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One-Pot Synthesis of Mixed Superphanes with CpCo-Capped Cyclobutadiene- and Cyclopentadienone Rings

Rolf Roers, Frank Rominger and Rolf Gleiter*

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

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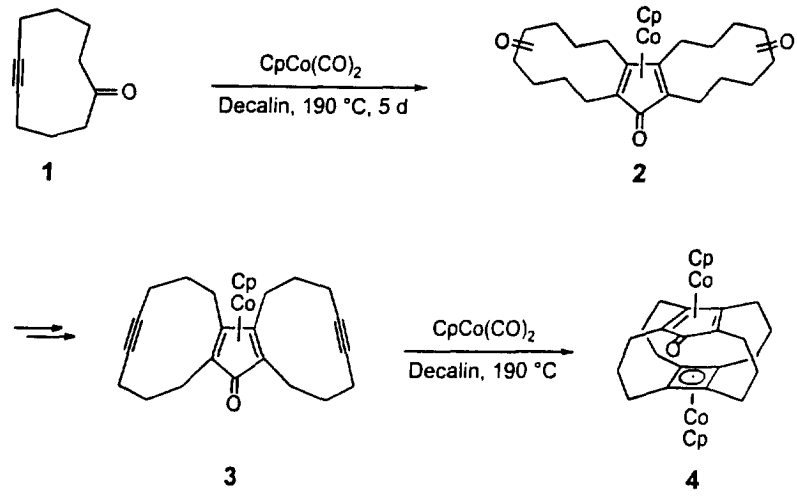
Abstract: A one-pot synthesis of mixed superphanes is reported in which CpCo-capped cyclobutadiene- and cyclopentadienone rings are connected by four pentamethylene and four heptamethylene chains, respectively.

Cyclophanes in which two cyclic conjugated π-systems face each other are ideal models for studying the interactions of two π-systems as a function of distance and intervening σ-skeleton.[1-3] For this reason a simple access to these systems is desirable. We here report a one-pot synthesis of cyclophanes consisting of one CpCo-capped cyclobutadiene system and one CpCo-capped cyclopentadienone system which are connected by four pentamethylene and four heptamethylene chains, respectively. The motivation for this study goes back to our recent report on the stepwise synthesis of **4** from 5-cyclodecynone (**1**) and dicarbonyl(η^5-cyclopentadienyl)cobalt ($CpCo(CO)_2$) as summarized in Scheme 1.[4]

Scheme 1



In order to obtain congeners of **4** in which the π-systems are further apart we went back to earlier investigations[5] which revealed a one-pot synthesis of CpCo-capped cyclobutadiene-superphanes, when heating 1,6-cyclodecadiyne[6], 1,8-cyclotetradecadiyne (**5**),[7] and 1,10-cyclooctadecadiyne (**6**) with $CpCo(CO)_2$.[8] Heating of **5** and **6** with $CpCo(CO)_2$ at 140 °C in xylene for five days afforded the superphanes **7**[9] and **8**[9], respectively, in 5 % yield (s. Scheme 2).

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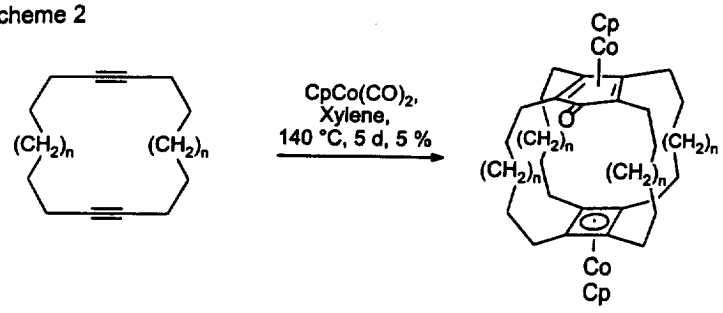
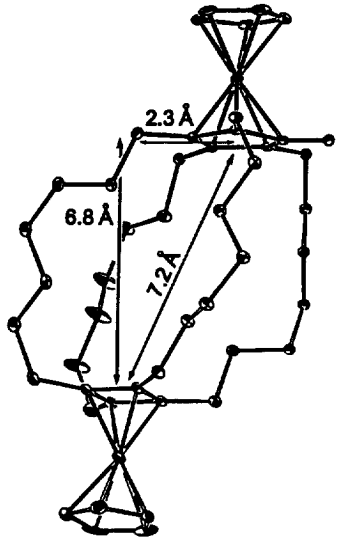
Scheme 2



n = 1, 3
5, 6

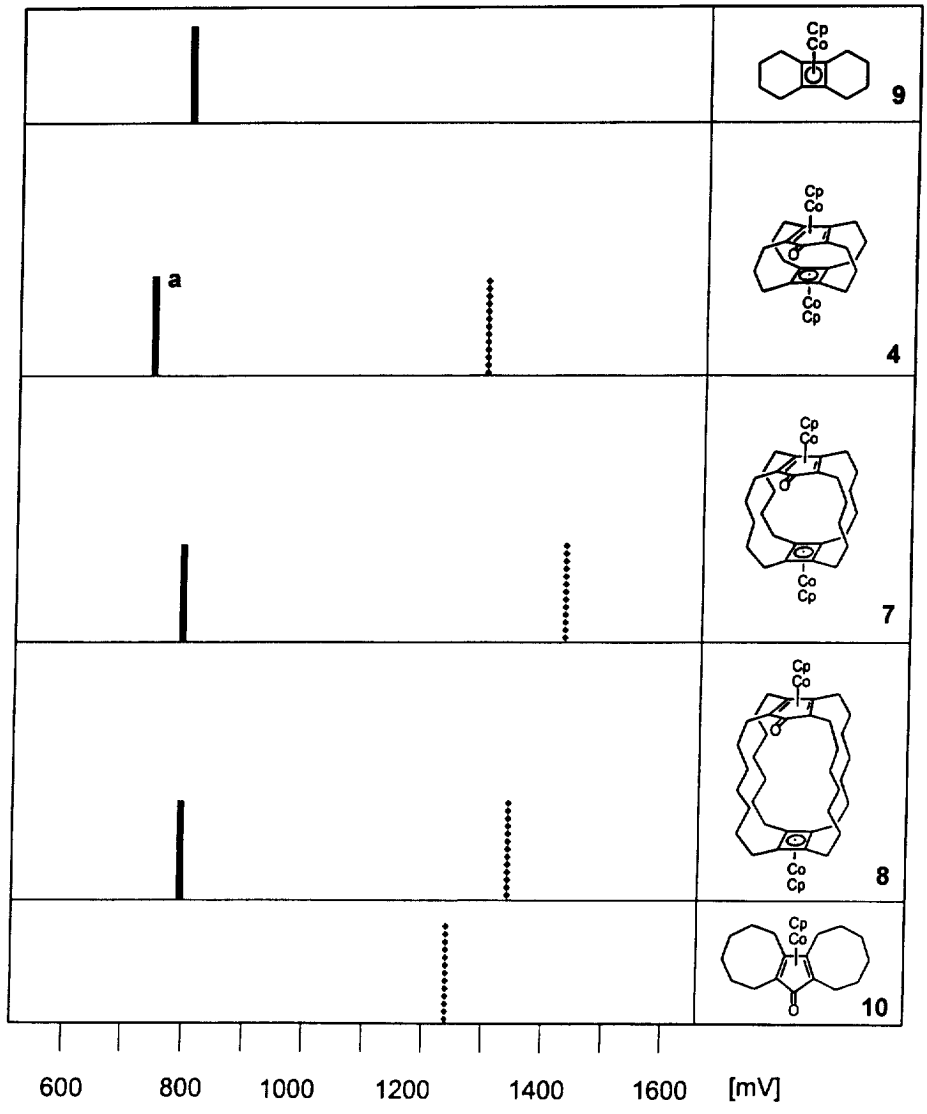
n = 1, 3
7, 8



8

Figure 1. Molecular structure of **8**[10]

An X-ray investigation of single crystals of **8** (Figure 1)[10] reveals that the centers of the two π-units are slipped by 2.3 Å. The separation between the centers of both parallel planes amounts to 7.2 Å. This slipped arrangement of both π-units reminds to the molecular structure of the CpCo-capped bis(cyclobutadiene)superphane with four heptamethylene bridges[8]. In this case X-ray investigations revealed that one of the two independent molecules in the unit cell shows a similar molecular structure as **8**. By means of cyclic voltammetry (CV) we studied the interactions between the two π-units in the mixed superphanes **4**,**7** and **8** (Figure 2)[13]. For comparison we also included in our studies the CV data of **9** and **10**. Only the first oxidation potentials below 1000 mV were reversible. A comparison between the first oxidation potentials of **4**,**7**,**8** and **9** shows that those of **7** and **8** are not influenced by the CpCo-complexed cyclopentadienone ring. We ascribe this to the large distance between both π-units in **7** and **8**. However, in **4**, where the distance between the π-units amounts to 3 Å, the first oxidation potential is shifted to lower values compared to **9**. These findings parallel those reported for the CpCo-capped bis(cyclobutadiene) superphanes[14]. Due to the irreversibility of the oxidation process above 1200 mV it seems not appropriate to draw any conclusion from these data.



[a] reversible for 0-1000 mV; irreversible for 0-1500 mV

Figure 2. Comparison between the CV data of **4**,**7**,**8**,**9** and **10**. The full bars represent reversible potentials, the broken bars irreversible potentials.

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[9] Most relevant analytical data **7** and **8**.

7: $C_{39}H_{51}Co_2O$ [M+H], calc. 653.2604, found 653.2608. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.58 (s, 5H), 4.39 (s, 5H), 2.93 - 2.88 (m), 2.73 - 2.68 (m), 2.62 - 2.57 (m), 2.30 - 2.21 (m), 2.14 - 2.02 (m), 1.68 - 1.52 (m), 1.44 - 1.37 (m), 1.31 - 0.84 (m) (together 40H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.9 (s), 93.2 (s), 85.6 (s) 84.0 (d), 81.7 (s), 81.6 (d), 79.7 (s), 30.7 (t), 30.0 (t), 29.4 (t), 27.8 (t), 27.7 (t), 27.3 (t), 26.6 (t), 26.2 (t), 26.1 (t), 23.9 (t).

8: $C_{47}H_{67}Co_2O$ [M+H], calc. 765.3856, found 765.3828. ^{1}H NMR (300 MHz, CDCl3): δ = 4.55 (s, 5H), 4.43 (s, 5H), 2.92 - 2.85 (m), 2.40 - 2.37 (m), 2.22 - 1.87 (m), 1.42 - 1.11 (m), 0.89 - 0.85 (m) (together 56H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8 (s), 92.4 (s), 82.8 (d), 81.8 (s), 80.1 (d), 79.3 (s), 78.9 (s), 31.4 (t), 31.0 (t), 30.9 (t), 30.5 (t), 30.1 (t), 29.5 (t), 28.2 (t), 27.6 (t), 27.0 (t), 26.8 (t), 26.5 (t), 26.1 (t), 24.4 (t).

[10] **8**: $C_{49}H_{76}Co_2O_4$, M = 846.96, crystal dimensions 0.3x0.2x0.1 mm^3, crystal system monoclinic, space group $P2_1/c$, Z = 4, a = 22.3360(5), b =9.4181(1), c = 22.4097(5), β = 103.947(10), V=4575.19(15) Å^3, F(000) = 1824, ρ_{calc} = 1.23 g/cm^3, $2\Theta_{max}$ = 51.2°. Radiation Mo Kα, λ = 0.71073 Å, 0.3° ω-*scans* with CCD area detector, T = 200K, 33004 reflections measured, 7963 unique, 5808 observed ($I > 2\sigma(II)$), intensities were corrected for Lorentz and polarisation effects, an empirical absorption correction was applied using SADABS[11] based on the Laue symmetry of the reciprocal space, μ = 77 mm^{-1}, T_{min} = 0.85, T_{max} = 0.94, structure solved by direct methods and refined against F^2 with a full matrix least-squares algorithm using the SHELXTL Plus (5.03) software package,[12] 556 parameters refined. Hydrogen atoms were treated using appropriate riding models, final residual values R(F) = 0.047, wR(F^2) = 0.103, residual electron density -0.46 to 0.52 e/ Å^3. Details of the crystal structure determinations of **8** may be obtained from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB 21 E10 (UK) on quoting the full journal citations.

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[13] The electrochemical measurements were performed with the METROHM potentiostat system PGSTAT20. As working electrode a METROHM disc electrode was used (diameter = 0.3 cm, glassy carbon). The Ag/AgCl reference electrode was separated from the solution by a fine grit and a luggin capillary. As electrolyte a 0.1 M solution of $(n\text{-Bu})_4N^+PF_6^-$ in CH_2Cl_2 was used. The potential of the ferrocene/ferrocenium (Fc/Fc^+) system was recorded at 721 mV with an error of ±0.5 mV vs. Ag/AgCl. All measurements were recorded at v = 100 mV/s.

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