A Heptamethylene Bridged Superphane of a Co(C_5H_5)-Stabilized Cyclobutadiene Complex

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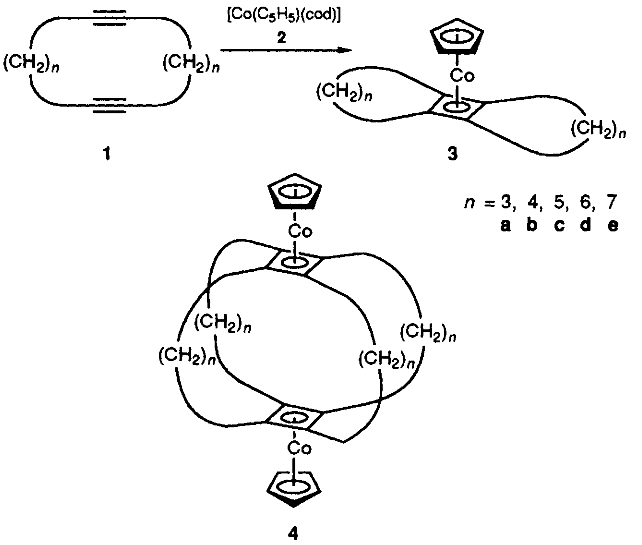
The reaction of cyclooctadeca-1,10-diyne with (η^4-cyclooctadiene)(η^5-cyclopentadienyl)cobalt gives in low yields the Co(C_5H_5)-stabilized cyclobutadiene superphane with four heptamethylene bridges.

In his seminal paper on the conformation of polycyclic ring systems, J. Dale showed that if one connects two π-systems with uneven chains of equal length a strain-free zig-zag conformation of the chains is adopted.[1] In the case of even chains no strain-free conformation is possible. This might be one of the reasons why the formation of superphanes of metal-stabilized cyclobutadiene has been reported only from cyclodeca-1,6-diyne **1a**[2] and cyclotetradeca-1,8-diyne **1c**.[3] In both cases the four chains between the cyclobutadiene moieties adopt a strain-free conformation.

In the case of cyclododeca-1,7-diyne **1b** only the intramolecular cyclization product **3b** has been found.[4] The observations so far[5] suggest that for cyclohexadeca-1,9-diyne **1d** only the intramolecular product **3d** should be formed while for cyclooctadeca-1,10-diyne **1e** the superphane **4e** seems a likely product. To probe these assumptions we have synthesized **1d** and **1e** using known procedures.[6] In the case of **1e** we could grow single crystals. The molecule has crystallographically



1 **3** **4**

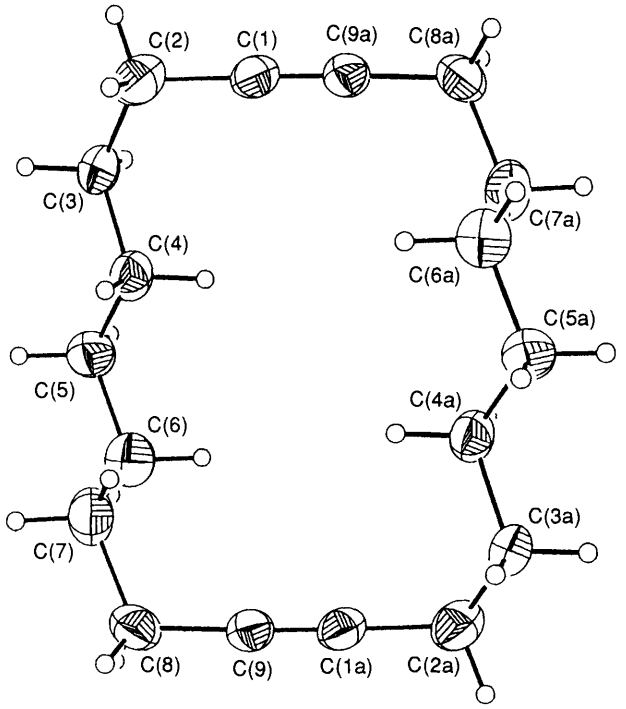


Fig. 1 Molecular structure of **1e**. Selected distances (Å): C(1)–C(9a), 1.167(5), C(1)–C(2) 1.476(5), C(2)–C(3) 1.537(5), C(3)–C(4) 1.511(5), C(4)–C(5) 1.529(5), C(5)–C(6) 1.534(5), C(6)–C(7) 1.478(6), C(7)–C(8) 1.540(5), C(8)–C(9) 1.462(5), C(1)–C(9) 7.118; angles (°) C(2)–C(1)–C(9a) 179.1(0.4).

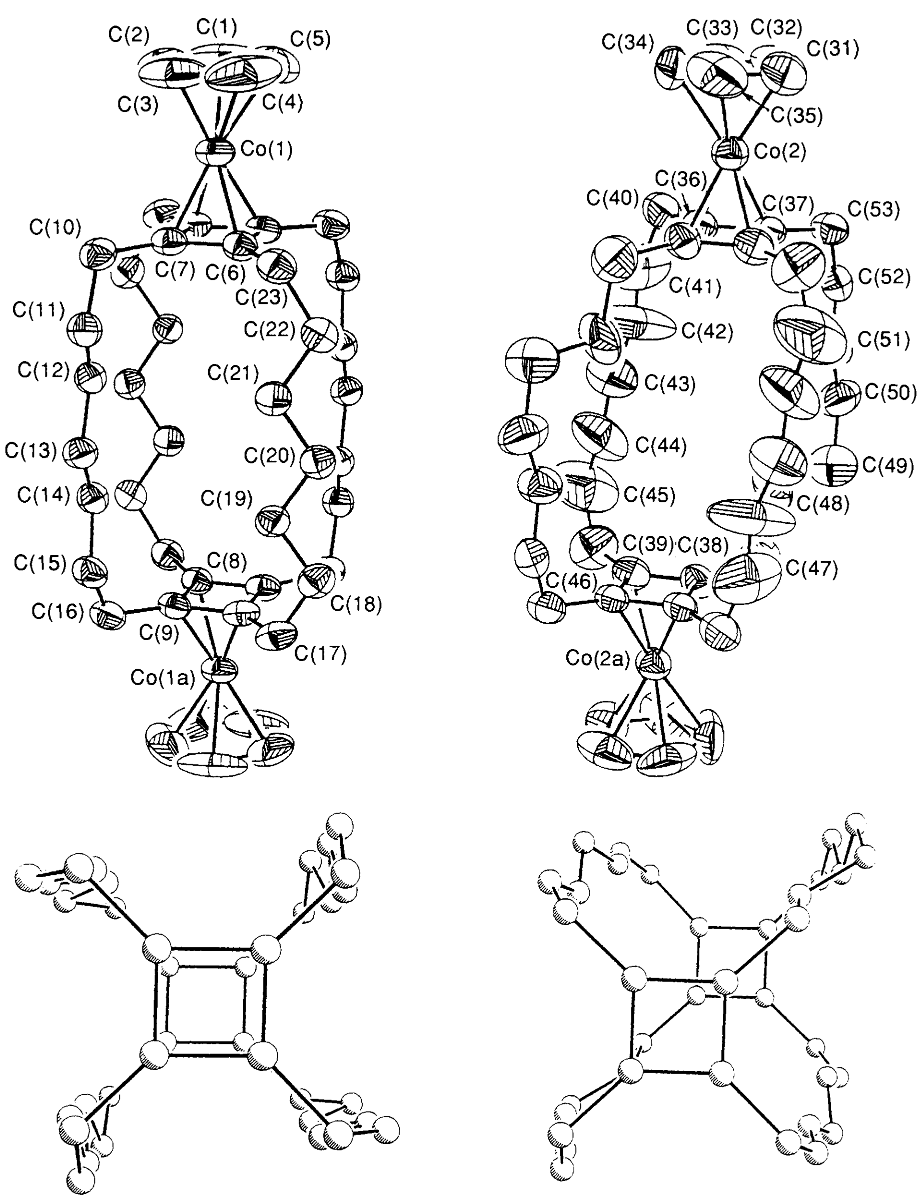


Fig. 2 Side view (top) and top view (bottom) of two independent molecules of **4e** in the unit cell. In the top view the Co(C_5H_5) moieties have been omitted. For clarity only the heavy atoms have been drawn. Selected distances (Å) left side: C_5H_5 ring C–C (av.) 1.335(23) centre of C_5H_5 ring–Co(1) 1.671; centre of cyclobutadiene unit–Co(1) 1.671; cyclobutadiene ring C–C (av.) 1.465(8), centre butadiene–centre butadiene: 7.83, butadiene C–CH_2 (av.) 1.500(8); Right side C_5H_5 ring, C–C (av.) 1.326(18), centre of C_5H_5 ring–Co(2) 1.672, centre of cyclobutadiene unit–Co(2): 1.672; cyclobutadiene ring (av.) 1.455(8) centre butadiene–centre butadiene: 7.44, butadiene–CH_2: 1.499(8).

imposed inversion symmetry; an X-ray analysis† confirms the predicted zig-zag conformation of the chains which separate the triple bonds by 7.12 Å (Fig. 1).

The reaction of **1e** with (η^4-cycloocta-1,5-diene)(η^5-cyclopentadienyl)cobalt{[Co(C_5H_5)(cod)], **2**} (5 days in nonane, reflux) gives (η^4:η^4-[7_4]cyclobutadienophane)bis(η^5-cyclopentadienyl)cobalt **4e**‡ in 0.5–1% yield, the main product being a dark polymer. X-Ray investigations on single crystals of **4e**† reveal two molecules in the unit cell (Fig. 2)

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† *Crystal data* **1e**: $C_{18}H_{28}$ crystallized from tetrahydrofuran (THF), space group *Pbca* (the space group has previously been published[6]), a = 9.305(4), b = 9.492(3), c = 17.821(5) Å, V = 1574.0 Å^3; Z = 4, Mo-Kα radiation, λ = 0.71072 Å. Intensity data were collected on a SYNTEX R3 diffractometer. Of 1854 reflections collected, 859 were with $I > 2\sigma(I)$ and 766 were considered unique with $I > 2.5\sigma(I)$. The structure was solved by direct methods (SHELXTL PLUS). R = 0.074, R_W = 0.065. The weighting scheme used was $1/\sigma^2$ (F).

4e: $C_{46}H_{66}Co_2$ crystallized by sublimation, space group $P\bar{1}$, a = 9.843(4), b = 10.386(4), c = 21.317(5) Å, α = 92.51(3), β = 95.74(3), γ = 112.06(3)°, V = 2001.7 Å^3; Z = 2, Mo-Kα radiation, λ = 0.71072 Å. Intensity data were collected on an SYNTEX R3 diffractometer. Of 8156 reflections collected, 5440 were with $I > 2\sigma(I)$ and 4950 were considered unique with $I > 2.5\sigma(I)$. The structure was solved by Patterson–Fourier carried out with SHELXTL PLUS. R = 0.068, R_W = 0.073. The weighting scheme used was $1/[\sigma^2(F) + 0.0003F^2]$.

For both structures (**1e**, **4e**) the H atoms were located by option HFIX, using the riding model with fixed isotropic thermal parameters U = 0.08. In both cases empirical absorption corrections (ψ-scans) were applied. For both structures atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No 1.

‡ *Selected spectroscopic data* **4e**: ^{1}H NMR (in C_6D_6, 300 MHz) δ 4.54 (s, 10H), 2.24 (m, 16H), 1.37 (s, 20H) and 1.23 (s, 20H); ^{13}C NMR (in C_6D_6, 75.47 MHz) δ 80.93, 79.55, 31.72, 31.05, 29.50, 27.69; *m/z* 737 (M + 1), 736(M,base), 612 [M − Co(C_5H_5)]. **3d**: ^{1}H NMR (in $CDCl_3$, 300 MHz) δ 4.61 (s, 5H), 2.16 (s, 4H), 1.91 (s, 4H), 1.46 (s, 16H); ^{13}C NMR (in $CDCl_3$, 50.32 MHz) δ 79.13, 78.86, 26.73, 26.05, 25.24; *m/z* 341(M + 1), 340(M), 216[M − Co(C_5H_5)].

whose Co···Co axes are inclined to each other by 109.6°. For one of the molecules the centres of the parallel Co(C_5H_5)-cyclobutadiene units are on top of each other leading to a pinwheel like conformation and a zig-zag arrangement of the heptamethylene chains [Fig. 2(*a*)]. The dihedral angle between C(6), C(23), C(17) and C(21), C(22), C(23) amounts to 51°. The two cyclobutadiene units are separated by 7.83 Å. For the other molecule the centres of the cyclobutadiene units are displaced parallel to each other by 1.02 Å, the zig-zag arrangement of the heptamethylene chains is similar to **1**. The distance between the centres of the two cyclobutadiene units amounts to 7.44 Å. The reaction of **1d** with **2** (2 days in n-nonane, reflux) gives (η^5-cyclopentadienyl)(η^4-tricyclo-[8.6.0.0.^{2,9}]hexadeca-1,8-diene)cobalt **3d**‡ (5% yield)[7] along with the polymeric material.

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References

1 J. Dale, *Angew. Chem.*, 1966, **78**, 1070; *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 1000.
2 R. Gleiter, M. Karcher, M. L. Ziegler and B. Nuber, *Tetrahedron Lett.*, 1987, **28**, 195.
3 R. Gleiter, B. Treptow, D. Kratz and B. Nuber, *Tetrahedron Lett.*, 1992, **33**, 1733.
4 R. B. Krug and A. Efraty, *J. Am. Chem. Soc.*, 1972, **94**, 3021.
5 Review: R. Gleiter, *Angew. Chem.*, 1992, **104**, 29; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 27.
6 J. Dale, A. J. Hubert and G. S. D. King, *J. Chem. Soc.*, 1963, 73.
7 This product has been obtained also by dimerization of cyclooctyne, V. Schehlmann, Dissertation, University of Heidelberg, 1990.