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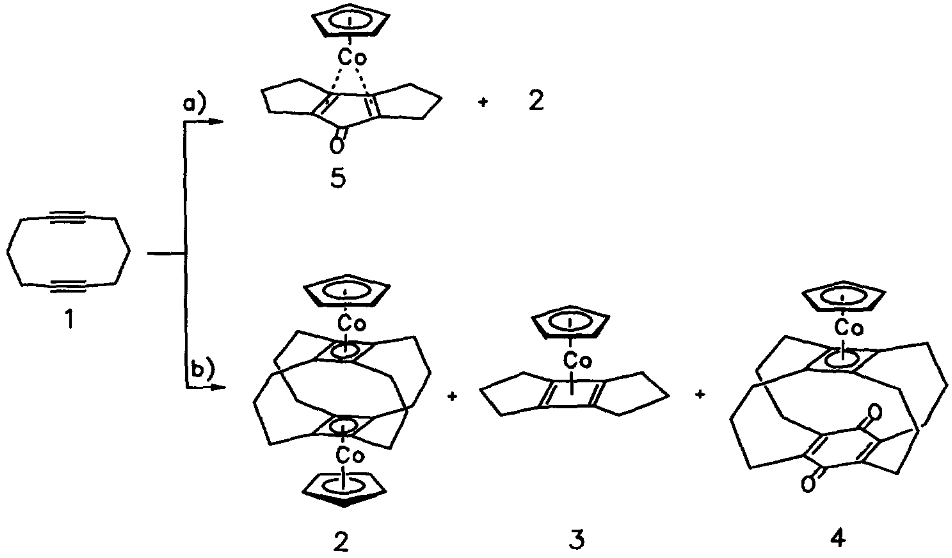
ISOLATION OF A DONOR-ACCEPTOR SUPERPHANE WITH A QUINONE AND A CpCo-CYCLOBUTADIENE UNIT

Rolf Gleiter and Detlef Kratz
Organisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, D-6900 Heidelberg, W. Germany

Abstract -
The reaction of cyclodeca-1,6-diyne with η^5-cyclopentadienylcobaltdicarbonyl not only yields the cyclobutadiene-derivatives **2** and **3** but also the fourfold bridged donor-acceptor superphane **4** as a side product.

The reaction of cyclodeca-1,6-diyne (**1**) with η^5-cyclopentadienylcobaltdicarbonyl ($CpCo(CO)_2$) in n-octane under reflux conditions gives the twofold CpCo-capped superphane of cyclobutadiene (**2**) and the cyclobutadiene

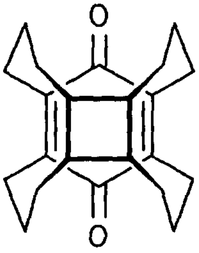


Scheme 1. a) in xylene, $CpCo(CO)_2$; b) in n-octane, $CpCo(CO)_2$

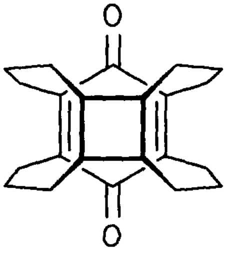
derivative **3** in yields of 12% and 6%, respectively (see Scheme 1).[1,2] Since the exclusive occurrence of η^4-cyclobutadiene complexes is rather the exception than the rule in such reactions[3] we have looked for other by-products.

Our search for further molecules was rewarded in so far as we found an additional side product (0.7%) whose analytical data are consistent with structure **4**. When the reaction is run in xylene under reflux conditions we were able to isolate the cyclopentadienone complex **5** in 5% yield (s. Scheme 1) next to **2** (1.7%). Although **4** is formed in very small yield it is of considerable interest with respect to its formation and its properties.

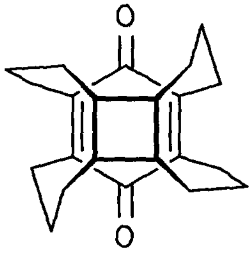
Preliminary X-ray results on **4** confirm our structural assignment.[4] The distance between the plane of the cyclobutadiene ring and the plane defined by the two C,C-double bonds of the quinone ring is found to be 2.95 Å. The quinone ring exhibits a tublike conformation in which the two CO groups are bent out of the plane of the quinone ring by $\approx 30^{\circ}$. From the three possible conformations (**a**-**c**) of the trimethylene chains, conformation **a** is preferred in the solid state.



a



b



c

A similar tublike conformation of the p-benzoquinone ring has been found in the case of p-quinoide compounds that are coordinated by a metal fragment (e.g. CpCo, CpRh)[5] or in the case of [2.2] and [3.3] quinocyclophanes.[6] The tublike conformation also accounts for the observation that the quinone moiety of **4** is not CpCo-complexed as is usually the case when quinones are formed in reactions of acetylenes and $CpCo(CO)_2$.[3] We ascribe the red colour of **4** to a charge transfer transition from the η^4-complexed cyclobutadiene moiety to the nonplanar p-benzoquinone part. In Figure 1 we have compared the electronic spectra of **4** (λ_{max} = 424 nm, log ϵ = 3.07) with those of tetramethylbenzoquinone (**6**) (λ_{max} = 430, log ϵ = 1.38) and η^5-cyclopentadienyl-tetraethyl-η^4-cyclobutadienecobalt (**7**) (λ_{max} = 380 nm, log ϵ = 1.68).[7] A very broad longwavelength absorption, typical for charge transfer complexes of quinone[8] is found. The nonplanarity of the quinone moiety in **4** rationalizes the observation that the longwavelength band in **4** occurs approximately at the same energy as in planar **6**.

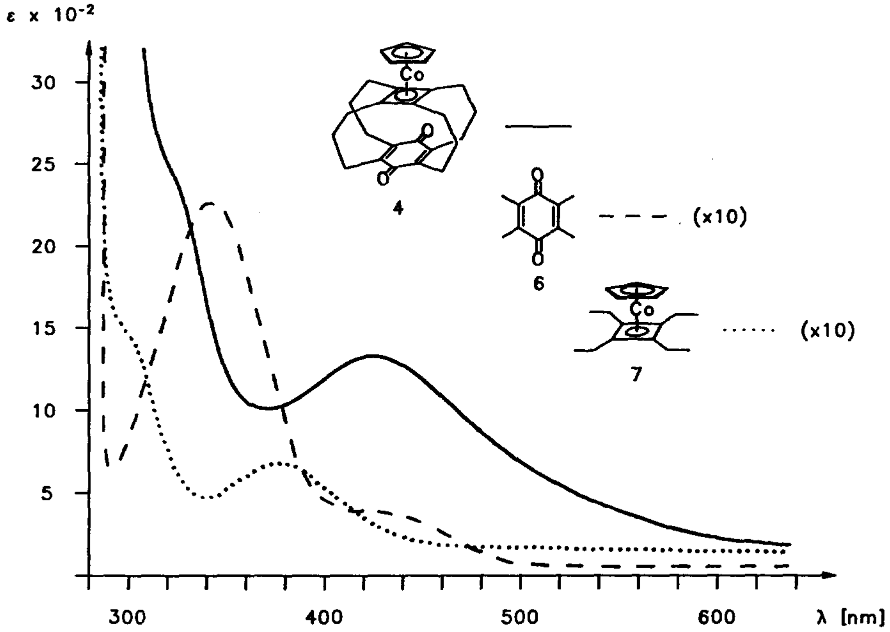


Fig. 1 Electronic absorption spectra of **4**, **6** and **7** in methylene chloride. The spectra of **6** and **7** are magnified by 10 for clarity.

Most relevant analytical data of **4** and **7**.

4: mp. > 250°C; **^{1}H-NMR** (300 MHz, $CDCl_3$): δ = 4.31 (s, 5H), 2.72 (m, 4H), 2.43 (m, 4H), 2.25 (m,8H), 1.66 (m, 4H), 1.52 (m, 4H); **^{13}C-NMR** (75.47 MHz, $CDCl_3$): δ = 26.35 (CH_2), 26.39 (CH_2), 26.71 (CH_2), 80.76 (CH), 82.25 (C), 143.74 (C=C), 190.78 (C=O); **MS** (EI): m/z 444 (M^+, 12%), 388 (M^+-(2x C=O), 17), 322 (M^+-(C_5H_6, 2x C=O), 16), 189 ($Co(C_5H_5)_2{}^+$, 12), 180 (CoC_5H_5, 2x C=O), 24), 152 (59), 124 (CoC_5H_5), 71), 91 (46), 59 (Co, 100), 44 (C_3H_8, 63); **IR** (KBr): ν [cm^{-1}] = 2926 (CH_2), 2860 (CH_2), 1646 (C=O), 1620 (C=O), 1547, 1455, 1432, 1268, 1237, 799; **UV/VIS** (CH_2Cl_2): λ_{max}[nm] (lgϵ) = 266 (4.12), 320 (3.38), 424 (3.07).

7: **^{1}H-NMR** (200 MHz, C_6D_6) δ = 4.67 (s, 5H), 1.95 (q, ^3J(H,H) = 7.5 Hz, 8H), 1.06 (t, ^3J(H,H) = 7.5 Hz, 12H); **^{13}C-NMR** (75.46 MHz, C_6D_6): δ = 15.48 (CH_3), 21.20 (CH_2), 80.35 (CH), 80.51 (C); **GC-MS** (EI): m/z 288 (M^+, 100%), 273 (M^+-CH_3, 11), 259 (M^+-C_2H_5, 71), 189 ($Co(C_5H_5)_2{}^+$, 8), 124 (CoC_5H_5, 44), 91 (8), 59 (Co, 25); **IR** (CH_2Cl_2): ν [cm^{-1}] = 2866 (CH_2), 1757, 1684, 1608, 1460, 1368, 819; **UV/VIS** (CH_2Cl_2): λ_{max}[nm] (lgϵ) = 234 (3.08), 264 (3.24), 298 (2.03), 380 (1.53).

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7 Synthesis of **7**: In 500 ml degassed decaline 1.6 g (6.89 mmol) CpCo (C_8H_{12}) are heated at 150° C. Under exclusion of air 2.16 g (28.3 mmol) 3-hexyne is added dropwise within 48 h. After further heating at 150°C for 12 h the solvent is removed and the residue is dissolved in n-pentane and chromatographed on Al_2O_3 (III). One obtains 1.6 g **7** (80%) as a yellow oil that solidifies at ≈ -10°C.

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