: C, 54.26%; H, 7.60%. **6**: ^{1}H-NMR ($CDCl_3$) δ 9.46 (s, 1 H, aldehyde–H), 4.98 (s, 5 H, Cp–H), 3.06–4.15 (q, 2 H, $J = 12.7$ Hz, CH_2), 0.09, 0.01 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$) δ 193.6 (1 C, aldehyde–C) 97.1, 76.2, 74.5, 71.8 (4 C, cyclobutadiene–C), 80.3 (5 C, Cp–C), 58.9 (1 C, CH_2), 1.49, 0.79 (6 C, TMS–C); IR ν 3418, 2955, 1631, 1247, 840, 755, 692 cm^{-1}; m.p. 130 °C; MS (EI): *m*/*z* Calc. for M^+($C_{17}H_{27}O_2CoSi_2$) 378.10, Found 378; Anal. Calc. for $C_{17}H_{27}O_2CoSi_2$: C, 53.97%; H, 7.14%; Found: C, 54.02%; H, 7.11%.

The oxidation of 520 mg (1.37 mmol) of the *para*-diol **4b** furnished first **7** (145 mg, 28%), then **8** (31.0 mg, 6%). **7**: ^{1}H-NMR ($CDCl_3$) δ 9.99 (s, 2 H, aldehyde–H), 4.46 (s, 5 H, Cp–H), 0.11, (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$) δ 191.7 (2 C, aldehyde–C), 81.1, 80.2 (4 C, cyclobutadiene–C), 80.5 (5 C, Cp–C), 1.09 (6 C, TMS–C); IR ν 2958, 2898, 2825, 1667, 1651, 1247, 830, 758, 695 cm^{-1}; MS (EI) *m*/*z* Calc. for M^+($C_{17}H_{25}O_2CoSi_2$) 376.10, Found 376; Anal. Calc. for $C_{17}H_{25}O_2CoSi_2$: C, 54.26%; H, 6.65%; Found: C, 54.29%; H, 6.55%. **8:** ^{1}H-NMR ($CDCl_3$) δ 9.82 (s, 1 H, aldehyde–H), 4.90 (s, 5 H, Cp–H), 4.24 (s, 2 H, CH_2), 0.2, 0.12 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$) δ 195.6 (1 C, aldehyde–C), 81.0, 80.7, 80.2, 67.6 (4 C, cyclobutadiene–C), 81.7 (5 C, Cp–C), 59.6 (1 C, CH_2), 1.87, 1.48 (6 C, TMS–C); IR ν 2954, 2898, 1657, 1246, 842 cm^{-1}; MS (EI) *m*/*z* Calc. for M^+($C_{17}H_{25}O_2CoSi_2$) 378.10, Found 378; Anal. Calc. for $C_{17}H_{25}O_2CoSi_2$: C, 53.97%, H, 7.14%; Found: C, 54.01%; H, 7.17%. **12:** From 464 mg (1.24 mmol) of **11**, 0.23 g of **12** (50%) was obtained after purification with chromatography on silica gel using CH_2Cl_2 as eluent. ^{1}H-NMR ($CDCl_3$) δ 9.63 (s, 1 H, aldehyde–H), 4.94 (s, 5 H, Cp–H), 3.19 (s, 1 H, alkyne–H), 0.19, 0.16 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$) δ 190.4 (1 C, aldehyde–C), 80.9 (5 C, Cp–C), 80.6, 79.6, (2 C, alkyne–C), 85.6, 79.3, 73.3, 68.3 (4 C, cyclobutadiene–C), 0.86, 0.46 (6 C, TMS–C); MS (EI) *m*/*z* Calc. for M^+ ($C_{18}H_{25}OCoSi_2$) 372.10, Found 372.

3.5. *Synthesis of [(η^4-C)-1,2-(bistrimethylsilyl)-3,4-($CHCCl_2$)$_2$]Co(η^5-C_5H_5)* **9**

Triphenylphosphine (1.05 g, 3.99 mmol) and CCl_4 (310 mg, 2.00 mmol) were dissolved in 5 ml of THF. After stirring for 2 h at room temperature, 48.0 mg (1.96 mmol) Magnesium was added and after stirring for an additional 30 min, 250 mg (0.66 mmol) of **5** were added to the dark mixture. After 18 h the reaction mixture was filtered over silica gel/$MgSO_4$ (1:1). For further purification the crude product was chromatographed over silica gel with hexane to yield **9** (177 mg, 53%). ^{1}H-NMR ($CDCl_3$) δ 6.28 (s, 2 H, vinyl-H), 4.89 (s, 5 H, Cp–H), 0.16 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$) δ 127.1 (2 C, vinyl–C), 80.4 (5 C, Cp–C), 0.99 (6 C, TMS–C); IR ν 2955, 2899, 1600, 1441, 1247, 855, 840, 812 cm^{-1}; MS (EI): *m*/*z* Calc. for M^+($C_{19}H_{25}CoSi_2Cl_4$) 510.32, Found 510.

3.6. *Synthesis of 1,2-diethynyl(cyclobutadiene)-cyclopentadienyl-cobalt* **1**

A total of 1.24 g (2.43 mmol) of **9** was dissolved in 100 ml THF and cooled to −78°C. After the dropwise addition of 13.4 ml (21.4 mmol) *n*-BuLi the mixture was allowed to warm to room temperature and stirring was continued for an additional hour. After aqueous workup and concentration of the organic extracts in vacuo the product **1** was chromatographed on silica gel with hexane for further purification. The product was obtained as yellow crystalline material (216 mg, 25%) after removal of solvent. **1**: ^{1}H-NMR ($CDCl_3$) δ 4.91 (s, 5 H, Cp–H), 3.15 (s, 2 H, alkyne–H), 0.17 (s, 18 H, TMS–H).

3.7. *General procedure for the synthesis of 1,2-diethynyl(cyclobutadiene)- cyclopentadienyl-cobalt* **1**, *1-ethynyl-2-methanoyl(cyclobutadiene)cyclopentadienyl-cobalt* **11** *and α-ethynyl-ω-[(2-ethynyl-3,4-bis(trimethylsilyl)cyclobutadiene-1-yl) (cyclopentadienyl)cobalt]-{[1,2-(3,4-bis(trimethylsilyl)(cyclobutadieneylene) (cyclopentadienyl)cobalt](butadiyn-1,4-diyl)* **14**

To 1 eq. of the respective aldehydes in 5 ml of methanol were added 2 eq. of dimethyl-(1-diazo-2-oxopropyl)phosphonate (**10**) and 2.5 eq. of K_2CO_3 successively at 0°C. The reaction mixture was allowed to warm to room temperature overnight and then partitioned between saturated aqueous $NaHCO_3$ and CH_2Cl_2. The combined extracts were dried and after concentration chromatographed on silica gel with hexane/acetone mixtures. **1:** Following the general procedure 215 mg (0.56 mmol) of **5** were dissolved in 5 ml of methanol. Chromatography with hexanes furnished **1** (148 mg, 75%); ^{1}H-NMR ($CDCl_3$) δ 4.91 (s, 5 H, Cp–H), 3.15 (s, 2 H, alkyne–H), 0.17 (s, 18 H, TMS–H). **11:** In analogy to the general procedure 1.11 g (2.94 mmol) of **6** were used to furnish 710 mg, (63%) of **11** after purification; ^{1}H-NMR ($CDCl_3$) δ 4.9 (s, 5 H, Cp–H), 4.08 (m, 2 H, CH_2), 3.09 (s, 1 H, alkyne–H), 0.21, 0.13 (s, 18 H, TMS–H); ^{13}C-NMR ($CDCl_3$) δ 91.4, 70.6, 69.0, 64.4 (s, 4 C, cyclobutadiene–C), 81.0, 79.3 (s, 2 C, alkyne–C), 80.4 (s, 5 C, Cp–C), 0.9, 0.8 (s, 6 C, TMS–C); IR ν 3308, 2955, 1246, 1164, 1002, 842, 811, 753 cm^{-1}; MS (EI): m/z Calc. for M$^+$ ($C_{18}H_{27}OCoSi_2$) 374.52, Found 374; Anal. Calc. for $C_{17}H_{27}OCoSi_2$: C, 57.75%; H, 7.22%; Found: C, 57.84%; H, 7.26%. **14:** According to the general procedure 80.0 mg (0.11 mmol) of **13** were dissolved in methanol. Chromatography of **14** was carried out with hexanes/acetone (6%) to yield 76% (60 mg); ^{1}H-NMR (C_6D_6) δ 4.68 (s, 10 H, Cp-H), 2.78 (s, 2 H, alkyne–H), 0.15, 0.14, 0.13 (s, 36 H, TMS–H); ^{13}C-NMR (C_6D_6) δ 81.4, 81.4 (d, 10 C, Cp–C), 80.4, 80.3, 80.2, 80.2, 80.2, (s, 8 C, alkyne–C), 77.9, 77.8, 73.2, 73.1, 73.0, 68.2, 68.1, 67.0, 66.9 (s, 8 C, cyclobutadiene–C), 0.13, 0.10 (s, 12 C, TMS–C); IR ν 3310, 2955, 2898, 2094, 1247, 1167, 1108, 843, 813, 752 cm^{-1}; MS (EI): m/z Calc. for M$^+$($C_{38}H_{48}Co_2Si_4$) 734.9, Found 734.0; Anal. Calc. for $C_{38}H_{48}Co_2Si_4$: C, 62.13%; H, 6.54%; Found: C, 62.21%; H, 6.55%.

*3.8. Coupling of **12** to **13***

$Cu(OAc)_2$ (1.46 g, 8.01 mmol) and 0.20 g (60.0 mmol) **12** were dissolved in 100 ml of acetonitrile and refluxed for 5 h. After aqueous workup and concentration of the organic extracts in vacuo the residue is chromatographed on silica gel with CH_2Cl_2 to yield **13** (110 mg, 55%). **13:** ^{1}H-NMR (C_6D_6) δ 9.69 (s, 2 H, aldehyde–H), 5.03 (s, 10 H, Cp–H), 0.25, 0.21 (s, 36 H, TMS–H); ^{13}C-NMR (C_6D_6) δ 190.3 (s, 2 C, aldehyde–C), 81.0 (s, 10 C, Cp–C), 79.2, 78.2, 74.9, 68.0 (s, 4 C, cyclobutadiene–C), 0.8, 0.5 (s, 12 C, TMS–C); MS (EI): m/z Calc. for M$^+$($C_{36}H_{48}O_2Co_2Si_4$) 742.98, Found 742; Anal. Calc. for $C_{36}H_{48}O_2Co_2Si_4$: C, 58.22%; H, 6.47%; Found: C, 58.29%; H, 6.54%.

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[5] Crystal data for **2b**: monoclinic, $C2/c$ $a = 63.539(1)$ $b = 9.5030(1)$ $c = 30.2495(5)$ $\beta = 115.873(3)$, $V = 16434.1$, Dx 1.230, μ 9.510 cm^{-1}, 17773 unique reflections measured, 11417 observed. No absorption correction, structure was solved by heavy atom method (Dirdif), Refinement on F, with anisotropic temperature factors for Co, Si, O, C, except for the disordered cp rings which were refined with one common isotropic temp. factor for each ring; H atoms were refined with fixed isotropic TF in the riding mode. Final $R = 0.059$, $R_w = 0.064$. Further details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre on quoting the names of the authors, and the journal citation.

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[8] Crystal data for **6**: monoclinic, $P2_1/c$ $a = 8.662(9)$ $b = 10.817(9)$ $c = 21.46(2)$ $\beta = 98.52(8)$, $V = 1988.7$, Density 1.265, μ 9.877 cm^{-1}, 2236 reflections measured. Final $R = 0.038$, $R_w = 0.045$. Further details of the crystal structure investigation may be obtained from the Cambridge Crystallographic Data Centre on quoting the depository number CCDC 102511, the names of the authors, and the journal citation.

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