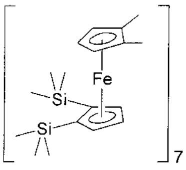
Beltlike Macrocycles with Four and Eight (Cyclopentadienyl)(cyclobutadienyl)cobalt Building Blocks, Formed by Stepwise Oligomerization of 1,6-Cyclodecadiyne Units**

Rolf J. Schaller, Rolf Gleiter,* Jasmin Hofmann, and Frank Rominger

Dedicated to Professor Walter Siebert
on the occasion of his 65th birthday

The synthesis and properties of macrocyclic compounds are important topics in supramolecular chemistry.[1] Beltlike macrocycles with various properties can be constructed by combining different bridges and rings.[2] These systems range from pure hydrocarbons, such as deltaphane,[3a] and collarene[3b], to polyazacycles,[3c] cyclodextrins,[3d] and calixarenes[3e], to name but a few. The acceptor properties of the interior of the belt depend upon the properties of these rings and bridges. Beltlike cyclophanes composed of redox-active π systems warrant special interest. To date, two such systems have been described, with ferrocene (**1**)[4] and (η^5-cyclopentadienyl)(cyclobutadienyl)cobalt [CpCo(cbd)][5] (**2** and **3**) as building blocks.



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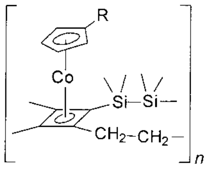
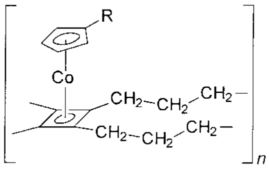


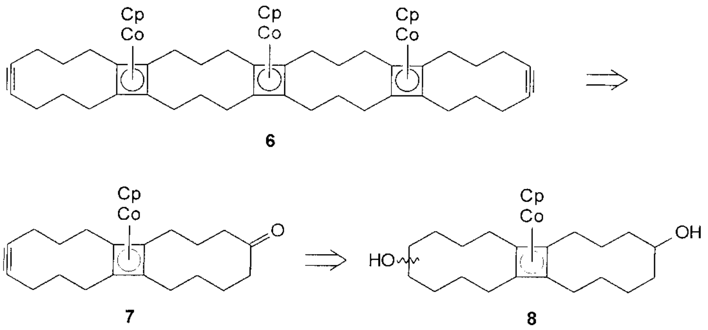
2: $n = 3$
3: $n = 4$
$R = CO_2CH_3$



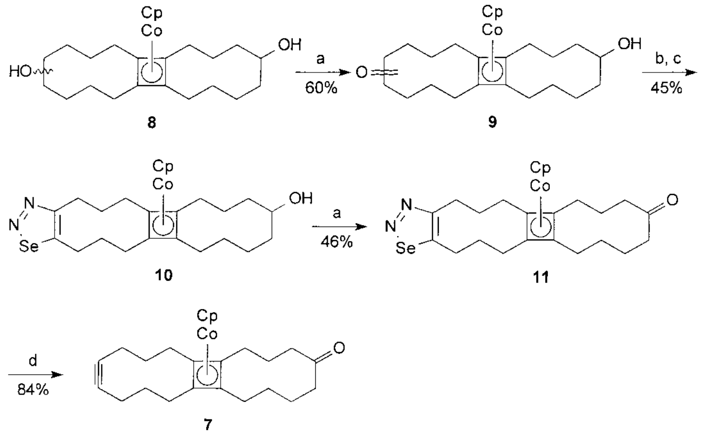
4: $n = 4$
5: $n = 8$
$R = H, CO_2CH_3$

Both systems were generated by one-pot reactions. This procedure places severe limitations on the variety of ring-size and ligands. Herein, we report on a stepwise approach to beltlike macrocycles with [CpCo(cbd)] as the π system and trimethylene units as bridges.

The heptacyclic, threefold {CpCo}-capped cyclobutadiene derivative **6**, which can be prepared by cobalt-mediated dimerization of **7**, is a key compound in the stepwise construction of **4** and **5** (Scheme 1).



Scheme 1. Retrosynthesis of the threefold {CpCo} capped cyclobutadiene derivative **6**.



Scheme 2. Synthetic route to **7**. a) $Al(iOPr)_3$, $(CH_3)_2CO$, 110 °C, toluene, 1 day; b) semicarbazide acetate, EtOH, 90 °C, 2 h; c) SeO_2, HOAc, 40 °C, 5 h; d) Cu, 190 °C, 15 min.

The tricyclic system **7** can be synthesized from the diol **8**, the preparation of which has been reported from 5-cyclodecinol.[6] Scheme 2 shows a synthetic pathway from **8** to **7**. One of the alcohol groups of **8** was selectively oxidized with acetone/aluminum tripropan-2-olate (Oppenauer procedure[7]) to afford **9**, which was converted to selenadiazole **10** in two steps.[8] First, the semicarbazone was prepared from **9** by using semicarbazide acetate. Subsequent reaction of the semicarbazone with selenium dioxide in glacial acetic acid yielded the selenadiazole **10**.[7] Only the regioisomer shown was found. The conformation of one of the ten-membered rings in **10** is very similar to the lowest energy conformation of 1,6-cyclodecadiene. Thus it seems reasonable to assume that the regioisomer **10** is the major product.[6] Oppenauer oxidation of **10** gave ketone **11**,[7] the thermolysis of which in presence of finely divided copper powder yielded **7**,[9] a key product in the synthesis of **4** ($n = 4$). The cobalt-mediated dimerization of **7** yielded three ketones (**12**), which were regioisomeric with respect to their {CpCo} fragments.[7] The *syn* isomer was transformed into bisselenadiazole **13**, analogously to **9** by reaction with semicarbazide acetate followed by SeO_2.[7] Flash thermolysis of **13** in the presence of finely divided copper yielded **6**[9] (Scheme 3).

It is noteworthy that 25 % of the dimerization product of **7** was the *syn* isomer **12** (with respect to the positions of the {CpCo} fragments of the isomers). This is one third of the total yield. For steric reasons, we expected a lower yield than this. We ascribe the unexpected yield to the conformation of **7**. X-ray structural analysis of **7** (Figure 1, top) reveals that both the alkyne chain and the chain containing the oxo group adopt positions in the same half-space. Consequently, the triple bond is shielded from "back-side" attack. These steric constraints slightly favor *syn* attack on the {CpCo} moiety.

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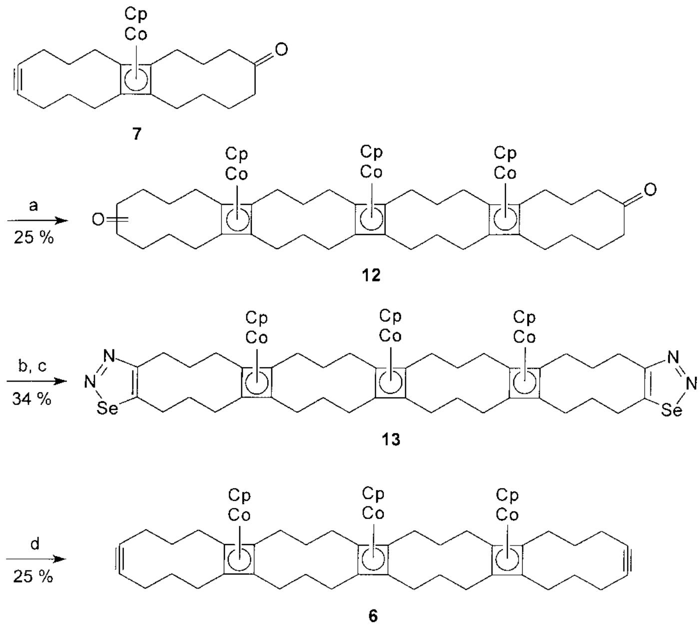
Supporting information for this article is available on the WWW under http://www.angewandte.com or from the author.



Scheme 3. Synthetic route to **6**. a) [CpCo(cod)], decalin, 170 °C, 1 day; b) semicarbazide acetate, EtOH, 90 °C, 4 h; c) SeO_2, HOAc, 40 °C, 6 h; d) Cu, 190 °C, 30 min.

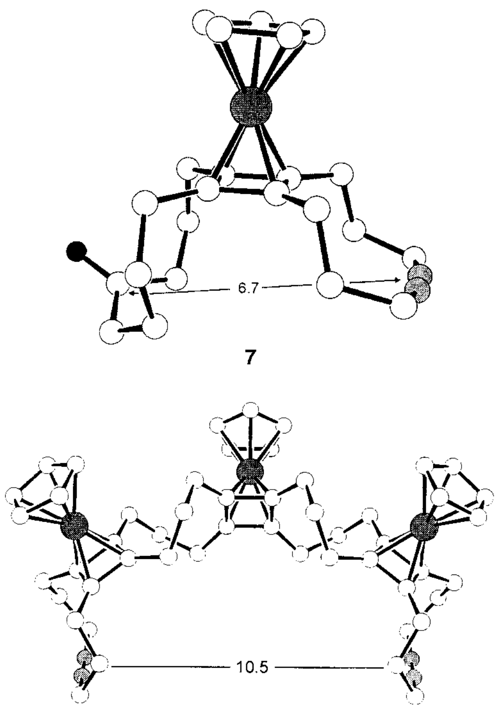
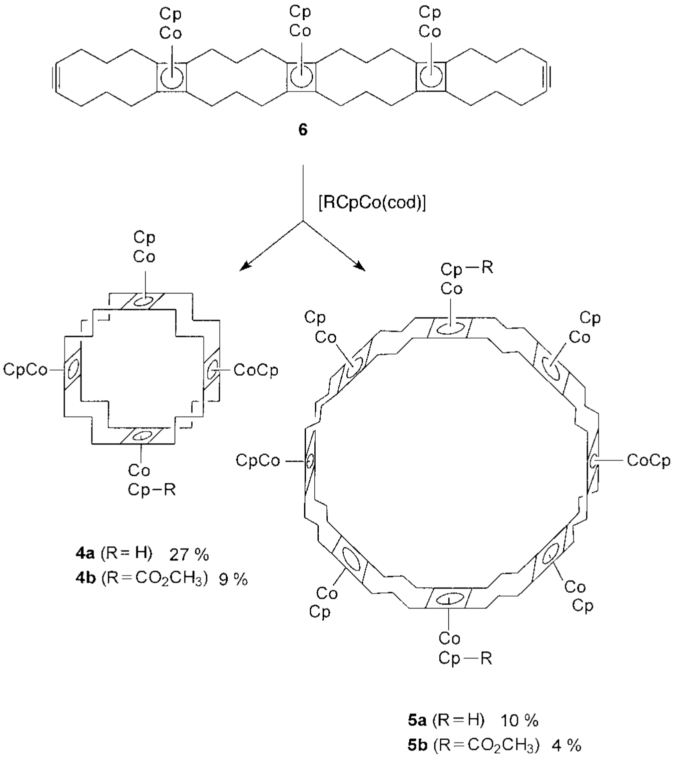


Figure 1. Structures of **6** and **7** (ORTEP plot; thermal ellipsoids for 50% probability). The hydrogen atoms are omitted for clarity. The Co atoms and the sp carbon atoms are represented as gray circles, the oxygen atom as a black circle (distances in Å).

The observed *syn–anti* ratio of 1:2 suggests that several conformations of **7** exist in solution.

The conformation of **6** in the solid state is also interesting (Figure 1, bottom). The *syn* position of all three {CpCo} fragments forces the two alkyne chains towards each other, which leads to a distance of about 10.5 Å, in a tweezerlike arrangement.[2, 10] The flexibility of the ten-membered-ring units should provide enough mobility to allow the possibility of a cobalt-induced ring closure and formation of inclusion complexes.

The reaction of **6** with [RCpCo(cod)] (R = H or CO_2CH_3; cod = cyclooctadiene) at high dilution afforded two compounds in each case (Scheme 4). The masses calculated for the main products of the intramolecular ring closure were in accord with those for the tetramers **4a** and **4b**, determined by high-resolution mass spectrometry.[11] The high level of symmetry in **4a** results in only four signals in the ^{13}C NMR spectrum. The signal for the sp hybridized carbon atoms in the cyclobutadiene unit is observed at $\delta = 84.0$; those for the Cp carbon atoms are shifted up field, to $\delta = 80.3$. Signals arising from both methylene-carbon atoms appear at $\delta = 32.4$ and $\delta = 28.4$, in a ratio of 1:2. In the ^1H NMR spectrum, a singlet is observed at $\delta = 4.57$, which is attributed to the cyclopentadienyl protons, and the signals from the two methylene groups occur at $\delta = 2.37$ and $\delta = 2.04$. The side products of the intermolecular [2+2] cycloaddition had masses of exactly twice those of **4a** and **4b**, respectively. Based on the analytical data, we assign the octameric structures **5a** and **5b** to these products, respectively[10]. Quasi-linear oligomers were not detected.



Scheme 4. Reaction of **6** with [RCpCo(cod)].

The stepwise approach described permits the synthesis of macrocyclic systems of the types **4** and **5**. This widens the potential for the synthesis of even-numbered beltlike cyclophanes containing organometallic π systems. It should now be possible to study the acceptor properties of the interior of such a cavity.

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[7] Relevant analytical data of **9**–**13** can be found in the Supporting Information.

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[9] Relevant analytical data for **6** and **7**. Compound **6**: yellow needles, m.p.: 139 °C; IR (KBr): $\tilde{\nu} = 2920$ (CH_2), 1630 cm^{-1} (C=C); UV (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 364 (2.35), 302 (3.24), 268 nm (4.31); ^1H NMR (500 MHz, C_6D_6): $\delta = 4.88$ (s, 5H; CH), 4.70 (s, 10H; CH), 2.17–1.75 (m, 48H; CH_2); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 82.9$ (C_{cbd}), 81.9 ($C_{\equiv}$), 80.2 (C_{Cp}), 79.8 (C_{cbd}), 79.5 (C_{Cp}), 79.0 (C_{cbd}), 32.0 (CH_2), 27.7 (CH_2), 25.5 (CH_2), 25.1 (CH_2), 24.1 (CH_2), 19.4 (CH_2); HRMS (FAB) calcd for $C_{55}H_{63}Co_3$: 900.2926, found: 900.2861; elemental analysis [%] calcd for $C_{55}H_{63}Co_3 \cdot 2\,CH_2Cl_2$: C 63.94, H 6.31, found: C 63.71, H 6.23; X-ray structure analysis of $C_{56}H_{65}Cl_2Co_3$: $M_r = 985.77$, $\mu = 1.184$ mm^{-1}, $\rho_{calcd} = 1.378$ $g\,cm^{-3}$, orthorhombic, space group *Pnma*, $Z = 4$, $a = 18.1815(3)$, $b = 30.8148(5)$, $c = 8.4824(1)$ Å, $V = 4752.34(12)$ Å^3, crystal dimensions $0.36 \times 0.30 \times 0.02$ mm^3, $T = 200(2)$ K, $\lambda = 0.71073$ Å, Θ-range 2.24–27.48°, $-23 \leq h \leq 23$, $-40 \leq k \leq 39$, $-11 \leq l \leq 10$; 46290 reflections collected, 5531 unique reflections, 2889 observed reflections with $I > 2\sigma(I)$, transmission max/min 0.98/0.86, an empirical absorption correction was applied by using SADABS,[12] based on the Laue symmetry of the reciprocal space. The structure was refined against F^2 with a full-matrix least-squares algorithm, $R(F) = 0.054$, $\omega R_2(F^2) = 0.092$. Hydrogen atoms were included in calculated positions. Special position of the molecule on a crystallographic mirror plane, one equivalent of dichloromethane is cocrystallized. Compound **7**: orange crystals; m.p.: 144 °C; IR (KBr): $\tilde{\nu} = 2931$ (CH_2), 1699 cm^{-1} (C=O); UV (CH_2Cl_2): λ_{max} ($\log\varepsilon$) = 380 (2.75), 300 (2.20), 268 nm (4.42); ^1H NMR (300 MHz, C_6D_6): $\delta = 4.45$ (s, 5H; CH), 2.83–1.15 (m, 26H; CH_2); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 211.7$ (C=O), 82.8 (C_{cbd}), 82.3 (C_{cbd}), 81.5 (C_{Cp}), 80.9 (C_{cbd}), 79.0 ($C_{\equiv}$), 45.2 (CH_2), 36.2 (CH_2), 29.3 (CH_2), 27.6 (CH_2), 26.4 (CH_2), 24.4 (CH_2), 23.9 (CH_2), 22.9 (CH_2), 20.8 (CH_2), 20.2 (CH_2); HRMS (FAB) calcd for $C_{25}H_{31}CoO$: 406.1706, found: 406.1711; elemental analysis [%] calcd for $C_{25}H_{31}CoO$: C 73.87, H 7.69; found: C 73.76, H 7.66. X-ray structure analysis of $C_{25}H_{31}CoO$: $M_r = 406.43$, $\mu = 0.848$ mm^{-1}, $\rho_{calcd} = 1.316$ $g\,cm^{-3}$, orthorhombic, space group *Pbca*, $Z = 8$, $a = 14.4938(1)$, $b = 10.3639(1)$, $c = 27.4912(1)$ Å, $V = 4103.87(5)$ Å^3, crystal dimensions $0.26 \times 0.18 \times 0.06$ mm^3, $T = 200(2)$ K, $\lambda = 0.71073$ Å, Θ-range 1.48–25.60°, $-17 \leq h \leq 17$, $-12 \leq k \leq 12$, $-32 \leq l \leq 32$; 28757 reflections collected, 3684 unique reflections, 2418 observed reflections with $I > 2\sigma(I)$, transmission max/min 0.95/0.80, an empirical absorption correction was applied by using SADABS,[12] based on the Laue symmetry of the reciprocal space. The structure was refined against F^2 with a full-matrix least-squares algorithm, $R(F) = 0.041$, $\omega R_2(F^2) = 0.094$. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were refined isotropically. CCDC-173922 (**7**) and CCDC-173921 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[11] Relevant analytical data of **4** and **5**. **4a**: HRMS (FAB) calcd for $C_{60}H_{68}Co_4$: 1024.2649; found: 1024.2693; ^1H NMR (500 MHz, C_6D_6): $\delta = 4.57$ (s, 20H; CH), 2.37 (m, 16H; CH_2), 2.04 (m, 32H; CH_2); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 84.0$ (C_{cbd}), 80.3 (C_{Cp}), 32.4 (CH_2), 28.3 (CH_2). **4b**: HRMS (FAB) calcd for $C_{62}H_{70}Co_4O_2$: 1082.2704, found: 1082.2699. **5a**: HRMS (FAB) calcd for $C_{120}H_{137}Co_8$: 2049.5376, found: 2049.5371. **5b**: HRMS (FAB) calcd for $C_{124}H_{140}Co_8O_4$: 2164.5408, found: 2164.5391.

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A *trans*-Platinum(II) Complex as a Single-Molecule Insulator**

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The use of single molecules as the ultimate tiny building blocks for electronic circuits would be an enormous step in terms of size reduction. This visionary concept in molecular electronics has its roots in theoretical studies of the 1970s.[1] A profound understanding of the correlation between the molecular structure and physical properties of single molecules is absolutely necessary for the design of such electronic circuits.[2] Numerous predictive correlation studies have been elaborated on the basis of electrochemical and/or spectroscopic investigations in solutions of different types of molecular wires[3] and monodisperse oligomers,[4] such as *trans*-platinum-linked oligo(tetraethenylethenes).[5]

Studies on electron transport through single-layer molecular films have been carried out between metallic electrodes.[6] Scanning tunneling microscopy has been used to investigate single or small numbers of molecules,[7] for example, in the switching behavior of molecular films supporting gold nanoclusters.[8] However, there are only a few studies on electron transport through single molecules which are covalently linked between two electrodes. Mechanically controlled break junctions have proven to be a very powerful tool for such investigations.[9] In previous work we studied the current through conjugated organic molecules[10] and generated

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