ORGANOMETALLICS

Volume 17, Number 3, February 2, 1998

# Communications

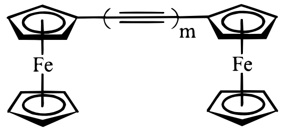
## Synthesis and Electrochemical Properties of Butadiyne-Bridged Cyclopentadienylcobalt−Cyclobutadiene Complexes

Holger Schimanke and Rolf Gleiter*

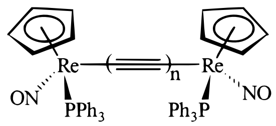
*Organisch Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*

*Received September 3, 1997*[⊗]

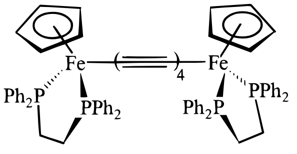
*Summary: The first cobalt $\eta^5$-cyclopentadienyl $\eta^4$-cyclopentadienyl derivative bridged by a butadiyne unit has been synthesized. Electrochemical (CV) studies reveal two oxidation potentials at 846 and 947 mV, respectively.*



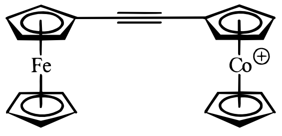
**1** (m = 1)
**2** (m = 4)



**3** (n = 1-10)



**4**



**5**

Binuclear complexes with two different redox sites in close proximity are of current interest to basic and applied research.[1] Since the first generation of the mixed-valence ion of diferrocenylacetylene (**1**) in 1974,[2] the interest in these compounds has dramatically increased.[3−5] As the ferrocenyl moiety is stable in both the neutral and oxidized forms, binuclear species with ferrocene termini have been studied intensively. It also was shown that oligoyne chains can be stabilized by organometallic fragments either by direct linking of the sp carbon to the metal as in **3**[5] or by joining the triple-bonded system to the ligand system as in **2**.[6] This led to the syntheses of long carbon chains, as exemplified by **4**.[7] So far mainly Fe, Ru, Cr, and Re have been the metals used in building binuclear complexes. Alkynes with end-capping cobalt compounds are rare[8] and have been commonly used with a cobaltocene moiety as in

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.

[1] Astruc, D. *Electron Transfer and Radical Processes in Transition Metal Chemistry*, VCH: New York, 1995. Brown, D. B., Ed. *Mixed Valence Compounds*; Reidel: Dordrecht, Holland, 1980.

[2] Le Vanda, C.; Cowan, D. O. *J. Am. Chem. Soc.* **1974**, *96*, 6728.

[3] Kramer, J. A.; Hendrickson, D. N. *Inorg. Chem.* **1980**, *19*, 3330.

[4] Lavastre, O.; Plass, J.; Bachmann, P.; Salaheddine, A.; Moinet, C.; Dixneuf, P. H. *Organometallics* **1997**, *16*, 184.

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

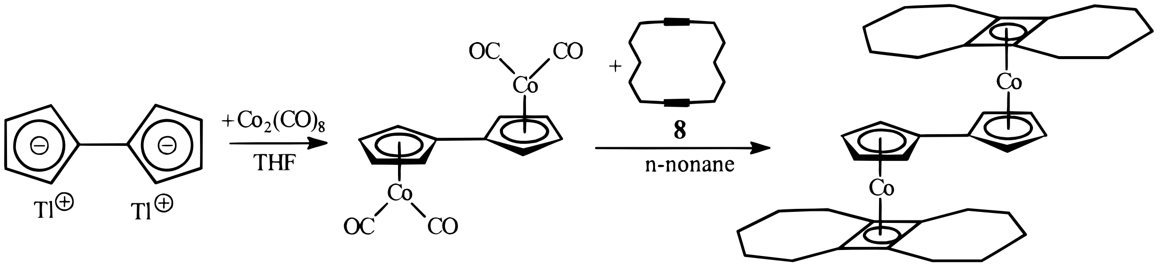
[6] Yuan, Z.; Marder, T. B. *J. Organomet. Chem.* **1993**, *452*, 115.

[7] Lapinte, C.; Coat, F. *Organometallics* **1996**, *15*, 477.

[8] Altmann, M.; Enkelmann, V.; Bunz, U. W. F. *Chem. Ber.* **1996**, *129*, 269.

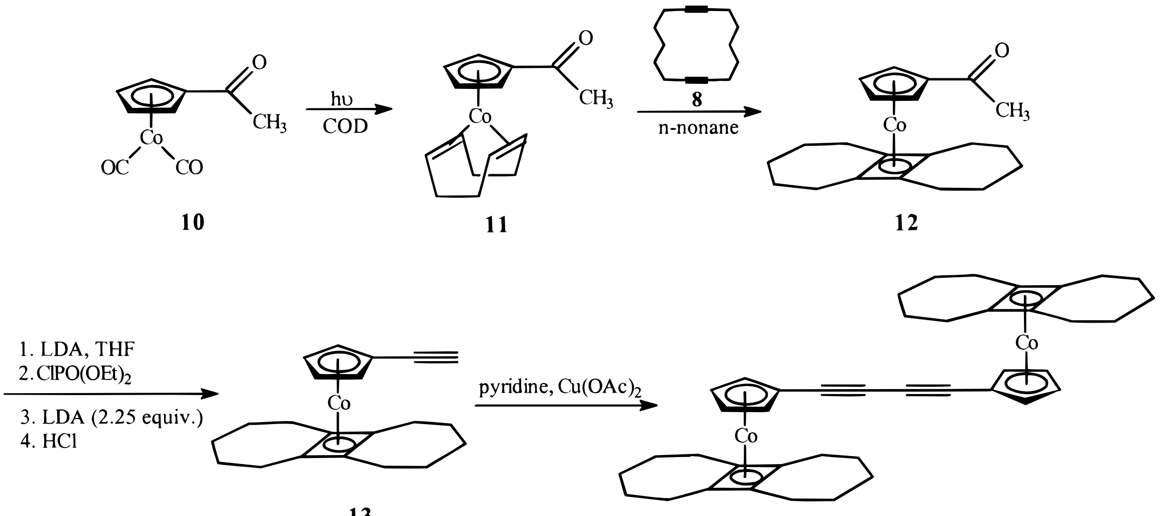
S0276-7333(97)00777-2 CCC: $15.00
Publication on Web 01/07/1998

**Scheme 1**



6 7 9

**Scheme 2**



14

**5**.[9] No binuclear alkyne-bridged cobalt complexes linked by cyclopentadienyl ligands are known to us.

We present here the synthesis and the electrochemical properties of a butadiyne terminated with an ($\eta^5$-cyclopentadienyl){(1,2,8,9-$\eta$)tricyclo[7.5.0.0$^{1,7}$]tetradeca-1,8-diene}cobalt moiety (CpCoCbd) on each side. We have chosen the CpCoCbd fragment because of its well-known redox properties[10] in mononuclear as well as in binuclear compounds and its easy availability. It can be synthesized[11] by the reaction of CpCoL$_2$ complexes with 1,8-cyclotetradecadiyne (**8**).[12] As a reference compound for our electrochemical studies, we prepared the dicobalt fulvalene complex **9**. Reaction of the dicobalt fulvalene tetracarbonyl complex **7**, which was prepared by conversion of the dithallium salt **6** of the fulvalene dianion with Co$_2$(CO)$_8$,[13] with 1,8-cyclotetradecadiyne in refluxing nonane gave ($\eta^5$:$\eta^5$-fulvalene){(1,2,8,9-$\eta$)-tricyclo[7.5.0.0$^{1,7}$]tetradeca-1,8-diene}dicobalt (**9**)[14] in 8% yield (Scheme 1). No byproduct of low molecular weight could be isolated.

The synthesis of our target molecule **14**, which contains the two redox centers at a larger distance, is summarized in Scheme 2. The starting material was ($\eta^5$-acetylcyclopentadienyl)dicarbonylcobalt (**10**),[15] which was converted to the corresponding 1,5-cyclooctadiene (COD) complex **11**[16] in 92% yield by irradiation of **10** in the presence of COD at 288 nm. Heating of **11** with 1,8-cyclotetradecadiyne in refluxing nonane afforded the cyclobutadiene complex **12**[17] in 22% yield. The acetyl group in **12** could be converted to the ethynyl group in 28% yield by a protocol described by Negishi.[18] The oxidative coupling of **13**[19] to our target molecule **14**[20] was achieved in 82% yield by following the procedure of Eglinton.[21]

---

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

[10] Gleiter, R.; Röckel, H.; Pflästerer, G.; Treptow, B.; Kratz, D. *Tetrahedron Lett.* **1993**, 558.

[11] Gleiter, R.; Pflästerer, G. *Organometallics* **1993**, *12*, 1886.

[12] Gleiter, R.; Merger, R.; Treptow, B.; Wittwer, W.; Pflästerer, G. *Synthesis* **1993**, 558.

[13] Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82.

[14] A 1.9 g (5.1 mmol) amount of 1,8-cyclotetradecadiyne (**8**) and 1.5 g (5.1 mmol) of ($\eta^5$:$\eta^5$-fulvalene)tetracarbonyldicobalt (**7**) were refluxed in 60 mL of *n*-nonane for 24 h. All volatiles were removed under vacuum and adsorbed on 3 mL of Celite. Purification by column chromatography on alumina (deactivated with 6% water, eluent: *n*-pentane) yielded 215 mg (8%) of an air-sensitive, yellow solid. Spectroscopic data for **9**: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.89 (m, 4 H), 4.62 (m, 4 H), 1.89−1.77 (m, 20 H), 1.52 (m, 16 H), 0.86 (m, 4 H); $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 80.1, 79.8, 79.1, 77.3, 30.9, 30.4, 27.9; UV/vis (*n*-pentane) $\lambda_{max}$ (log $\epsilon$) 266 (4.56), 300 (3.13), 382 (266); HRMS (EI, 70 eV) calcd for C$_{38}$H$_{48}$CO *m/z* 622.2420, found *m/z* 622.2426.

[15] Hart, P. W.; Rausch, M. D. *J. Organomet. Chem.* **1997**, *527*, 43.

[16] A 4.5 g (20.1 mmol) amount of ($\eta^5$-acetylcyclopentadienyl)-dicarbonylcobalt (**10**) was dissolved in 200 mL of 1,5-cyclooctadiene and the solution was irradiated with a low-pressure mercury lamp for 72 h. After the solvent was removed under vacuum, the black solid obtained was purified by column chromatography (alumina, deactivated with 6% water, eluent: ether). The first fraction yielded 6.0 g (92%) of an air-sensitive, red solid. Spectroscopic data for **11**: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.20−5.18 (m, 2 H), 4.17−4.15 (m, 2 H), 3.50 (m, 4 H), 2.69 (s, 3 H), 2.41−2.35 (m, 4), 1.69−1.62 (m, 4 H); $^{13}$C NMR (75.4 MHz, CDCl$_3$) $\delta$ 194.7, 97.1, 88.7, 82.7, 68.7, 31.6, 27.0; UV (*n*-pentane) $\lambda_{max}$ (log $\epsilon$) 244 (4.13), 264 (4.01), 334 (3.43); HRMS (EI, 70 eV) calcd for C$_{15}$H$_{19}$CoO *m/z* 274.0765, found *m/z* 274.0768.

**Table 1. Oxidation Potentials of 9, 13, and 14 in $CH_2Cl_2$ vs SCE**

| compd | $E_1$ (mV) | $E_2$ (mV) | $\Delta E$ (mV) |
|---|---|---|---|
| **9** | 540 | 725 | 185 |
| **14** | 846 | 947 | 101 |
| **13** | 857 | | |

In contrast to a binuclear fulvene complex studied by Geiger,[22] we found only two reversible one-electron oxidations at higher potentials for compound **9**. The potentials for all compounds are given in Table 1. The moderate difference of 185 mV for **9** between $E_2$ and $E_1$ is commonly associated with a class II valence-trapped system.[23] The radical cation of compound **9** was ESR silent at 104 K. Comparing the cyclic voltammetric data of the acetylene compounds **13** and **14**, we observed reversible one-electron oxidation for each cobalt atom. We found a potential at 857 mV for **13**. In the binuclear complex **14** two potentials were observed at 846 and 947 mV. Apparently, in the radical cationic state the two metallic centers interact via the butadiyne chain. Coulomb effects can be excluded, because both Co centers are far removed. Although the compounds gave no ESR signals at 104 K, the cyclic voltammetric results of **14** are in good agreement with a valence-trapped compound.

**Acknowledgment.** Financial support from the Deutsche Forschungsgemeinschaft (Grant No. SFB 247), the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft, Ludwigshafen, Germany, is gratefully acknowledged.

OM970777+

---

(17) A 5.3 g (28 mmol) amount of 1,8-cyclotetradecadiyne (**8**) and 8.5 g (31 mmol) of ($\eta^5$-acetylcyclopentadienyl)($\eta^4$-1,5-cyclooctadiene)-cobalt (**11**) were refluxed in 60 mL of *n*-nonane for 5 days. All volatiles were removed under vacuum and adsorbed on 3 mL of Celite. Purification by column chromatography on alumina (6% water/94% *n*-pentane → 1/1 *n*-pentane/ether) yielded 2.4 g (22%) of a yellow solid. Spectroscopic data for **12**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.35−5.33 (m, 2 H), 4.87−4.85 (m, 2 H), 2.20 (s, 3 H), 1.94−1.79 (m, 10 H), 1.58−1.45 (m, 8 H), 0.91−0.81 (m, 2H); $^{13}$C NMR (75.4 MHz, $CDCl_3$) $\delta$ 195.4, 83.8, 82.1, 80.5, 79.8, 30.3, 29.8, 27.3, 26.9; UV/vis ($CHCl_3$) $\lambda_{max}$ (log $\epsilon$) 262 (4.18), 286 (3.90), 326 (3.47), 388 (3.03); HRMS (EI, 70 eV) calcd for $C_{21}H_{27}CoO$ *m/z* 354.1397, found *m/z* 354.1405. Anal. Calcd for $C_{21}H_{27}CoO$: C, 71.16; H, 7.68. Found: C, 71.08; H, 7.56.

(18) Negishi, E.; King. A. O. *Org. Synth.* **1986**, *64*, 44; *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, p 63.

(19) To a solution of 2.82 mmol of freshly prepared LDA in 10 mL of THF was added 1 g (2.82 mmol) of ($\eta^5$-acetylcyclopentadienyl)-{(1,2,8,9-$\eta$)-tricyclo[7.5.0.0$^{1.7}$]tetradeca-1,8-diene}cobalt (**12**) in 3 mL of THF at −78 °C. After the mixture was stirred for 1 h, 0.4 mL (2.82 mmol) of diethyl chlorophosphate was added at the same temperature. The reaction mixture was kept for 1 h at −78 °C and then raised to 0 °C and stirred again for 60 min. After 5.64 mmol of LDA was added at −78 °C, the mixture was brought to room temperature within 2 h and hydrolyzed with 6 mL of degassed water. Then, ice-cold 2 N hydrochloric acid was added to pH 6. After 10 mL of a saturated aqueous solution of $NaHCO_3$ was added, the organic layer was extrated with ether and dried over $MgSO_4$. The yellow oil obtained after evaporation of the solvent was purified by column chromatography on alumina (deactivated with 6% water, eluent: *n*-pentane:ether 1:1). A 265 mg amount (28%) of a yellow, air-stable solid was obtained. Spectroscopic data for **13:** $^1$H NMR (200 MHz, $CD_2Cl_2$) $\delta$ 5.01−5.00 (m, 2 H), 4.74−4.73 (m, 2 H), 2.76 (s, 1 H), 2.00−1.94 (m, 10 H), 1.63−1.54 (m, 8 H), 0.95−0.87 (m, 2H); $^{13}$C NMR (50.3 MHz, $CD_2Cl_2$) $\delta$ 83.5, 81.6, 81.4, 80.0, 74.4, 73.7, 30.8, 30.5, 27.4; UV (*n*-pentane) $\lambda_{max}$ (log $\epsilon$) 222 (4.15), 270 (4.53), 300 (4.39); HRMS (EI, 70 eV) calcd for $C_{21}H_{25}Co$ *m/z* 336.1288, found *m/z* 336.1266.

(20) A 100 mg (0.3 mmol) amount of {$\eta^5$-ethynylcyclopentadienyl}-{(1,2,8,9-$\eta$)-tricyclo[7.5.0.0$^{1.7}$]tetradeca-1,8-diene}cobalt (**13**) was dissolved in a mixture of 5 mL of ether and 1.9 mL of ethanol. A 2.5 mL portion of freshly distilled pyridine was added. The reaction mixture was heated with an additional 540 mg (0.3 mmol) of copper(II) acetate at 53 °C for 3 h, and the mixture was poured into 10 mL of ether after cooling. The copper salts were separated by flash chromatography on Celite using ether. After evaporation of the solvents, the crude product was dissolved in 15 mL of ether and 5 mL of 1 N hydrochloric acid was added. The organic layer was separated, washed with aqueous $NaHCO_3$ solution, and dried with $MgSO_4$. Column chromatography on alumina (deactivated with 6% water, eluent: *n*-pentane:ether, 50:1) gave 24 mg of **14** in 82% yield by 15% turnover. Spectroscopic data for **14**: mp 249 °C dec; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.30−5.29 (m, 4 H), 5.04−5.02 (m, 4 H), 2.18−1.93 (m, 20 H), 1.62−1.47 (m, 16 H), 0.85 (m, 4H); $^{13}$C NMR (50.3 MHz, $CDCl_3$) $\delta$ 84.2, 82.0, 80.7, 80.0, 74.4, 73.7, 30.9, 30.5, 27.7; UV/vis ($CD_2Cl_2$) $\lambda_{max}$ (log $\epsilon$) 226 (4.77), 268 (4.75), 340 (4.35); HRMS (EI, 70 eV) calcd for $C_{42}H_{48}CO_2$ *m/z* 670.2414, found *m/z* 670.2419.

(21) Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3614. Eglinton, G.; McCrae, W. *Adv. Org. Chem.* **1963**, *4*, 225.

(22) Geiger, W. E.; Chin, T. T. *Organometallics* **1995**, *14*, 1316.

(23) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.