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Alkyne Substitution on Cobaltocenium Triflates

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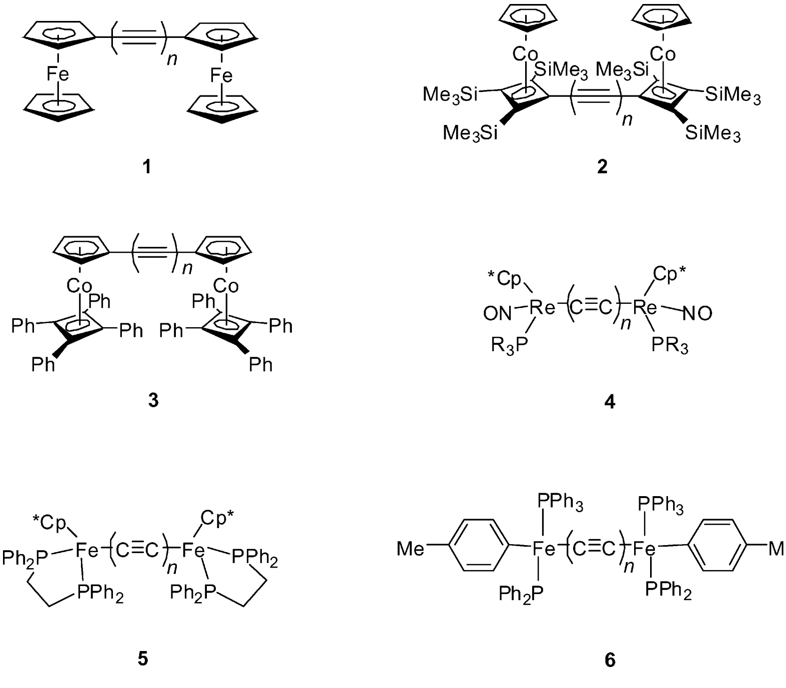
Cobaltocenium triflates consisting of a CpCo-capped η^5-1-trifluoromethylsulfonyloxy-2,3,4,5-tetrapropylcyclopentadienyl ring were substituted at the Cp ring by a trialkylsilylethynyl group to yield the R–CpCo capped tetra-*n*-propylcyclopentadienone with R = C_2SiMe_3 (**11a**) and R = C_2SiEt_3 (**11b**). The parent system with R = C_2H (**11c**) was generated by hydrolyzing the SiR_3 groups of **11a** and **11b**. The trialkylsilyl-1,3-butadiyne derivatives with alkyl = CH_3 (**11d**) and alkyl = C_2H_5 (**11e**) were derived from **11c** by using a Cadiot–Chodkiewicz coupling with bromo(triethylsilyl)acetylene. Removal of the $SiEt_3$ protecting group led to **11f**. The alkynes **11c** and **11f** could be dimerized to **13a** and **13b** by a Hay coupling. These results were confirmed by X-ray diffraction studies on the starting materials **7**, **8**, and **12** as well as the derivatives **11c**, **11f**, and **13a**.

Introduction

In material science, model systems with two redox-active centers are often connected with conjugated bridges such as polyalkenes and polyalkynes. Since the first investigations on diferrocenylalkynes[1,2] the interest in dinuclear complexes has increased considerably.[1–12] The most well-known species are diferrocenylalkynes (**1**)[1,2] and related species **2**–**6**[1–6] (Scheme 1). The metal centers can be connected through the ligands (see **1**–**3**)[2–4] or they can be bonded directly to the alkyne bridges (see **4**–**6**).[5–14] In both types bulky termini are connected by a carbon rod.

Recently we found a simple way of carrying out substitution reactions at the η^5-cyclopentadienyl ring of cobaltocenium triflates by an S_N' reaction.[15] In these species a nucleophile attacks the Cp ring of the cobaltocenium ion whereas the leaving group is situated at the other five-membered ring. This reaction is shown in Scheme 2.



Scheme 1. Model systems of two redox-active centers connected by alkyne units.

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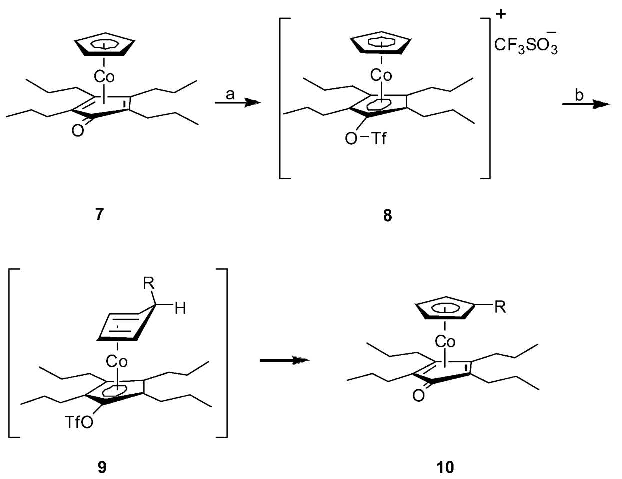


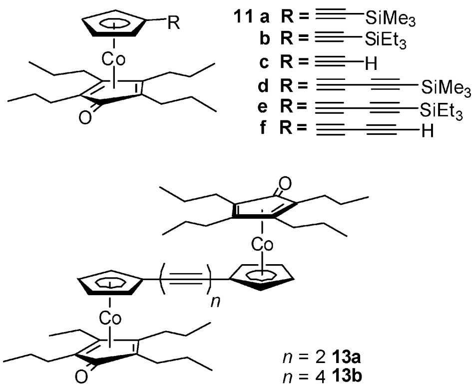
Scheme 2. Generation of **8** and S_N' substitution to yield **10**. (a) $(CF_3SO_2)_2O/CH_2Cl_2$/–50 °C); (b) RLi/THF/–30 °C.

The starting point is the readily available CpCo-capped cyclopentadienone complex **7**. Treatment of **7** with trifluoromethanesulfonic anhydride afforded the cobaltocenium triflate **8** in good yields. When the latter was treated with alkyl- and aryllithium compounds a substitution at the Cp ring occurred to give **10** in yields between 60 and 80%.[15] This reaction should also provide a simple means to prepare alkyne-substituted CpCo-capped cyclopentadienone complexes. In this paper we report on the synthesis and the properties of **11a**–**11f**, **12** as well as **13a** and **13b** (Schemes 3 and 4).

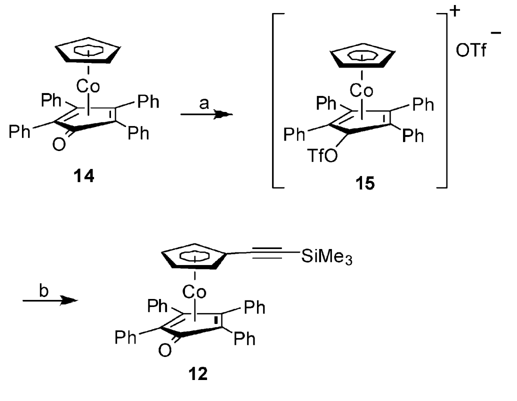
Results and Discussion

To obtain the alkynes **11a**–**11f** we followed the protocol shown in Scheme 2. The lithium salt of the monoprotected alkyne was treated with **8**. When we used trimethylsilylacetylene to prepare **11a** from **8** the yield was only 16%. To find out if other substituents at the cyclopentadienone ring of **8** can increase the yield we prepared the cobaltocenium triflate **15** from the readily available tetraphenyl-cyclopentadienone complex **14**[16] (Scheme 4) by treating **14** with trifluoromethanesulfonic anhydride at –30 °C. The resulting cobaltocenium salt **15** was treated with the in situ prepared lithium salt of trimethylsilyl acetylene (TMSA). The resulting tetraphenylcyclopentadienone complex **12** was obtained in 19% yield, indicating that the substituents at the cyclopentadienone ring were not responsible for the low yields. Better yields were obtained when we used triethylsilylacetylene instead of trimethylsilylacetylene. Starting from **8** we synthesized **11b** in 56% yield. For **11a** as well as for **11b** we were able to cleave the protecting groups by treating them with a 5 M aqueous solution of NaOH at room temperature. The yield of **11c** was >95%.

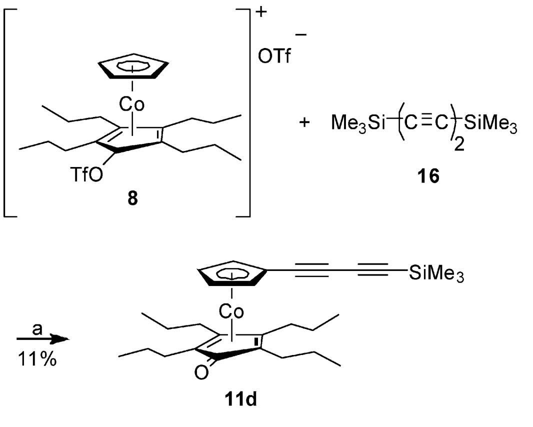
To synthesize the 1,3-butadiyne substituted derivatives **11d** and **11e** we first tried to react **8** with the lithium salt of trimethylsilyl-1,3-butadiyne. However, the yield was rather low (16%). In a second experiment we followed a suggestion in the literature[17] and tried to generate the anion of trimethylsilyl-1,3-butadiyne in situ from 1,4-bis(trimethylsilyl)-1,3-butadiyne (**16**) (Scheme 5) and methyllithium. The addition of a THF solution of **8** to the mixture resulted in only 11% of **11d** as a red oil. After these failures we used a stepwise approach. The key step in this protocol was a Cadiot–Chodkiewicz coupling reaction[18] between **11c** and bromo(triethylsilyl)acetylene in the presence of CuI and ethylamine. This protocol afforded **11e** in 80% yield as a red oil (Scheme 6). The parent system **11f** was generated by the treatment of **11e** with $(nBu)_4NF$ in THF as red crystals.



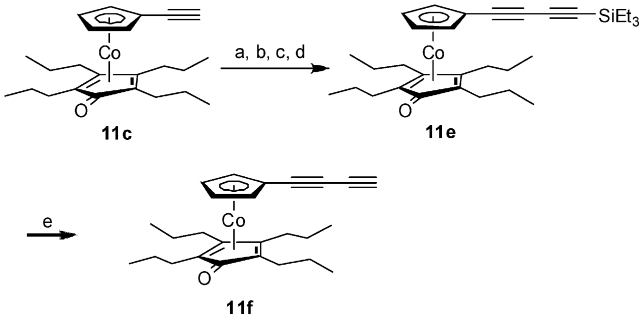
Scheme 3. Target molecules.



Scheme 4. (a) $(CF_3SO_2)_2O/CH_2Cl_2$/–50 °C; (b) $Me_3Si–C{\equiv}C–H/nBuLi$/THF/–30 °C.

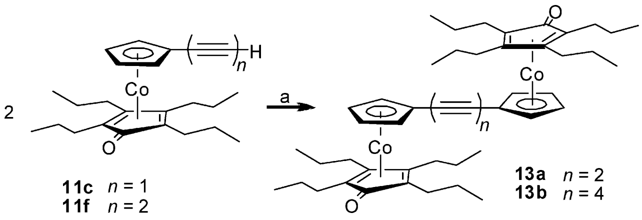


Scheme 5. (a) MeLi/LiBr/–50 °C/THF.



Scheme 6. (a) nBuLi/THF/–40 °C; (b) CuI/–15 °C; (c) $EtNH_2$/–25 °C; (d) Br–C≡C–$SiEt_3$/–25 °C, (e) 1 M $n$$Bu_4NF$/THF.

The alkynes **11c** and **11f** were ideal precursors to try an oxidative coupling reaction between the alkyne units. We chose the protocol suggested by Hay[19] using CuCl in the presence of pyridine (Scheme 7). For **11c** as well as **11f** the Hay protocol[19] proved to be very efficient. The products **13a** and **13b** could be isolated in yields of 80 and 90%, respectively.



Scheme 7. (a) CuCl/O_2/pyridine.

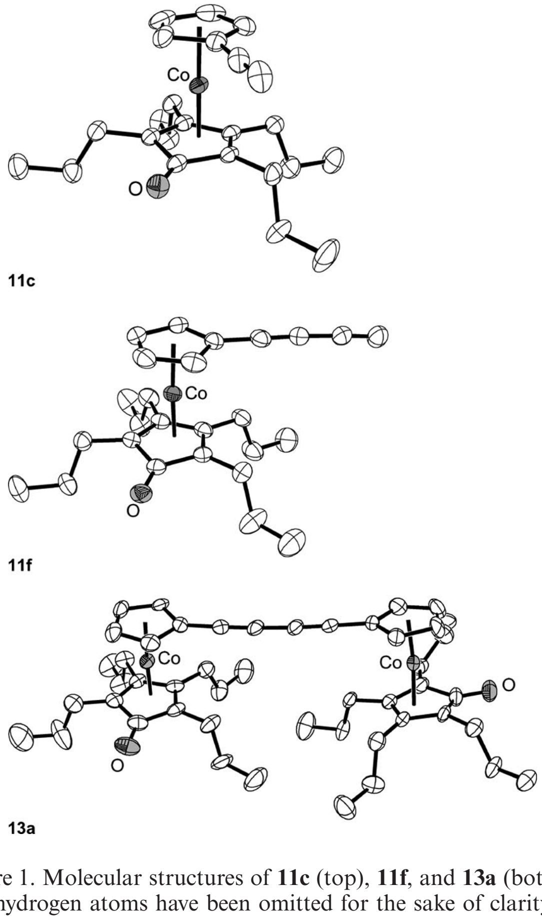


Figure 1. Molecular structures of **11c** (top), **11f**, and **13a** (bottom). The hydrogen atoms have been omitted for the sake of clarity.

For **7**, **8**, **11c**, **11f**, **12**, and **13a** we were able to isolate single crystals, which allowed us to carry out X-ray diffraction studies. In Figure 1 we show the molecular structures of **11c**, **11f**, and **13a**.

The distance between the cobalt center and the plane of the cyclopentadienyl unit is 1.67 Å for all three structures and is close to the values reported for other CpCo–cyclopentadienone complexes.[20] The same holds for the distance between the metal and the plane of the four alkyl-substituted carbon atoms of the cyclopentadienone unit, which was found to be 1.62 Å for **11c** and 1.63 Å for **11f** and **13a**. The distances between the Cp rings and the adjacent sp centers vary between 1.43 Å (**11c**, **11f**) and 1.42 Å (**13a**). The bond lengths of the alkyne units are 1.18 Å (**11c**), 1.20 Å, 1.38 Å, 1.18 Å (**11f**), and 1.19 Å, 1.39 Å, 1.19 Å (**13a**). The angles at the triple bonds deviate slightly from 180°. These values and angles are very similar to those of other alkyne chains between metallorganic units.[21]

Experimental Section

General Remarks: All melting points are uncorrected. The NMR spectra were measured with a Bruker Avance 300 spectrometer (^{1}H NMR at 300 MHz and ^{13}C NMR at 75 MHz) and a Bruker Avance 500 spectrometer (^{1}H NMR at 500 MHz and ^{13}C NMR at 125 MHz) using the solvent as internal standard (δ). The mass spectra refer to data from a JEOL JMS-700 instrument. IR spectra were recorded with a Bruker Vector 22 FT-IR spectrometer. All reactions were carried out in dried glassware under argon using dried and oxygen-free solvents.

[(2,3,4,5-η)-2,3,4,5-Tetrapropylcyclopenta-2,4-dien-1-one](η^5-cyclopentadienyl)cobalt(I) (7): A solution of $CpCo(CO)_2$ (6.1 g, 34 mmol) in decalin (150 mL) was heated at 190 °C. 4-Octyne (3.3 g, 30 mmol) dissolved in decalin (150 mL) was then added over 8 h. When the addition was completed the heating was continued for an additional 5 d. The reaction mixture was cooled to room temperature and then filtered through neutral alumina, activity III. The solvent decalin and unreacted $CpCo(CO)_2$ were extracted with petroleum ether as the eluent. The cyclopentadienone complex was chromatographed with CH_2Cl_2/MeOH (50:1) as a broad orange band. After removal of the solvent the crude product was purified again by column chromatography on neutral alumina, activity III, with CH_2Cl_2/MeOH (20:1) to yield complex **7** (3.0 g, 54%) as an orange-red solid; m.p. 113 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.97 (t, 6 H, CH_3), 0.99 (t, 6 H, CH_3), 1.41–1.45 (m, 6 H, CH_2), 1.67 –1.70 (m, 2 H, CH_2), 1.88–1.93 (m, 2 H, CH_2), 2.25–2.49 (m, 6 H, CH_2), 4.60 (s, 5 H, Cp_{CH}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.5 (CH_3), 15.6 (CH_3), 23.4 (CH_2), 25.2 (CH_2), 28.5 (CH_2), 29.1 (CH_2), 82.6 (C_{cpd}), 83.0 (Cp_{CH}), 92.9 (C_{cpd}), 158.7 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3082 (m), 2960 (vs), 2935 (s), 2871 (s), 1575 (vs), 1466 (s), 1377 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 288 (4.45), 362 (3.57), 420 (3.32) nm. HRMS (FAB): calcd. 373.1942; found 373.1916. $C_{22}H_{33}CoO$ (372.43): calcd. C 70.95, H 8.93; found C 70.84, H 8.95.

(η^5-1-Trifluoromethylsulfonyloxy-2,3,4,5-tetrapropylcyclopentadienyl)(η^5-cyclopentadienyl)cobalt(III) Trifluoromethansulfonate (8): The cyclopentadienone complex **7** (2.5 g, 6.7 mmol), dissolved in dichloromethane (20 mL), was added to a cooled (–50 °C) solution of trifluoromethanesulfonic anhydride (2.8 g, 10.1 mmol) in dry dichloromethane (70 mL) over a period of 15 min. The mixture was warmed and stirred for 12 h at room temperature. After evaporation of the solvent, ether (100 mL) was added. The precipitate was filtered off and recrystallized from CH_2Cl_2/Et_2O. Complex **8** (3.59 g, 82%) was obtained as a yellow solid; m.p. 161 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, 6 H, CH_3), 1.07 (t, 6 H, CH_3), 1.41–1.56 (m, 8 H, CH_2), 2.44–2.72 (m, 8 H, CH_2), 5.59 (s, 5 H, Cp_{CH}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4 (CH_3), 14.7 (CH_3), 24.0 (CH_2), 25.1 (CH_2), 26.1 (CH_2), 27.4 (CH_2), 88.2 (Cp_{CH}), 95.6 (C_{cpd}), 98.9 (C_{cpd}), 118.1 (C_{OTf}) ppm. IR (KBr): $\tilde{\nu}$ = 3102 (w), 2969 (m), 2880 (w), 1631 (w), 1466 (m), 1421 (s), 1269 (s), 1224 (s), 1141 (s) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 288 (4.55) nm. HRMS (FAB): calcd. 505.1434; found 505.1455. $C_{24}H_{33}CoF_6O_6S_2$ (654.56): calcd. C 44.04, H 5.08; found C 44.21, H 5.26.

(η^5-1-Trifluoromethylsulfonyloxy-2,3,4,5-tetraphenylcyclopentadienyl)(η^5-cyclopentadienyl)cobalt(III) Trifluoromethansulfonate (15): The cyclopentadienone complex **14**[16] (1 g, 1.9 mmol), dissolved in dichloromethane (20 mL), was added to a cooled (–50 °C) solution of trifluoromethanesulfonic anhydride (0.8 g, 2.9 mmol) in dry dichloromethane (50 mL) over a period of 15 min. The mixture was warmed and stirred for 12 h at room temperature. After evaporation of the solvent, ether (100 mL) was added. The precipitate was filtered off and recrystallized from CH_2Cl_2/Et_2O to yield **15** (1.13 g, 75%) as a yellow solid; m.p. 189 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 5.94 (s, 5 H, Cp_{CH}), 7.01–7.02 (m, 4 H, CH_{arom}), 7.15–7.22 (m, 4 H, CH_{arom}), 7.30–7.33 (m, 2 H, CH_{arom}), 7.44–7.49 (m, 10 H, CH_{arom}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 90.7 (Cp_{CH}), 95.9 (C_{cpd}), 98.2 (C_{cpd}), 116.6 (C_{OTf}), 124.6 (C_{arom}), 126.2 (C_{arom}), 129.1 (CH_{arom}), 129.4 (CH_{arom}), 130.5 (CH_{arom}), 131.1 (CH_{arom}), 131.3 (CH_{arom}), 131.3 (CH_{arom}), 131.7 (CH_{arom}) ppm. IR (KBr): $\tilde{\nu}$ = 3101 (w), 2932 (s), 2861 (m), 1631 (m), 1464 (m), 1414 (s) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 256 (4.28), 352 (4.09), 402 (3.43) nm. HRMS (FAB): calcd. 641.0808; found 641.0815.

Procedure for the (Trialkylsilyl)alkynyl-Substituted RCpCo-Capped Cyclopentadienone Complexes 11a–11f and 12: *n*-Butyllithium (2.29 mmol, 1.6 M solution) was slowly added to a solution of (trialkylsilyl)acetylene (3.06 mmol) in 60 mL of THF at –30 °C. The mixture was stirred at this temperature for 90 min and then a solution of the cobaltocenium salt **8** (1.53 mmol) in THF (30 mL) was added over a period of 10 min. After it was warmed overnight and stirred further at room temperature for 48 h, the mixture was hydrolyzed with a saturated NH_4Cl solution (30 mL), the layers were separated, and the aqueous layer was washed three times with ether. Once the combined organic layers had been dried with $MgSO_4$, the solvent was removed and the crude mixture was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (30:1).

[(2,3,4,5-η)-2,3,4,5-Tetrapropylcyclopenta-2,4-dien-1-one](η^5-trimethylsilylethynylcyclopentadienyl)cobalt(I) (11a): Complex **11a** (114 mg, 16%) was obtained as a dark-red oil. ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.25 [s, 9 H, $Si(CH_3)_3$], 0.96–1.04 (m, 12 H, CH_3), 1.45–1.49 (m, 6 H, CH_2), 1.63–1.65 (m, 2 H, CH_2), 1.90–1.93 (m, 2 H, CH_2), 2.27–2.43 (m, 6 H, CH_2), 4.61–4.62 (m, 2 H, Cp_{CH}), 4.73–4.74 (m, 2 H, Cp_{CH}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = –0.4 [$Si(CH_3)_3$], 14.5 (CH_3), 14.6 (CH_3), 22.6 (CH_2), 24.2 (CH_2), 27.0 (CH_2), 27.1 (CH_2), 78.7 (C_{sp}), 82.6 (C), 84.2 (Cp_{CH}), 85.0 (Cp_{CH}), 92.7 (C), 94.7 (C), 98.5 (C), 157.0 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2960 (vs), 2933 (s), 2872 (s), 2152 (m), 1557 (vs), 1456 (s), 1250 (s) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 302 (4.18), 370 (3.45), 412 (3.09) nm. HRMS (FAB): calcd. 469.2337; found 469.2339.

[(2,3,4,5-η)-2,3,4,5-Tetrapropylcyclopenta-2,4-dien-1-one](η^5-triethylsilylethynylcyclopentadienyl)cobalt(I) (11b): Complex **11b** (437 mg, 56%) was obtained as a dark-red oil. ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.87 (q, 6 H, $SiCH_2$), 1.15 (t, 9 H, $SiCH_2CH_3$), 1.20 (t, 6 H, CH_3), 1.24 (t, 6 H, CH_3), 1.56–1.70 (m, 6 H, CH_2), 1.78–1.87 (m, 2 H, CH_2), 2.08–2.14 (m, 2 H, CH_2), 2.45–2.52 (m, 2 H, CH_2), 2.56–2.64 (m, 4 H, CH_2), 4.85–4.86 (m, 2 H, Cp_{CH}), 4.92–4.93 (m, 2 H, Cp_{CH}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 4.7 ($SiCH_2$), 7.7 ($SiCH_2CH_3$), 14.9 (CH_3), 15.0 (CH_3), 22.9 (CH_2), 24.6 (CH_2), 27.5 (CH_2), 27.6 (CH_2), 79.1 (C_{sp}), 82.3 (C), 84.5 (Cp_{CH}), 85.2 (Cp_{CH}), 92.3 (C), 92.9 (C), 100.2 (C), 158.9 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2958 (vs), 2934 (vs), 2873 (vs), 2153 (s), 1571 (vs), 1457 (s), 1237 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 272 (4.00), 304 (4.24), 372 (3.52), 416 (3.14) nm. HRMS (FAB): calcd. 511.2806; found 511.2823. $C_{30}H_{47}CoOSi$ (510.72): calcd. C 70.55, H 9.28; found C 70.49, H 9.30.

[(2,3,4,5-η)-2,3,4,5-Tetrapropylcyclopenta-2,4-dien-1-one](η^5-ethynylcyclopentadienyl)cobalt(I) (11c): NaOH (0.95 mmol, 5 M solution) was added to a solution of **11b** (439 mg, 0.86 mmol) in methanol (10 mL). After 15 min water and ether were added, the layers were separated, and the aqueous layer was washed three times with ether. The combined organic layers were dried with $MgSO_4$, the solvent was removed, and the crude mixture was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (20:1). Complex **11c** (337 mg, 99%) was obtained as a dark-red solid; m.p. 115 °C. ^1H NMR (500 MHz, CD_2Cl_2): δ = 0.97 (t, 6 H, CH_3), 1.01 (t, 6 H, CH_3), 1.40–1.49 (m, 6 H, CH_2), 1.63–1.66 (m, 2 H, CH_2), 1.85–1.91 (m, 2 H, CH_2), 2.24–2.30 (m, 2 H, CH_2), 2.35–2.43 (m, 4 H, CH_2), 3.03 (s, 1 H, $C\equiv CH$), 4.67–4.68 (m, 2 H, Cp_{CH}), 4.70–4.71 (m, 2 H, Cp_{CH}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 14.9 (CH_3), 14.9 (CH_3), 22.8 (CH_2), 24.5 (CH_2), 27.6 (CH_2), 27.7 (CH_2), 77.4 (CH_{sp}), 77.7 (C_{sp}/Cp_C), 78.0 (C_{sp}/Cp_C), 82.1 (C_{cpd}), 84.2 (Cp_{CH}), 85.4 (Cp_{CH}), 93.0 (C_{cpd}), 159.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3061 (m), 2958 (s), 2934 (s), 2871 (m), 2098 (w), 1570 (vs), 1467 (m), 1229 (w), 1120 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 298 (4.24), 368 (3.42), 416 (5.05) nm. HRMS (FAB): calcd. 397.1942; found 397.1928. $C_{24}H_{33}CoO$ (396.45): calcd. C 72.71, H 8.39; found C 72.29, H 8.29.

[(2,3,4,5-η)-2,3,4,5-Tetrapropylcyclopenta-2,4-dien-1-one](η^5-trimethylsilylbutadiynylcyclopentadienyl)cobalt(I) (11d): MeLi/LiBr (2.53 mmol, 1.5 M in THF) was added to a solution of bis(trimethylsilyl)acetylene (446 mg, 2.3 mmol) in ether (50 mL) at room temperature. After the mixture was stirred at this temperature overnight, it was cooled to –50 °C and a solution of the cobaltocenium salt **8** (1 g, 1.53 mmol) in THF (30 mL) was added over a period of 10 min. After it was warmed overnight and stirred further at room temperature for 48 h, the mixture was hydrolyzed with a saturated NH_4Cl solution (30 mL), the layers were separated, and the aqueous layer was washed three times with ether. The combined organic layers were dried with $MgSO_4$, the solvent was removed, and the crude mixture was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (30:1). Complex **11d** (83 mg, 11%) was obtained as a dark-red oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.20 [s, 9 H, $Si(CH_3)_3$], 0.96–0.99 (t, 6 H, CH_3), 1.00–1.03 (t, 6 H, CH_3), 1.40–1.49 (m, 6 H, CH_2), 1.64–1.72 (m, 2 H, CH_2), 1.84–1.89 (m, 2 H, CH_2), 2.20–2.27 (m, 2 H, CH_2), 2.33–2.44 (m, 4 H, CH_2), 4.67–4.68 (m, 2 H, Cp_{CH}), 4.76–4.77 (m, 2 H, Cp_{CH}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –0.3 [$Si(CH_3)_3$], 15.0 (CH_3), 15.1 (CH_3), 22.7 (CH_2), 24.3 (CH_2), 27.6 (CH_2), 27.6 (CH_2), 70.7 (C_{sp}), 71.7 (C_{sp}), 74.1 (C_{sp}), 76.6 (C_{sp}), 82.7 (C_{cpd}/Cp_C), 84.9 (Cp_{CH}), 85.6 (Cp_{CH}), 87.8 (C_{cpd}/Cp_C), 93.2 (C_{cpd}/Cp_C), 159.4 (C=O) ppm. HRMS (FAB): calcd. 493.2337; found 493.2325.

[(2,3,4,5-η)-2,3,4,5-Tetrapropylcyclopenta-2,4-dien-1-one](η^5-triethylsilylbutadiynylcyclopentadienyl)cobalt(I) (11e): *n*BuLi (0.95 mmol, 1.6 M in *n*-hexane) was slowly added to a solution of the complex **11c** (341 mg, 0.86 mmol) in THF (50 mL) at –35 °C. Subsequently, CuI (164 mg, 0.86 mmol) was added and the mixture was stirred for 10 min at –15 °C. After stirring at room temperature for 10 min, the suspension was cooled to –25 °C and freshly distilled ethylamine (2 mL) as well as bromo(triethylsilyl)acetylene (208 mg, 0.95 mmol) in THF (5 mL) were added. After further stirring for 12 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 ether and drying of the combined organic layers with $MgSO_4$. Purification by column chromatography on silica gel with CH_2Cl_2/MeOH (30:1) yielded the complex **11e** (349 mg, 79%) as a dark-red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.66 (q, 6 H, $SiCH_2$), 0.99 (t, 9 H, $SiCH_2CH_3$), 1.02 (t, 6 H, CH_3), 1.04 (t, 6 H, CH_3), 1.43–1.53 (m, 6 H, CH_2), 1.67–1.74 (m, 2 H, CH_2), 1.87–1.93 (m, 2 H, CH_2), 2.24–2.30 (m, 2 H, CH_2), 2.37–2.48 (m, 4 H, CH_2), 4.72–4.73 (m, 2 H, Cp_{CH}), 4.80–4.81 (m, 2 H, Cp_{CH}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 4.3 ($SiCH_2$), 7.5 ($SiCH_2CH_3$), 15.0 (CH_3), 15.1 (CH_3), 22.7 (CH_2), 24.3 (CH_2), 27.6 (CH_2), 27.7 (CH_2), 70.9 (C_{sp}), 74.4 (C_{sp}), 76.8 (C_{sp}), 83.0 (C), 85.0 (Cp_{CH}), 85.6 (Cp_{CH}), 88.2 (C), 88.9 (C), 93.3 (C), 158.7 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3099 (w), 2958 (vs), 2873 (vs), 2208 (s), 2104 (m), 1567 (vs), 1466 (s), 1378 (w), 1235 (w) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 274 (4.07), 298 (4.19), 308 (4.20), 376 (3.58), 420 (3.12) nm. HRMS (FAB): calcd. 535.2806; found 535.2809.

[(2,3,4,5-η)-2,3,4,5-Tetrapropylcyclopenta-2,4-dien-1-one](η^5-butadiynylcyclopentadienyl)cobalt(I) (11f): nBu_4NF (0.74 mmol, 1.5 M in THF) was added to a solution of **11e** (358 mg, 0.67 mmol) in THF (10 mL). After 5 h the mixture was hydrolyzed with a saturated NH_4Cl solution (30 mL), the layers were separated, and the aqueous layer was washed three times with ether. The combined organic layers were dried with $MgSO_4$, the solvent was removed, and the crude mixture was purified by column chromatography on silica gel with CH_2Cl_2/MeOH (20:1). Complex **11f** (182 mg, 65%) was obtained as a dark-red air-sensitive solid; m.p. 124 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.98 (t, 6 H, CH_3), 1.03 (t, 6 H, CH_3), 1.42–1.52 (m, 6 H, CH_2), 1.62–1.68 (m, 4 H, CH_2), 1.85–1.90 (m, 2 H, CH_2), 2.24–2.44 (m, 4 H, CH_2), 2.57 (s, 1 H, $C{\equiv}CH$), 4.74–4.75 (m, 4 H, Cp_{CH}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 15.0 (CH_3), 15.1 (CH_3), 22.8 (CH_2), 24.6 (CH_2), 27.7 (CH_2), 27.9 (CH_2), 68.2 (CH_{alkyne}), 70.7 (C_{sp}/Cp_C),70.7 (C_{sp}/Cp_c), 73.2 (C_{sp}/Cp_C), 76.4 (C_{sp}/Cp_C), 82.6 (C_{cpd}), 85.0 (Cp_{CH}), 86.0 (Cp_{CH}), 93.7 (C_{cpd}), 159.5 (C=O) ppm. IR (film): $\tilde{\nu}$ = 3071 (m), 2960 (s), 2931 (s), 2870 (m), 2213 (w), 2045 (w), 1627 (m), 1573 (vs), 1463 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 266 (4.14), 300 (4.39), 360 (3.72), 374 (3.80), 418 (3.72) nm. HRMS (FAB): calcd. 421.1942; found 421.1942.

[(2,3,4,5-η)-2,3,4,5-Tetraphenylcyclopenta-2,4-dien-1-one](η^5-trimethylsilylethynylcyclopentadienyl)cobalt(I) (12): Complex **12** (87 mg, 19%) was obtained as a dark-red solid; m.p. 208 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.12 [s, 12 H, $Si(CH_3)_3$], 4.91–4.92 (m, 2 H, Cp_{CH}), 4.94–4.96 (m, 2 H, Cp_{CH}), 7.15–7.29 (m, 16 H, CH_{arom}), 7.60–7.62 (m, 4 H, CH_{arom}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = –0.4 [$Si(CH_3)_3$], 78.9 (C_{sp}), 81.9 (C), 87.3 (Cp_{CH}), 87.4 (Cp_{CH}), 94.3 (C), 97.9 (C), 98.1 (C), 127.5 (CH_{arom}), 127.9 (CH_{arom}), 128.0 (CH_{arom}), 128.1 (CH_{arom}), 131.0 (CH_{arom}), 132.1 (CH_{arom}), 132.2 (C_{arom}), 133.0 (C_{arom}), 157.0 (CO) ppm. IR (KBr): $\tilde{\nu}$ = 3042 (w), 2919 (m), 2850 (m), 1634 (s), 1545 (w), 1502 (w), 1462 (w), 1447 (w), 1385 (w), 1250 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 270 (4.23), 346 (4.11), 402 (2.97) nm. HRMS (FAB): calcd. 605.1710; found 605.1736.

Procedure for the Alkyne-Bridged Cyclopentadienone Complexes 13a and 13b: A solution of CuCl [**13a**: 15 mg (0.15 mmol), **13b**: 10 mg (0.10 mmol)] in dry pyridine (15 mL), saturated with oxygen, was added to a Schlenk flask. The alkynyl complex [**11c**: 150 mg (0.38 mmol), **11f**: 105 mg (0.25 mmol)] was added to this mixture and oxygen was passed through the mixture for 24 h. After removal of the pyridine under vacuum, the crude product was purified by column chromatography on neutral alumina, activity III, CH_2Cl_2/MeOH (50:1).

Bis{[(2,3,4,5-η)-2,3,4,5-tetrapropylcyclopenta-2,4-dien-1-one](η^5-ethynylcyclopentadienyl)cobalt(I)} (13a): Complex **13a** (119 mg, 79%) was obtained as a dark-red solid; m.p. 166 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (t, 12 H, CH_3), 1.0 (t, 12 H, CH_3), 1.41–1.48 (m, 12 H, CH_2), 1.65–1.71 (m, 4 H, CH_2), 1.83–1.89 (m, 4 H, CH_2), 2.22–2.28 (m, 4 H, CH_2), 2.34–2.44 (m, 8 H, CH_2), 4.71–4.76 (m, 8 H, Cp_{CH}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.0 (CH_3), 15.1 (CH_3), 22.6 (CH_2), 24.3 (CH_2), 27.6 (CH_2), 27.7 (CH_2), 73.9 (C_{sp}/Cp_C), 75.4 (C_{sp}/Cp_C), 77.0 (C_{sp}/Cp_C), 82.8 (C_{cpd}), 84.9 (Cp_{CH}), 85.5 (Cp_{CH}), 93.2 (C_{cpd}), 159.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2960 (m), 2933 (s), 2871 (m), 2151 (w), 1588 (vs), 1464 (s), 1379 (m), 1119 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 286 (4.48), 382 (4.02), 442 (3.55) nm. HRMS (FAB): calcd. 791.3649; found 791.3662.

Bis{[(2,3,4,5-η)-2,3,4,5-tetrapropylcyclopenta-2,4-dien-1-one](η^5-butadiynylcyclopentadienyl)cobalt(I)} (13b): Complex **13b** (93 mg, 89%) was obtained as a dark-red solid; m.p. 159 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 0.99 (t, 12 H, CH_3), 1.04 (t, 12 H, CH_3), 1.39–1.53 (m, 12 H, CH_2), 1.60–1.70 (m, 4 H, CH_2), 1.85–1.91 (m, 4 H, CH_2), 2.24–2.45 (m, 12 H, CH_2), 4.80–4.81 (m, 8 H, Cp_{CH}) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ = 14.9 (CH_3), 15.0 (CH_3), 22.8 (CH_2), 24.6 (CH_2), 27.8 (CH_2), 27.9 (CH_2), 63.9 (C_{sp}), 66.3 (C_{sp}/Cp_C), 74.0 (C_{sp}/Cp_C), 74.0 (C_{sp}/Cp_C), 75.8 (C_{sp}/Cp_C), 82.8 (C_{cpd}), 85.6 (Cp_{CH}), 86.4 (Cp_{CH}), 94.1 (C_{cpd}), 159.6 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3066 (w), 2959 (vs), 2932 (s), 2870 (s), 2198 (vs), 2123 (w), 2077 (w), 1592 (vs), 1466 (s), 1377 (m) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 244 (4.79), 258 (4.79), 312 (4.78), 334 (4.68), 398 (4.43), 430 (4.30), 488 (3.94) nm. HRMS (FAB): calcd. 839.3649; found 839.3680.

X-ray Structure Analyses: The reflections were collected with a Bruker Smart CCD diffractometer at 200 K equipped with a Mo-K_α radiation source and a graphite monochromator (λ = 0.71073 Å). The 0.3° omega-scans that were taken covered a whole sphere in reciprocal space in each case. Intensities were corrected for Lorentz and polarization effects, and an absorption correction was applied using the SADABS program based on the Laue symmetry of the reciprocal space, except for **13a** where no absorption correction was applied because of insufficient data quality. The structures were solved by direct methods, and the structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique against F^2. All hydrogen atoms were treated using appropriate riding models. Structure solution and refinement were carried out with the SHELXTL (5.10) software package.[22]

Crystallographic data and details of the data collection and the refinement procedure are given below. CCDC-674040 (for **7**), -674041 (for **8**), -674042 (for **12**), -674043 (for **11c**), -674044 (for **11f**), and -674045 (for **13a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/conts/retrieving.html (or, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

7: Orange crystal (needle), dimensions 0.41 × 0.10 × 0.08 mm, crystal system monoclinic, space group $P2_1/c$, $Z = 8$, $a = 7.8532(1)$ Å, $b = 19.0327(3)$ Å, $c = 27.5571(3)$ Å, $\alpha = 90°$, $\beta = 90.5370(10)°$, $\gamma = 90°$, $V = 4118.71(9)$ Å^3, $\rho = 1.201$ g cm^{-3}, $\theta_{\max} = 26.35°$, 39017 reflections measured, 8397 unique [R(int) = 0.0714], 5504 observed [$I > 2\sigma(I)$], $\mu = 0.84$ mm^{-1}, $T_{\min} = 0.73$, $T_{\max} = 0.94$, 433 parameters refined, goodness of fit 1.01 for observed reflections, final residual values $R(F) = 0.040$, $wR(F^2) = 0.074$ for observed reflections, residual electron density –0.29 to 0.27 e Å^{-3}.

8: Yellow crystal (polyhedron), dimensions 50 × 26 × 15 mm, crystal system monoclinic, space group $P2_1/n$, $Z = 4$, $a = 13.9634(2)$ Å, $b = 12.8101(2)$ Å, $c = 16.9600(2)$ Å, $\alpha = 90°$, $\beta = 106.755(1)°$, $\gamma = 90°$, $V = 2904.89(7)$ Å^3, $\rho = 1.497$ g cm^{-3}, $\theta_{\max} = 27.48°$, 29561 reflections measured, 6655 unique [R(int) = 0.0377], 5340 observed [$I > 2\sigma(I)$], $\mu = 0.81$ mm^{-1}, $T_{\min} = 0.75$, $T_{\max} = 0.89$, 386 parameters refined, goodness of fit 1.03 for observed reflections, final residual values $R(F) = 0.031$, $wR(F^2) = 0.077$ for observed reflections, residual electron density –0.29 to 0.40 e Å^{-3}.

11c: Orange crystal (polyhedron), dimensions 32 × 16 × 07 mm, crystal system monoclinic, space group $P2_1/c$, $Z = 4$, $a = 13.3378(1)$ Å, $b = 7.8770(1)$ Å, $c = 21.1540(3)$ Å, $\alpha = 90°$, $\beta = 101.9460(10)°$, $\gamma = 90°$, $V = 2174.35(4)$ Å^3, $\rho = 1.211$ g cm^{-3}, $\theta_{\max} = 27.48°$, 21820 reflections measured, 4982 unique [R(int) = 0.0495], 3695 observed [$I > 2\sigma(I)$], $\mu = 0.80$ mm^{-1}, $T_{\min} = 0.74$, $T_{\max} = 0.95$, 244 parameters refined, goodness of fit 1.02 for observed reflections, final residual values $R(F) = 0.036$, $wR(F^2) = 0.076$ for observed reflections, residual electron density –0.34 to 0.26 e Å^{-3}.

11f: Red crystal (polyhedron), dimensions 0.45 × 0.26 × 0.14 mm, crystal system monoclinic, space group $P2_1/c$, $Z = 8$, $a = 17.5063(3)$ Å, $b = 15.8730(3)$ Å, $c = 18.9913(3)$ Å, $\beta = 117.2720(10)°$, $V = 4690.64(14)$ Å^3, $\rho = 1.191$ g cm^{-3}, $\theta_{\max} = 27.46°$, 47930 reflections measured, 10738 unique [R(int) = 0.0530], 6874 observed [$I > 2\sigma(I)$], $\mu = 0.74$ mm^{-1}, $T_{\min} = 0.71$, $T_{\max} = 0.91$, 513 parameters refined, goodness of fit 1.02 for observed reflections, final residual values $R(F) = 0.037$, $wR(F^2) = 0.083$ for observed reflections, residual electron density –0.53 to 0.47 e Å^{-3}.

12: Dark-red crystal (polyhedron), dimensions 0.38 × 0.22 × 0.13 mm, crystal system triclinic, space group $P\bar{1}$, $Z = 2$, $a = 10.0788(3)$ Å, $b = 12.6156(3)$ Å, $c = 13.4032(3)$ Å, $\alpha = 76.4710(10)°$, $\beta = 71.8860(10)°$, $\gamma = 81.5640(10)°$, $V = 1569.76(7)$ Å^3, $\rho = 1.279$ g cm^{-3}, $\theta_{\max} = 27.50°$, 15558 reflections measured, 7123 unique [R(int) = 0.0293], 5642 observed [$I > 2\sigma(I)$], $\mu = 0.61$ mm^{-1}, $T_{\min} = 0.77$, $T_{\max} = 0.93$, 382 parameters refined, goodness of fit 1.02 for observed reflections, final residual values $R(F) = 0.034$, $wR(F^2) = 0.079$ for observed reflections, residual electron density –0.41 to 0.28 e Å^{-3}.

13a: Red crystal (polyhedron), dimensions 0.16 × 0.29 × 0.50 mm, crystal system monoclinic, space group $C2/c$, $Z = 24$, $a = 23.3709(3)$ Å, $b = 40.0736(5)$ Å, $c = 32.4767(4)$ Å, $\beta = 110.0080(10)°$, $V = 28580.5(6)$ Å^3, $\rho = 1.279$ g cm^{-3}, $\theta_{\max} = 23.26°$, 105915 reflections measured, 20533 unique [R(int) = 0.1542], 10978 observed [$I > 2\sigma(I)$], $\mu = 0.91$ mm^{-1}, 1551 parameters refined, goodness of fit 1.01 for observed reflections, final residual values $R_1(F) = 0.092$, $wR(F^2) = 0.242$ for observed reflections, residual electron density –1.18 to 2.98 e Å^{-3}.

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