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Synthesis and Properties of Superphanes with Cyclopentadienone Units

Rolf Roers, Frank Rominger, Christoph Braunweiler and Rolf Gleiter*
Organisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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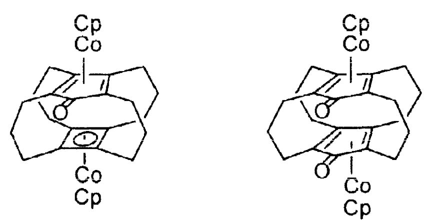
Abstract: A metal supported [2+2+1]cycloaddition of two cyclic alkynes and one CO group is the key step for the preparation of the first superphanes (**1**, **2**) with a metal-capped cyclopentadienone ring. Cyclic voltammetry reveals a strong interaction between the two π-systems in **2**.

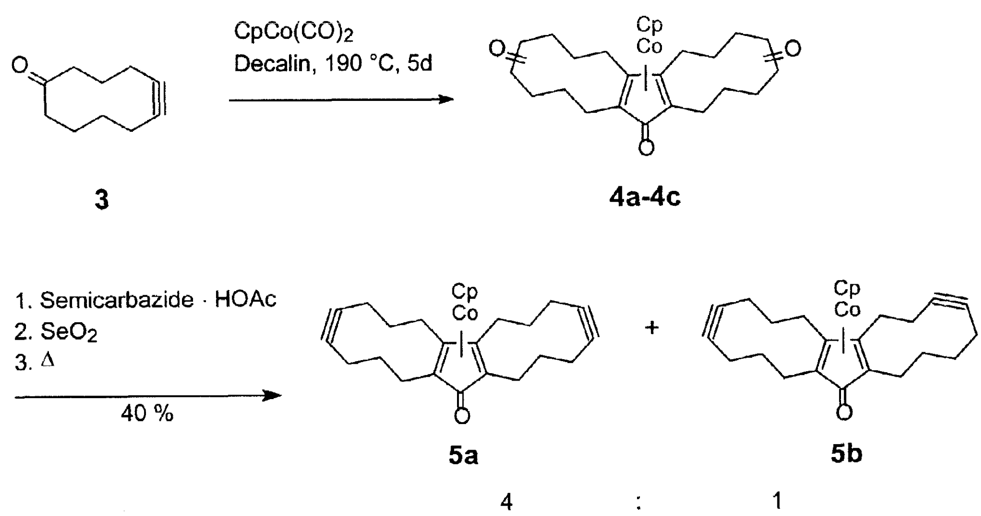
There are many examples of cyclophanes with heterocyclic five-membered 6π-units,[1,2] but there is only one report of cyclophanes with cyclopentadienone rings as building blocks.[3] In connection with our studies on phanes with three- and four-membered rings[4] we have developed a general route to cyclophanes containing cyclopentadienone rings as building units. In this paper we report on the synthesis of **1** and **2**, the first superphanes containing metal stabilized cyclopentadienone rings.



1 **2**

To construct the cyclopentadienone unit we made use of the transition metal supported [2+2+1]cycloaddition of two alkynes and one CO group to cyclopentadienone.[5] Starting point of our synthesis was 5-cyclodecynone (**3**)[6] which was transformed to a mixture of isomeric tricyclic cyclopentadienone complexes **4a** - **4c** in 60% yield when heated with dicarbonyl(η^5-cyclopentadienyl)cobalt ($CpCo(CO)_2$) in decalin at 190 °C for five days. The isomeric complexes of **4** were transferred to a mixture of isomeric

Scheme 1



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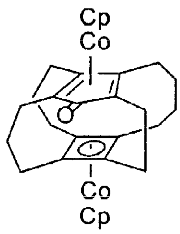
tricyclic diynes following a procedure which was used earlier to synthesize the corresponding cyclobutadiene complexes to the tricyclic diynes.[7] In this protocol the isomeric bissemicarbazones were transformed to the bisselenadiazoles following a procedure proposed by Lalezari.[8] Thermolysis of the bisselenadiazoles yielded the bisalkynes. The main products **5a**[9] and **5b** were separated by HPLC.

The mixture of **5a/5b** was heated for five days in decalin at 190 °C in presence of $CpCo(CO)_2$. The resulting mixture of products was separated by HPLC into a main component (**1**, 20%)[9] and a minor one. The analytical properties of the latter are in agreement with either the structure of **6** or the structure of **7**.



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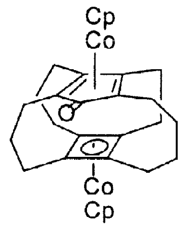

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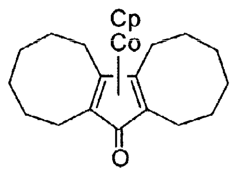
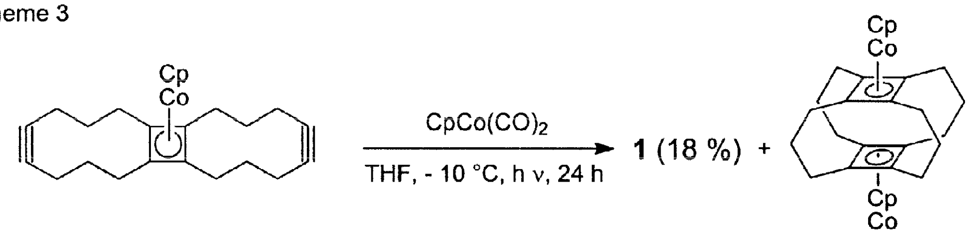


10

Scheme 2

$$\mathbf{1} \xleftarrow[\text{Decalin, 190 °C, 5d}]{CpCo(CO)_2} \mathbf{5a,5b} \xrightarrow[\text{THF, 30 °C, h}\nu]{CpCo(CO)_2} \mathbf{2}$$

Scheme 3



8 **9**

To confirm the structural assignment of **1** it was also independently synthesized. We obtained **1** in 18% yield by irradiation of the tricyclic diyne **8**[7] in the presence of $CpCo(CO)_2$.

The irradiation of the mixture of **5a/5b** in the presence of $CpCo(CO)_2$ in THF at 30 °C gave red crystals in 25% yield to which we assigned the structure of superphane **2**. The structural assignment of **2** is based on spectroscopic data.[9] The *syn*-configuration is deduced from the four signals of the bridging sp^3 carbon centers in the ^{13}C NMR spectrum because in the case of the *trans*-isomer only three signals are expected for the sp^3 carbon centers. X-ray investigations on single crystals of **2** (see Figure 1)[10] reveal two cyclopentadienone units oriented parallel at a distance of 3 Å. The carbonyl groups adopt the *syn*-configuration in the solid state.

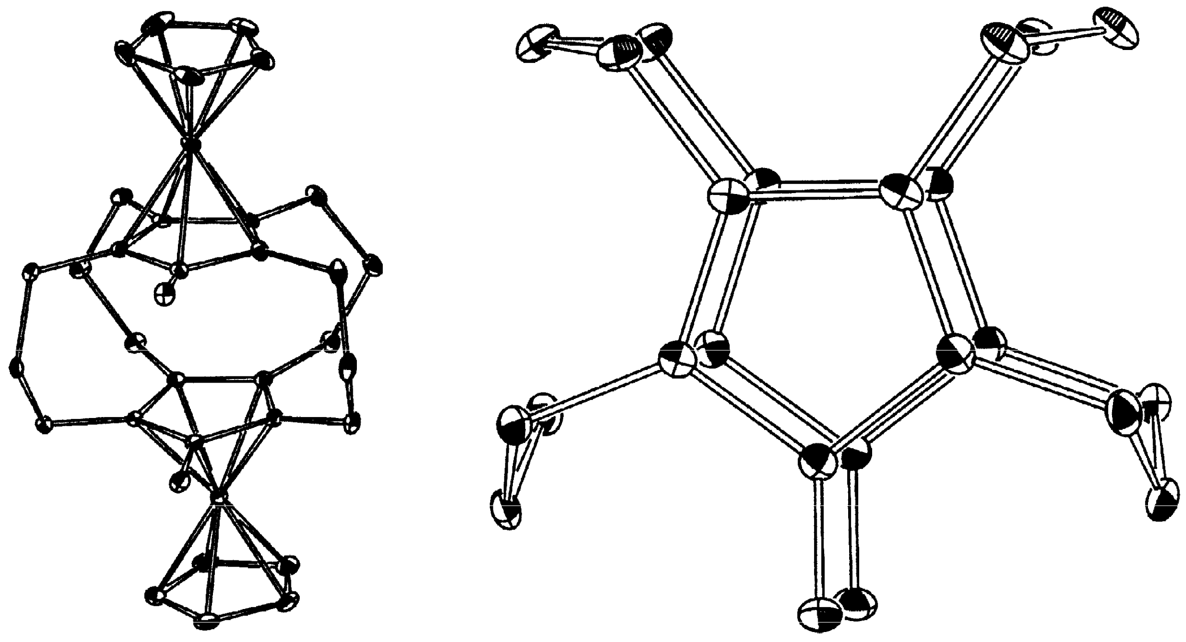


Figure 1. Molecular structure of **2** (ORTEP-PLOT).[10] Side view (left) and top view (right). In the latter case the CpCo units were omitted for the sake of clarity.

Table 1. Oxidation potentials of **1**, **2** and **10**[13] in methylene chloride.

compound	E_1 (mV)	E_2 (mV)
1	734	1291[a]
2	1198[a]	1511[a]
10	1233[a]	-

[a] irreversible oxidation

The interaction of the two CpCo(CpO) units in **2** can be seen from the comparison of the CV data of **2** with **10**. The first oxidation potential of **2** occurs at a lower value (1198 mV) than in **10** (1233 mV). As anticipated, the second oxidation of **2** occurs at a considerably higher value (1511 mV) than the first one due to the interaction of the positively charged CpCo(CpO) moiety with the neutral one in **2**. The energy difference between the first and second oxidation potentials of **2** (313 mV) is similar to that recorded for **9** (445 mV) and points to a strong interaction between both CpCo(CpO) units in **2**.

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9 Most relevant analytical data of **1**, **2**, and **5a**.

1: $C_{31}H_{35}Co_2O$ [M+H], calc. 541.1351, found 541.1365, +1.3 mmu. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.49 (s, 5H), 4.34 (s, 5H), 2.95 - 2.84 (m), 2.78 - 2.68 (m), 2.58 - 2.49 (m), 2.34 - 2.24 (m), 2.13 - 1.79 (m) (together 24H). ^{13}C NMR (75.0 MHz, $CDCl_3$): δ = 152.4 (s), 90.8 (s), 84.3 (s), 82.1 (s), 81.6 (d), 80.2 (d), 76.75 (s), 26.3 (t), 26.0 (t), 25.4 (t), 24.8 (t), 23.0 (t), 20.5 (t). λ_{max} [nm] lgε = 232(4.3), 290(4.3), 358(4.3).

2: $C_{32}H_{35}Co_2O_2$ [M+H], calc. 569.1301, found 569.1326, +2.5 mmu. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.52 (s, 10H), 3.14 - 3.10 (m), 2.81 - 2.63 (m), 2.29 - 2.14 (m), 1.72 - 1.67 (m) (together 24H). ^{13}C NMR (125.75 MHz, $CDCl_3$): δ = 149.1 (s), 89.7 (s), 87.4 (s), 82.3 (d), 25.3 (t), 24.1 (t), 23.1 (t), 20.6 (t). λ_{max} [nm] lgε = 220(4.1), 260(3.6), 326(4.2), 420(3.2).

5a: $C_{26}H_{30}CoO$ [M+H], calc. 417.1628, found 417.1611, -1.7 mmu. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.55 (s, 5H), 2.98 - 2.88 (m, 4H), 2.72 - 2.66 (m, 4H), 2.43 - 2.36 (m, 4H), 2.14 - 2.04 (m, 4H), 1.86 - 1.77 (m, 4H), 1.52 - 1.50 (m, 4H). ^{13}C NMR (75.0 MHz, $CDCl_3$): δ = 157.7 (s), 94.1 (s), 84.1 (s), 84.0 (s), 83.3 (d), 82.7 (s), 29.9 (t), 26.6 (t), 24.6 (t), 24.1 (t), 19.8 (t), 19.0 (t). λ_{max} [nm] lgε = 224(4.2), 292(4.4), 351(3.6), 364(3.7), 418(3.4).

10 **2**: $C_{32}H_{34}Co_2O_2$, M = 640.52, crystal dimensions 0.30x0.30x0.12 mm^3, crystal system monoclinic, space group $P2_1/n$, z = 4, a = 9.3822(1), b = 18.8319(3), c = 16.1949(2) $Å^3$, F(000) = 1344, ρ_{calc} = 1.52 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, 20550 reflections measured, 4859 unique, 4050 observed ($I>2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[11] based on the Laue symmetry of the reciprocal space, μ = 1.239 mm^{-1}, T_{min} = 0.74, T_{max} = 0.89, 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] 441 parameters refined. Hydrogen atoms were treated using appropriate riding models, final residual values R(F) = 0.025, wR(F^2) = 0.059, residual electron density -0.32 to 0.25 e/ $Å^3$. Details of the crystal structure determinations of **2** 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 (radius ≈ 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 ferrocen/ferrocenium (Fc/Fc^+) system was recorded at 721 mV with an error of± 5 mV vs. Ag/AgCl. All measurements were recorded at v = 100 mV/s.