Oligoalkyne-Bridged (η^4-Cyclobutadiene)(η^5-cyclopentadienyl)cobalt Fragments − Syntheses and Properties

Joerg Classen,[a] Rolf Gleiter,*[a] and Frank Rominger[a]

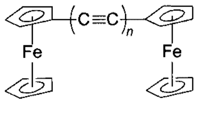
Dedicated to Professor Dwaine O. Cowan

Keywords: Alkynes / Conjugation / Electron transfer / Rod-like molecules / Cobalt

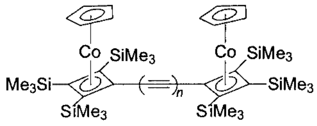
The syntheses of (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt units bridged by buta-1,3-diyne, octa-1,3,5,7-tetrayne, and dodeca-1,3,5,7,9,11-hexayne units (**15**, **18**, **21**) are reported. All three species could be obtained by Hay coupling of the corresponding mono-, di-, and triyne units **14**, **17**, and **20**. In the case of **14–17** and **21**, the molecular structures were confirmed on the basis of X-ray studies on single crystals. Cyclic voltammetry revealed a weak interaction between the metal centers of **15** and no interaction between the metal centers of **18** and of **21**.

Introduction

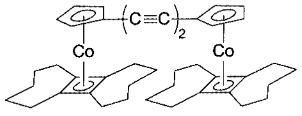
Transition metal complexes with two redox centers are of current interest in basic and applied research.[1] Since the first investigation of biferrocene,[1,2] biferrocenylene,[3,4] and diferrocenylacetylene[5,6] almost 30 years ago, the interest in dinuclear complexes has increased considerably.[7−20] Of current interest are species with rigid alkyne units between the metal units. The metal centers can be connected through the ligands as in **1−3**, or they can be connected directly to the alkyne bridges as in **4** and **5**.[13−20] In both types, voluminous termini are connected with a rigid carbon rod. The most frequent metal species to mark the end of the rod are iron- and rhenium-based fragments. In this paper we report on the synthesis, structural and spectroscopic properties of molecular wires consisting of C_4 to C_{12} chains bridging two (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadiene)cobalt units.



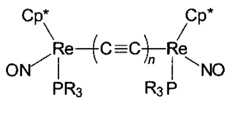
1



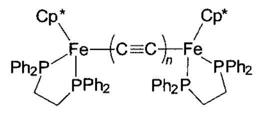
2



3



4



5

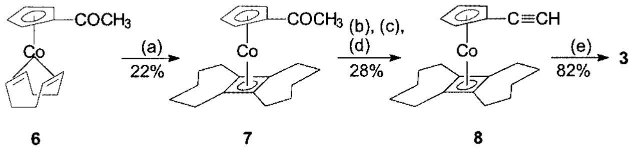
Syntheses of 14−20

Initiated by electrochemical studies on species with (η^4-cyclobutadiene)(η^5-cyclopentadienyl)cobalt fragments, we synthesized **3** and compared its electrochemical properties with related species. The synthesis of **3** is briefly outlined in Scheme 1 and has been described in the literature.[11] The further extension of the length of the alkyne bridges was hampered by the two low yielding steps for obtaining the starting material **8** (Scheme 1).[11] The replacement of the cyclooctadiene unit in **6** by a tricyclo[7.5.0.0^{1,7}]tetradeca-1,8-diene group could only be achieved in 22% yield.[11] Furthermore, the conversion of the acetyl group in **7**[11] to the alkyne unit according to a protocol described by Negishi, furnished **8** in only 28% yield.[11] In order to obtain higher yields of the starting material we replaced 1,8-cyclotetradecadiyne by the less expensive tolan and chose a different route to generate the alkyne unit. Our synthesis of the monoalkyne complex **14** is summarized in Scheme 2. The dicarbonyl(η^5-methoxycarbonylcyclopentadienyl)cobalt complex **9**[21] was converted into the metallocene **10**,[22,23] and subsequently reduced to the alcohol **11**[24] according to known procedures. The conversion into the aldehyde **12**[25] was accomplished with $BaMnO_4$ oxidation,[26] followed by a Wittig reaction with (chloromethyl)-triphenylphosphonium chloride, giving a 1:1 mixture of (*E*)/(*Z*)-alkenes **13**.[24] Treatment of the mixture with potassium

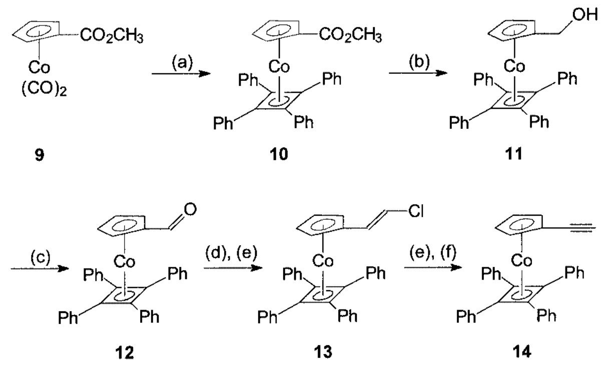
---

[a] Organisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

tert-butoxide yielded a mixture of the (*E*) diastereomer and the alkyne **14**.[24] After separation of **14**, the (*E*) diastereomer was treated with phenyllithium at room temperature, giving **14** again. The overall yield of the five steps shown in Scheme 2 was 10%. The structure of **14** could be confirmed by a diffraction analysis on single crystals.

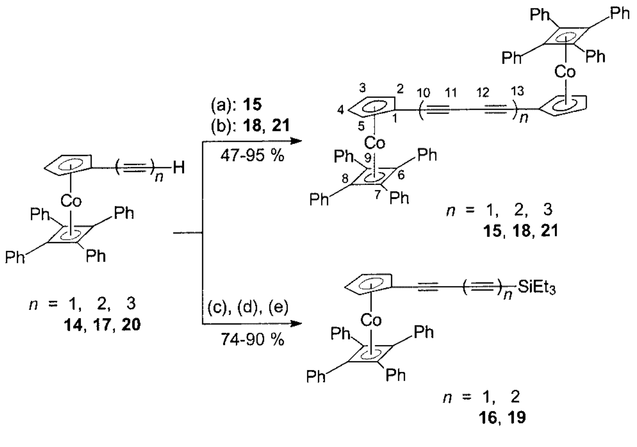


Scheme 1. Preparation of **3**: a) 1,8-cyclododecadiyne; b) LDA/THF; c) $ClPO(OEt)_2$; d) LDA, HCl; e) $Cu(OAc)_2$, pyridine



Scheme 2. Preparation of **14**: a) tolan, xylene, 120 °C; b) $LiAlH_4$/ether; c) $BaMnO_4$; d) $ClCH_2P(C_6H_5)_3{}^+Cl^-$; e) KO*t*Bu; f) C_6H_5Li

To transform **14** into its dimer **15**, we tested the protocols of Eglinton[27,28] and Hay.[29] The reaction of **14** with dry copper(II) acetate and dry pyridine at 90 °C was not successful, only decomposition of the starting material was observed. We were able to isolate 93% of the dimer **15** using the coupling reported by Hay[29] (Scheme 3). The structure of **15** could be confirmed by X-ray investigations on single crystals (see below).



Scheme 3. Synthesis of **15**, **16**, **18**, **19**, **21**: a) CuCl/pyridine + O_2; b) CuCl/TMEDA + O_2 c) *n*BuLi; d) CuCl; e) Br−C≡C−$SiMe_3$, $EtNH_2$

In order to obtain longer chains we had to find a reasonable path to elongate **14** by one ethynyl unit. This could be achieved by a modified Cadiot−Chodkiewicz reaction[13,14,30−33] involving **14** and (triethylsilyl)ethynyl bromide,[32,33] as shown in Scheme 3 in 90% yield. The parent compound **17** could be obtained by solvolysis of **19** with 5 M NaOH[10,34] in DMF.

Coupling of **17** to the dimer with four alkyne units could be achieved with Cu^I in the presence of tetramethylethylenediamine (TMEDA) (Scheme 3) and oxygen. The moderate yield of this product **18** can be attributed to the instability of **17** under the coupling conditions. The yield of **18** could be increased to 95% when **17** was produced in situ and not isolated.

Compound **21** was prepared by the elongation of the alkyne chain of **17** by one unit using the homocoupling protocol as shown in Scheme 3. As a side reaction, **18** could be isolated, therefore the yield of **19** was lower (74%) relative to the coupling reaction which led to **16**. In order to obtain **21**, the triethylsilyl group of **19** was removed by NaOH in DMF in situ, followed by a Cadiot−Chodkiewicz reaction (Scheme 3). In this case the product was obtained in 47% yield. The single crystals obtained of **21** were of poor quality. Therefore, the X-ray data can only be used as proof of the constitution and conformation of the end groups.

Structural Investigations

We were able to isolate single crystals for **14**−**17** and **21**. In Figures 1 and 2 we display as examples the molecular structures of **15** and **17**. Selected bond lengths of **14**−**17** are summarized in Table 1. The asymmetric unit of **14** contains two independent molecules, one of them is disordered with respect to the position of the alkyne unit attached to the Cp ring. The alkyne unit can be located at two adjacent Cp carbon atoms with nearly the same occupancies. In the discussion only the results of the non-disordered molecule are considered.

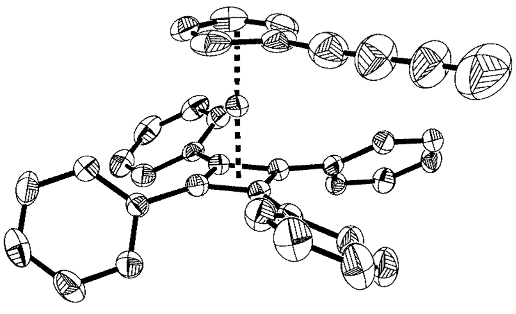


Figure 1. ORTEP plot (50% probability) of the molecular structure of **17**

The mean distances between the cobalt atom and the cyclopentadienyl (Cp) ring (1.68 Å for all structures) are slightly shorter than between the cobalt atom and the cyclobutadiene (Cb) unit (1.69 Å for all structures). These values are close to those reported for (η^4-cyclobutadiene)(η^5-

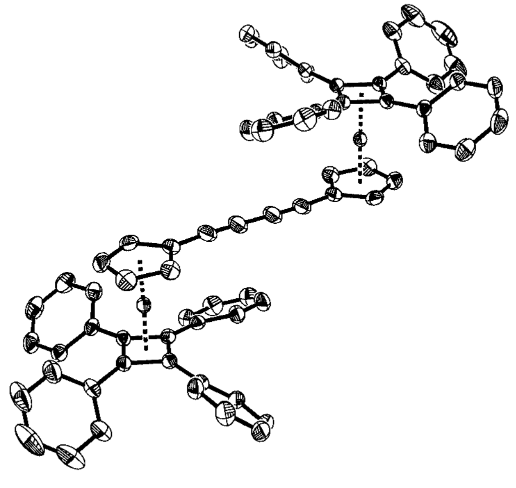


Figure 2. ORTEP plot (50% probability) of the molecular structure of **15**

Table 1. Selected bond lengths [Å] and bond angles [°] of **14**−**17**; for the numbering see Scheme 3

	14	15	16	17
Cp−Co (mean values)	1.675(3)	1.675(2)	1.679(2)	1.682(4)
Cb−Co (mean values)	1.691(3)	1.693(2)	1.692(2)	1.693(3)
C1−C10	1.443(6)	1.418(3)	1.422(3)	1.425(6)
C10−C11	1.143(7)	1.197(3)	1.204(3)	1.247(7)
C11−C12		1.378(4)	1.387(3)	1.319(7)
C12−C13			1.192(3)	1.275(9)
C1−C10−C11	175.6(7)	175.7(2)	178.4(2)	177.7(5)
C10−C11−C12		178.7(3)	179.4(2)	178.9(7)
C11−C12−C13			179.4(2)	176.3(8)

cyclopentadienyl)cobalt,[35] where the mean distance between the Cp ring and the cobalt atom is 1.66 Å, and the distance between the cobalt atom and the Cb ring is 1.68 Å.[34] The distances between the Cp ring and the sp carbon centers (C1−C10, Scheme 3) vary between 1.44 Å (**14**) and 1.42 Å (**15**−**17**). The bond length of the terminal triple bond in **14** [1.143(7) Å] is unrealistically short. This can be attributed to the librational shortening caused by the strong anisotropic motion of this molecular tail, which cannot be modeled correctly by an ellipsoid-shaped description. The distances found for the other triple bonds (C10−C11 and C12−C13) vary between 1.20 Å (**15**, **16**) and 1.28 Å (**17**). The angles at the triple bonds deviate slightly from 180°, as reported for other long alkyne chains.[32,33] The C−C bond lengths within the Cb and Cp rings are found to be equal. The phenyl rings are twisted out of the plane of the Cp ring in a propeller-like fashion (see Figure 2).

The molecular structure of **21** in the solid state is shown in Figure 3. In this molecule both tetraphenylcyclobutadiene units are far removed from each other, therefore they can adopt the *syn* conformation (Figure 3). The crystal data of **21** reveal *R* values that are too large to be used for a quantitative evaluation (cf. Table 2). This shortcoming is mainly due to three disordered dichloromethane molecules in the asymmetric unit. Nevertheless, **21** is the first example with a hexayne unit between two Cp ligands. It can be compared with $(CO)_2Cp^*Fe-(C{\equiv}C)_6-FeCp^*(CO)_2$, in which the C_{12} chain is bound directly to the metal centers.[36]

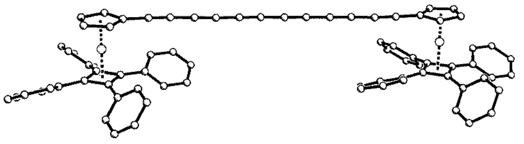


Figure 3. Molecular structure of **21** (ball-and-stick model)

Spectroscopic and Cyclovoltammetric Data

The NMR spectroscopic data of the new alkynes are listed in the Exp. Sect. The assignment of all ^{13}C signals was possible by carrying out a DEPT experiment. In Figure 4 the superimposed UV/Vis spectra of **15**, **18**, and **21** are shown. It demonstrates a shift to longer wavelengths of the absorbance bands with increasing chain length, as reported for related species.[10,13−17,36]

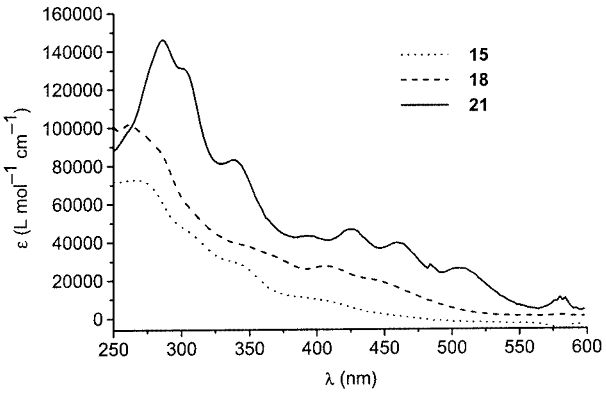


Figure 4. UV/Vis spectra of **15**, **18**, and **21**

In order to investigate the extent of metal−metal interaction in **15**, **18**, and **21**, cyclic voltammetric (CV) measurements were carried out. The uncertainty of the signals is somewhat larger (±25 mV) than usual (±15 mV), because of the low solubility of the samples in dichloromethane. As a reference, compound **14** was used, which is the simplest common building block of all three oligomers. The CV measurement of **14** shows a reversible oxidation at 540 mV (Figure 5). The CV of **15** reveals two oxidations, one at 490 mV, the second at 720 mV. The former is reversible, the latter is irreversible at different scan rates of up to 2 V/s.

The first oxidation of **15** was observed at a lower potential (by 50 mV) than that of the reference compound **14**. This result can be rationalized by assuming a lower HOMO energy due to the interaction of both metal fragments. The positive charge of the resulting radical cation is delocalized over both Co atoms through the alkyne backbone, resulting in a higher second oxidation potential. The potential separation of 230 mV suggests that the electronic interaction is relatively weak,[38] therefore, we assign **15** to class II in

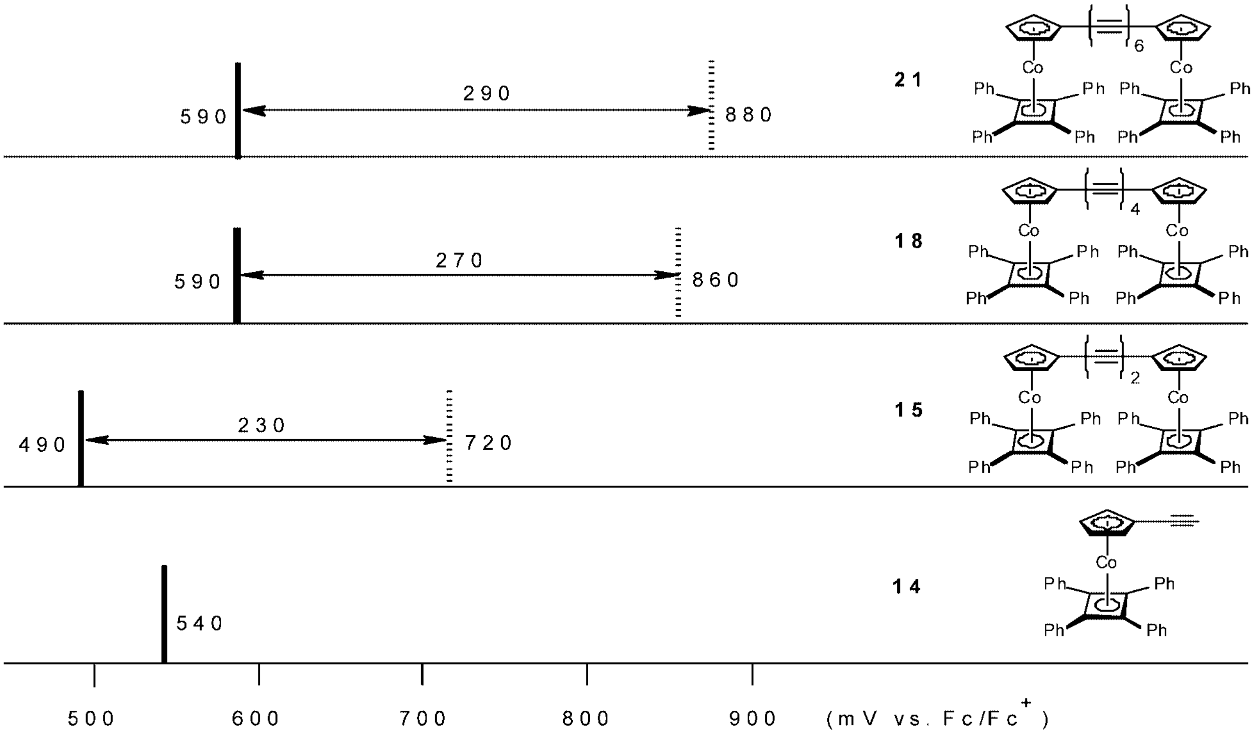


Figure 5. Comparison of the CV data of **14**, **15**, **18**, and **21**

the Robin and Day classification of mixed-valent compounds.[37]

A different situation is observed for **18** and **21**, where the first reversible oxidation potential is shifted towards a higher potential (by 50 mV) with respect to **14**. The second oxidation of **18** and **21** is irreversible at different scan rates of up to 2 V/s. The larger potential separation of 270 (**18**) and 290 mV (**21**) seems to indicate an increase in the electronic interaction with increasing alkyne chain length. However, a larger π-system is expected to result in a decrease in the HOMO energy, which in turn should cause a more facile oxidation. This contradiction can be explained by a reversible two-electron oxidation, where both Co atoms are oxidized to Co^{II} at similar potentials. At the second irreversible potential, an oxidation of one or both Co^{II} atoms to Co^{III} may occur. Another explanation is an ECE mechanism, where the first oxidation is followed by a chemical transformation, which renders the second oxidation irreversible. The latter complexes show no electronic interaction, so they can be assigned to class I in the Robin and Day classification of mixed-valent compounds.[37]

Concluding Remarks

Our goal was to find a reasonable path to prepare polyalkynes with (η^5-cyclopentadienyl)(η^4-tetraphenylcyclobutadienyl)cobalt fragments at both ends of the carbon rod. This could be achieved using **14** as a starting material. This compound was made available in five steps from **10**, with an overall yield of 10%. With **14** as the key intermediate, we were able to synthesize **15**, **18**, and **21**. The key steps were the Hay coupling reaction of the corresponding mono-, di-, and triyne units **14**, **17**, and **20**, respectively. The yields of **18** and **21** could be improved by preparing **17** and **20** in situ by deprotection of the protected diyne **16** and triyne **19**, respectively. By means of X-ray studies of the single crystals of **14**−**17** and **21** we could confirm the structure and conformation of the alkynes. For the polyyne part of all the studied samples, clear short−long C≡C−C bond alternation is observed. Our CV studies do not indicate a metal−metal interaction through the alkyne rod for **18** and **21**, whereas in **15**, where the distance between the metal centers is shorter, a slight shift with respect to **14** is observed.

Experimental Section

General Remarks: All melting points are uncorrected. The NMR spectra were measured with a Bruker Avance 500 spectrometer (^{1}H NMR at 500 MHz and ^{13}C NMR at 125.77 MHz) using the solvent as internal standard (δ). The mass spectra refer to data recorded with a JEOL JMS-700 instrument. IR spectra were recorded with a Bruker Vector 22. All reactions with CpCo(COD) were carried out in dried glassware under argon, using dried and oxygen-free solvents.

(η^5-Formylcyclopentadienyl)(η^4-tetraphenylcyclobutadienyl)cobalt(I) (12):[25] $BaMnO_4$ (2.0 g, 7.8 mmol) was added to a solution of **11** (200 mg, 0.4 mmol) in 100 mL of dichloromethane.[26] The suspension was stirred for 24 h under argon. After filtration, the solvent was removed to give 198 mg (99%) of **12** as an orange solid. ^{1}H NMR (CD_2Cl_2): δ = 4.91 (pt, 2 H, CpH), 5.23 (pt, 2 H, CpH), 7.21−7.34 (m, 12 H, *o,p*-ArH), 7.41−7.47 (m, 8 H, *m*-ArH), 9.31 (s, 1 H, CHO) ppm. ^{13}C NMR (CD_2Cl_2): δ = 77.5, 92.9 (s), 83.4, 88.9 (d, Cp), 127.3 (d, *p*-Ar), 128.5 (d, *o*-Ar), 129.1 (d, *m*-Ar), 135.2 (s, Ar), 190.9 (d, CHO) ppm.

[η^5-(*E*)-1-Chloroethenylcyclopentadienyl](η^4-tetraphenylcyclobutadienyl)cobalt(I) [(*E*)-13] and (η^5-Ethynylcyclopentadienyl)(η^4-tetraphenylcyclobutadienyl)cobalt(I) (14): Potassium *tert*-butoxide (106 mg, 1.0 mmol) was added to a solution of (chloromethyl)triphenylphosphonium chloride (350 mg, 1.0 mmol) in 20 mL of THF. At −70 °C, a cooled (−65 °C) solution of **12** (342 mg, 0.7 mmol) in 20 mL of THF was added to this solution. The resulting mixture was stirred for 30 min at −65 °C and then 30 min at room temperature. Subsequently, a solution of potassium *tert*-butoxide (106 mg, 1.0 mmol) in 20 mL of THF was added and the mixture refluxed for 17 h. After cooling and addition of 20 mL of distilled water, the layers were separated, and the aqueous layer was washed four times with diethyl ether. After drying ($MgSO_4$) of the combined organic layers, the solvent was removed and the crude mixture was purified by column chromatography on alumina (light petroleum ether to light petroleum ether/diethyl ether, 10:1). This procedure yielded 166 mg (46%) of (*E*)-**13** as a yellow solid. Following the isolation of (*E*)-**13**, 134 mg (39%) of the alkyne complex **14** was obtained as a yellow solid. ^{1}H NMR (CD_2Cl_2): δ = 4.63 (pt, 2 H, CpH), 4.67 (pt, 2 H, CpH), 5.84 (d, 1 H, C=CH), 5.93 (d, 1 H, C=CH), 7.19−7.30 (m, 12 H, *o,p*-ArH), 7.37−7.45 (m, 8 H, *m*-ArH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 76.2 (s), 81.1 (d, Cp), 84.8 (d, Cp), 93.1 (s), 115.8 (d, C=C), 126.7 (d, *p*-Ar), 127.2 (d, C=C), 128.4 (d, *o*-Ar), 129.1 (d, *m*-Ar), 136.1 (s, Ar).

Transformation of (*E*)-13 to 14: Phenyllithium (0.6 mL, 1.1 mmol, 1.8 M) was added to a solution of (*E*)-**13** (500 mg, 0.9 mmol) in 20 mL of THF. After stirring for 20 h, the mixture was hydrolyzed with 25 mL of brine. The aqueous layer was extracted four times with diethyl ether, the combined organic layers were dried ($MgSO_4$) and the solvent was removed. After purification by column chromatography on alumina (neutral, grade III, light petroleum ether), 275 mg (59%) of the alkyne **14** was obtained as a yellow solid, m.p. 148 °C. ^{1}H NMR (CD_2Cl_2): δ = 2.51 (s, 1 H, CCH), 4.62 (pt, 2 H, CpH), 4.79 (pt, 2 H, CpH), 7.23−7.28 (m, 12 H, ArH), 7.45−7.49 (m, 8 H, ArH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 76.4, 76.7, 78.2, 79.5 (s, cbd-C, Cp, C_{Alkyne}), 84.9 (d, Cp), 86.6 (d, Cp), 126.9 (d, *p*-Ar), 128.4 (d, *o*-Ar), 129.3 (d, *m*-Ar), 135.8 (s, Ar) ppm. IR (KBr): ṽ = 3056, 2924, 2109, 1628, 1600, 1498, 1445 cm^{-1}. HRMS (FAB): calcd. 504.1288; found 504.1273.

{μ-[Butadiynediylbis(η^5-cyclopentadienyl)]}bis(η^4-tetraphenylcyclobutadienyl)dicobalt(I) (15): A solution of CuCl (16 mg, 0.16 mmol) in 15 mL of dry pyridine, saturated with oxygen was added to a Schlenk flask. To this mixture **14** (209 mg, 0.4 mmol) was added, and oxygen was passed through the mixture for 46 h. After removal of the pyridine under vacuum, the crude product was purified by column chromatography on alumina (neutral, grade III) with light petroleum ether/diethyl ether (60:1), giving 192 mg (93%) of **15** as a yellow-orange solid, m.p. 240 °C. ^{1}H NMR (CD_2Cl_2): δ = 4.69 (pt, 4 H, CpH), 4.81 (pt, 4 H, CpH), 7.16−7.25 (m, 24 H, ArH), 7.39−7.47 (m, 16 H, ArH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 74.1, 76.4, 77.1, 78.5 (s, C_{Alkyne}, cbd-C, Cp), 84.9 (d, Cp), 87.3 (d, Cp), 126.9 (d, *p*-Ar), 128.5 (d, *o*-Ar), 129.2 (d, *m*-Ar), 135.5 (s, Ar) ppm. IR (KBr): ṽ = 3056, 2924, 2148, 1604, 1497, 1446 cm^{-1}. HRMS (EI): calcd. 1006.2420; found 1006.2432.

(η^4-Tetraphenylcyclobutadienyl)[η^5-(triethylsilylbutadiynyl)cyclopentadienyl]cobalt(I) (16): *n*-Butyllithium (645 mg, 1.5 mmol, 1.6 M solution) was slowly added to a solution of **14** (695 mg, 1.4 mmol) in 100 mL of THF, at −35 °C. Subsequently, CuCl (263 mg, 1.4 mmol) was added and the mixture was stirred for 30 min at −15 °C. After stirring at room temperature for 10 min, the suspension was cooled to −25 °C and freshly distilled ethylamine (5 mL) and bromo(triethylsilyl)acetylene (330 mg, 1.5 mmol) were added. After further stirring for 18 h, the hydrolysis was carried out with 50 mL of saturated NH_4Cl solution. The workup was completed by extraction of the aqueous layer with diethyl ether and drying of the combined organic layers with $MgSO_4$. Removal of the solvent gave a crude product. Further purification by column chromatography on silica with light petroleum ether/dichloromethane (7:1) yielded 804 mg (91%) of **16** as a yellow solid, m.p. 146 °C. ^{1}H NMR (C_6D_6): δ = 0.56 (q, CH_2, 6 H), 1.01 (t, CH_3, 9 H), 4.31 (pt, CpH, 2 H), 4.61 (pt, CpH, 2 H), 7.04−7.12 (m, 12 H, ArH), 7.54−7.59 (m, 8 H, ArH) ppm. ^{13}C NMR (C_6D_6): δ = 4.7 (t, CH_2), 7.7 (q, CH_3), 73.5, 74.5, 77.0, 77.7, 86.0, 91.1 (s, Cp, C_{Alkyne}, cbd-C,), 85.1 (d, Cp), 87.4 (d, Cp), 126.9 (d, *p*-Ar), 128.4 (d, *o*-Ar), 129.2 (d, *m*-Ar), 135.6 (s, Ar) ppm. IR (KBr): ṽ = 2955, 2874, 2206, 1630, 1499, 1460 cm^{-1}. HRMS (EI): calcd. 642.2153; found 642.2159. $C_{43}H_{39}CoSi$ (642.2): calcd. C 80.35, H 6.12; found C 80.10, H 6.32.

(η^5-Butadiynylcyclopentadienyl)(η^4-tetraphenylcyclobutadienyl)cobalt(I) (17): NaOH (0.3 mL of an aqueous 5 M solution) was added to a solution of **16** (337 mg, 0.5 mmol) in 30 mL of DMF. After 5 min, 2 M HCl was added until pH < 4 (ca. 2 mL). The resulting precipitate was filtered, washed extensively with water, dissolved in diethyl ether, and dried with $MgSO_4$. Removal of the solvent yielded 264 mg (95%) of **17** as a gold-colored, oxygen-sensitive solid. ^{1}H NMR ($CDCl_3$): δ = 2.32 (s, 1 H, CCH), 4.68 (pt, 2 H, CpH), 4.82 (pt, 2 H, CpH), 7.22−7.33 (m, 12 H, ArH), 7.43−7.49 (m, 2 H, ArH) ppm. ^{13}C NMR (C_6D_6): δ = 69.3, 69.7, 72.4, 73.4, 77.1, 77.2 (s, C_{Alkyne}, cbd-C, Cp), 85.2 (d, Cp), 87.3 (d, Cp), 126.9 (d, *p*-Ar), 128.4 (d, *o*-Ar), 129.2 (d, *m*-Ar), 135.6 (s, Ar) ppm. IR (KBr): ṽ = 3060, 2209, 1609, 1499 cm^{-1}. HRMS (FAB): calcd. 528.1289; found 528.1312.

{μ-[Octatetraynediylbis(η^5-cyclopentadienyl)]}bis(η^4-tetraphenylcyclobutadienyl)dicobalt(I) (18): NaOH (0.15 mL of 1 M solution) was added to a solution of **16** (145 mg, 0.23 mmol) in 15 mL of DMF. After 5 min, HCl (1.5 mL of 2 M solution) was added. The organic layer was washed three times with water and brine. The aqueous layer was extracted twice with diethyl ether, the combined organic layers were dried with $MgSO_4$ and concentrated to 20 mL. The solution was poured into a mixture of acetone (20 mL), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (14 mg) and CuCl (12 mg). After 4 h of passing oxygen through the mixture, hydrolysis with 30 mL of saturated NH_4Cl solution was carried out. After extraction of the aqueous layer with dichloromethane, the combined layers were adsorbed on silica. The purification by column chromatography on silica with light petroleum ether/dichloromethane (4:1) yielded 113 mg (95%) of **18** as an orange-red solid, m.p. 218 °C. ^{1}H NMR ($CDCl_3/CD_2Cl_2$, 2:1): δ = 4.74 (pt, 4 H, CpH), 4.89 (pt, 4 H, CpH), 7.23−7.36 (m, 24 H, ArH), 7.42−7.49 (m, 16 H, ArH) ppm. ^{13}C NMR ($CDCl_3/CD_2Cl_2$, 2:1): δ = 63.9, 66.1, 73.6, 74.9, 75.9, 77.2 (s, C_{Alkyne}, cbd-C, Cp), 85.3 (d, Cp), 87.5 (d, Cp), 126.7 (d, *p*-Ar), 128.1 (d, *o*-Ar), 128.7 (d, *m*-Ar), 134.8 (s, Ar) ppm. IR (KBr): ṽ = 3061, 2925, 2194, 1630, 1498, 1449 cm^{-1}. HRMS (FAB): calcd. 1055.2498; found 1055.2483.

(η^4-Tetraphenylcyclobutadienyl)[η^5-(triethylsilylhexatriynyl)cyclopentadienyl]cobalt(I) (19): *n*-Butyllithium (73 mg, 0.17 mmol of a 1.6 M solution) in *n*-hexane was slowly added to a cooled solution (−40 °C) of **17** (81 mg, 0.15 mmol) in 10 mL of THF. Subsequently, CuCl (30 mg, 0.16 mmol) was added. After stirring the mixture for a further 5 min at −30 °C, the stirring was continued at room temperature for 10 min. Subsequently, freshly distilled ethylamine (1 mL) and bromo(triethylsilyl)acetylene (70 mg, 0.25 mmol) were added at −25 °C. Stirring was continued for 50 min at that temperature and the mixture was then hydrolyzed with 15 mL of a saturated NH_4Cl solution. The extraction of the aqueous layer with diethyl ether and the removal of the solvent gave a crude product, which was further purified by column chromatography on silica with light petroleum ether/dichloromethane (5:1) gave 75 mg (74%) of **19** as a yellow-brown solid, m.p. 114 °C. ^{1}H NMR ($CDCl_3$): δ = 0.68 (q, 6 H, CH_2), 1.05 (t, 9 H, CH_3), 4.69 (pt, 2 H, CpH), 4.84 (pt, 2 H, CpH), 7.22−7.34 (m, 12 H, ArH), 7.43−7.48 (m, 8 H, ArH) ppm. ^{13}C NMR ($CDCl_3$): δ = 4.2 (CH_2), 7.4 (CH_3), 62.1, 65.3, 73.2, 74.2, 76.2, 76.9, 86.0, 89.7 (s, C_{Alkyne}, cbd-C, Cp), 85.2 (Cp), 87.3 (Cp), 126.7 (d, *p*-Ar), 128.1 (d, *o*-Ar), 128.8 (d, *m*-Ar), 134.9 (Ar) ppm. IR (KBr): $\tilde{\nu}$ = 2953, 2921, 2879, 2176, 2067, 1605, 1497, 1454 cm^{-1}. HRMS (FAB): calcd. 666.2153; found 666.2148. $C_{45}H_{39}CoSi$ (666.2): calcd. C 81.06, H 5.89; found C 81.19, H 6.15.

{μ-[Dodecahexaynediylbis(η^5-cyclopentadienyl)]}bis(η^4-tetraphenylcyclobutadienyl)dicobalt(I) (21): The removal of the protection group from **19** was achieved by adding NaOH (0.12 mL of a 5 M aqueous solution) to a solution of **19** (115 mg, 0.17 mmol) in 35 mL of DMF at room temp. After 5 min, the solution was acidified by adding HCl (35 mL of a 2 M aqueous solution). The resulting precipitate was filtered, washed extensively with water, and dissolved in diethyl ether. The aqueous layer was extracted twice with diethyl ether, the combined organic layers were dried with $MgSO_4$ and concentrated to 20 mL. The solution was poured into a solution of acetone (36 mL), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.053 mL) and CuCl (18 mg). After 80 min of passing oxygen through the mixture, 60 mL of diethyl ether and 50 mL of saturated NH_4Cl solution were added. The organic layer was washed twice with water. and the combined aqueous layers were washed with dichloromethane. The combined organic layers were dried with $MgSO_4$, absorbed on silica and purified by column chromatography on silica with light petroleum ether/dichloromethane (7:1), yielding 45 mg (47%) of **21** as a red solid, m.p. 210 °C. ^{1}H NMR (CD_2Cl_2: δ = 4.74 (pt, 4 H, CpH), 4.90 (pt, 4 H, CpH), 7.21−7.44 (m, 40 H, ArH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 64.0, 64.2, 64.3, 65.9, 73.4, 75.3, 76.4, 77.8 (s, cbd-C, Cp, C_{Alkyne}), 86.2 (d, Cp), 88.2 (d, Cp), 127.2 (d, *p*-Ar), 128.5 (d, *o*-Ar), 129.1 (d, *m*-Ar), 135.1 (s, Ar) ppm. IR (KBr): $\tilde{\nu}$ = 2148, 2041, 1630, 1498, 1261 cm^{-1}. HRMS (FAB): calcd. 1102.2393; found 1102.2366.

Cyclovoltammetry: The electrochemical measurements were performed with an Ecochem PGStat 20. A glassy carbon disk electrode with a 3 mm diameter was used as the working electrode. The Ag/AgCl reference electrode was separated from the solution by a G4-frit and a Haber−Luggin capillary. As the electrolyte, a 0.1 M solution of $nBu_4N^+PF_6^-$ in anhydrous, degassed CH_2Cl_2 was used. All reported potentials are referred to the Fc/Fc$^+$ couple, which

Table 2. Crystal data and structure refinement for **14**−**17** and **21**

	14	**15**	**16**	**17**	**21**
Empirical formula	$C_{35}H_{25}Co$	$C_{70}H_{48}Co_2$	$C_{43}H_{39}CoSi$	$C_{37}H_{25}Co$	$C_{78}H_{48}Co_2 \cdot 3CH_2Cl_2$
Formula mass	504.48	1006.94	642.76	528.50	1357.80
Temperature [K]	200(2)	200(2)	200(2)	200(2)	150(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	8	2	4	4	4
a [Å]	27.5105(2)	10.5359(3)	16.7032(2)	11.1526(2)	11.0730(1)
b [Å]	19.7683(2)	20.0926(6)	12.7019(2)	14.2496(2)	14.3480(2)
c [Å]	9.3815(1)	13.0286(4)	16.7817(1)	117.142(2)	41.4520(5)
β [°]	90	112.88(1)	106.524(1)	99.652(1)	94.286(1)
Volume [Å^3]	5102.00(8)	2540.92(13)	3413.40(7)	2685.71(7)	6567.3(1)
Density (calculated) [g/cm^3]	1.31	1.32	1.25	1.31	1.37
Absorption coefficient [mm^{-1}]	0.694	0.697	0.567	0.66	0.80
Crystal shape	polyhedron	irregular	polyhedron	lamina	lamina
Crystal size [mm]	0.38 × 0.33 × 0.11	0.4 × 0.3 × 0.2	0.42 × 0.30 × 0.30	0.46 × 0.28 × 0.03	0.38 × 0.32 × 0.10
θ range for data collection [°]	1.27 to 25.66	1.98 to 25.62	2.04 to 27.49	1.9 to 27.5	1.7 to 21.5
Index ranges	$-33 \leq h \leq 32$	$-12 \leq h \leq 12$	$-21 \leq h \leq 21$	$-14 \leq h \leq 14$	$-6 \leq h \leq 11$
	$-23 \leq k \leq 23$	$-23 \leq k \leq 23$	$-16 \leq k \leq 16$	$-8 \leq k \leq 8$	$-8 \leq k \leq 14$
	$-11 \leq l \leq 11$	$-15 \leq l \leq 15$	$-1 \leq l \leq 21$	$-22 \leq l \leq 22$	$-33 \leq l \leq 42$
Reflections collected	37314	18723	34497	27287	14892
Independent reflections	8350 [R(int) = 0.0298]	4429 [R(int) = 0.0274]	7828 [R(int) = 0.0319]	6170 [R(int) = 0.0594]	7505 [R(int) = 0.0661]
Observed reflections	7413 [$I > 2\sigma(I)$]	3813 [$I > 2\sigma(I)$]	6463 [$I > 2\sigma(I)$]	4180 [$I > 2\sigma(I)$]	6123 [$I > 2\sigma(I)$]
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	0.94 and 0.83	0.89 and 0.77	0.86 and 0.74	0.98 and 0.83	0.96 and 0.65
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	8350/221/672	4429/0/325	7828/7/424	6170/0/343	7505/73/821
Goodness-of-fit on F^2	1.03	1.09	1.02	1.03	1.26
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.036$	$R1 = 0.030$	$R1 = 0.037$	$R1 = 0.053$	$R1 = 0.130$
	$wR2 = 0.085$	$wR2 = 0.063$	$wR2 = 0.090$	$wR2 = 0.132$	$wR2 = 0.281$
Largest diff. peak and hole [e·Å^{-3}]	0.30 and −0.38	0.23 and −0.28	0.56 and −0.39	0.94 and −0.46	1.27 and −1.48

was used as an internal calibrant. All measurements were performed at room temperature.

X-ray Crystallography and Structure Solution: The crystallographic data were recorded with a Bruker Smart CCD diffractometer at 200 K for **14**−**17** and **21**. Relevant crystal and data collection parameters are given in Table 2. The structures were solved using direct methods (**14**−**16**, **21**) or the Patterson heavy atom method (**17**), least-squares refinement, and Fourier techniques. Structure solution and refinement were performed with SHELXTL.[39] CCDC-172774 (**14**), -172775 (**15**), -172776 (**16**), -172777 (**17**), and -172778 (**21**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

---

[1] D. Astruc, *Electron Transfer and Radical Processes in Transition Metal Chemistry*, VCH, New York, **1995**.

[2] D. B. Brown (Ed.), *Mixed Valence Compounds*, Reidel, Dordrecht, Netherlands, **1990**.

[3] D. O. Cowan, C. LeVanda, J. Park, F. Kaufman, *Acc. Chem. Res.* **1973**, *6*, 1−7.

[4] C. LeVanda, K. Bechgaard, D. O. Cowan, M. D. Rausch, *J. Am. Chem. Soc.* **1977**, *99*, 2964−2968.

[5] C. LeVanda, D. O. Cowan, C. Leitch, K. Bechgaard, *J. Am. Chem. Soc.* **1974**, *96*, 6788−6789.

[6] J. A. Kramer, D. N. Hendrickson, *Inorg. Chem.* **1980**, *19*, 3330−3337.

[7] O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P. H. Dixneuf, *Organometallics* **1997**, *16*, 184−189.

[8] Z. Yuan, G. Stringer, I. R. Jobe, D. Kreller, K. Scott, L. Koch, N. J. Taylor, T. B. Marder, *J. Organomet. Chem.* **1993**, *452*, 115−120.

[9] M. Wildschek, C. Rieker, P. Jaitner, H. Schottenberger, K. E. Schwarzhans, *J. Organomet. Chem.* **1990**, *396*, 355−361.

[10] M. Altmann, V. Enkelmann, U. H. F. Bunz, *Chem. Ber.* **1996**, *129*, 269−273.

[11] H. Schimanke, R. Gleiter, *Orgonometallics* **1998**, *17*, 275−277.

[12] M. I. Bruce, B. D. Kelly, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2000**, *604*, 150−156.

[13] M. Brady, W. Weng, Y. Zhou, J. W. Seyler, A. J. Amoroso, A. M. Arif, M. Böhme, G. Frenking, J. A. Gladysz, *J. Am. Chem. Soc.* **1997**, *119*, 775−788.

[14] T. Bartik, B. Bartik, M. Brady, R. Dembinski, J. A. Gladysz, *Angew. Chem.* **1996**, *108*, 467−469; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 414−417.

[15] F. Coat, C. Lapinte, *Organometallics* **1996**, *15*, 477−479.

[16] F. Paul, C. Lapinte, *Coord. Chem. Rev.* **1998**, *178*−*180*, 431−509.

[17] F. Paul, W. E. Meyer, L. Toupet, H. Jiao, J. A. Gladysz, C. Lapinte, *J. Am. Chem. Soc.* **2000**, *122*, 9405−9414.

[18] M. I. Bruce, *Coord. Chem. Rev.* **1997**, *166*, 91−119.

[19] M. I. Bruce, P. J. Low, K. Costuas, J.-F. Halet, S. P. Best, G. A. Heath, *J. Am. Chem. Soc.* **2000**, *122*, 1949−1962.

[20] U. H. F. Bunz, *Angew. Chem.* **1996**, *108*, 1047−1049; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 968−971.

[21] W. P. Hart, D. Shihua, M. D. Rausch, *J. Organomet. Chem.* **1985**, *282*, 111−121.

[22] S. T. Mabrouk, M. D. Rausch, *J. Organomet. Chem.* **1996**, *523*, 111−117.

[23] A. M. Stevens, C. J. Richards, *Organometallics* **1999**, *18*, 1346−1348.

[24] A. M. Stevens, C. J. Richards, *Tetrahedron Lett.* **1997**, *38*, 7805−7808.

[25] M. D. Rausch, R. A. Genetti, *J. Org. Chem.* **1970**, *35*, 3888−3897.

[26] H. Firouzabadi, E. Ghaderi, *Tetrahedron Lett.* **1978**, *9*, 839−840.

[27] O. M. Behr, G. Eglinton, A. R. Galbraith, R. A. Raphael, *J. Chem. Soc.* **1960**, 3614−3625.

[28] G. Eglinton, W. McCrae, *Adv. Org. Chem.* **1963**, *4*, 225−328.

[29] A. S. Hay, *J. Org. Chem.* **1960**, *25*, 1275−1276; A. S. Hay, *J. Org. Chem.* **1962**, *27*, 3320−3321.

[30] P. Cadiot, W. Chodkiewicz, in: *Chemistry of Acetylenes* (Ed.: H. G. Viehe), Marcel Dekker, New York, **1969**, pp. 597−647.

[31] W. Chodkiewicz, *Ann. Chim. Paris* **1957**, *2*, 819−869.

[32] R. Dembinski, T. Lis, S. Szafert, C. L. Mayne, T. Bartik, J. A. Gladysz, *J. Organomet. Chem.* **1999**, *578*, 229−246.

[33] B. Bartik, R. Dembinski, T. Bartik, A. M. Arif, J. A. Gladysz, *New J. Chem.* **1997**, *21*, 739−750.

[34] R. Eastmond, D. R. M. Walton, *Tetrahedron* **1972**, *78*, 4591−4599.

[35] P. E. Riley, R. E. Davis, *J. Organomet. Chem.* **1976**, *113*, 157−166.

[36] A. Sakurai, M. Akita, Y. Moro-oka, *Organometallics* **1999**, *18*, 3241−3244.

[37] M. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247−422.

[38] R. Gleiter, H. Röckel, G. Pflästerer, B. Treptow, D. Kratz, *Tetrahedron Lett.* **1993**, *34*, 8075−8078.

[39] G. M. Sheldrick, Bruker Analytical X-ray Division, Madison, WI, **1997**.

Received November 7, 2001
[I01442]