Threefold and Fourfold [2 + 2] Cycloadditions of Cyclic Diynes as a Consequence of Steric Effects: En Route to Polymers**

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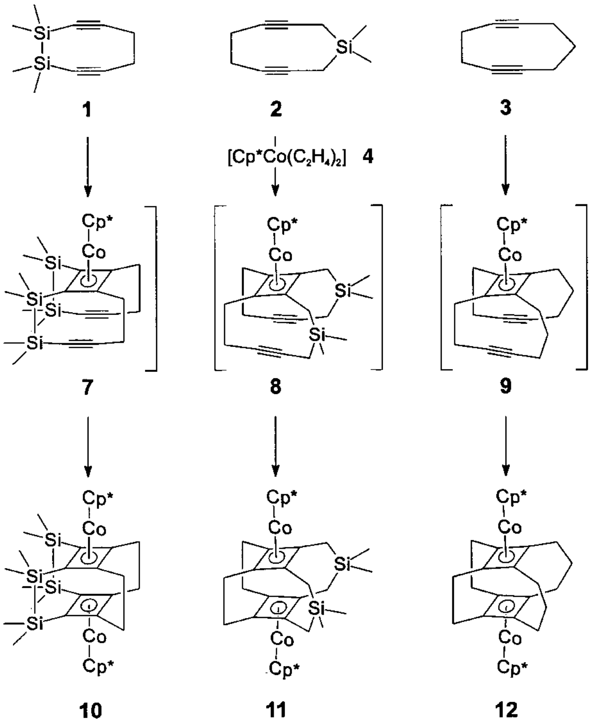
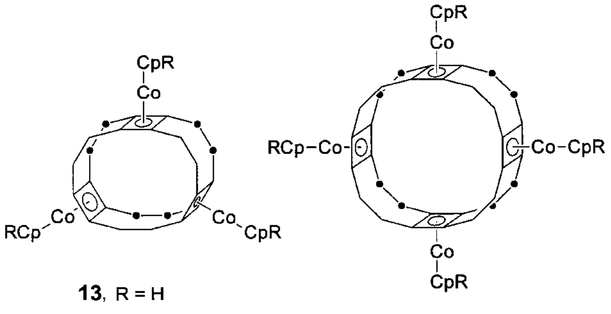
Cyclic diynes can react either in an intra- or intermolecular way with organometallic complexes. In the latter case defined oligomers or polymers may be formed. The polymers may consist of a ladder of metal-stabilized cyclobutadiene rings or a two-dimensional net of aromatic rings each of which are connected by hydrocarbon chains. It is important to know and understand the reaction mechanisms if the choice of the reaction pathway is to be controlled. A key intermediate in the reactions of two or more alkyne units with organometallic complexes is a metallacyclopentadiene species which has been proposed and substantiated by Yamazaki, Wakatsuki et al.[1] From this hypothesis we inferred for cyclic diynes two pathways: an intramolecular reaction path for large rings and an intermolecular route for smaller diynes.[2] In the latter case the degree of oligomerization was always two. When we used diynes which contained a disilyltetramethyl bridge on one side and a relatively long and flexible chain (C_4H_8, C_5H_{10}) on the other[3] the yield of superphanes was rather high. In our search for higher oligomers we reasoned that small chains on both sides or small chains on one side and a chain with bulky groups on the other might favor higher oligomers. In order to test these ideas we investigated the reaction of 1,1,2,2-tetramethyl-1,2-disilacycloocta-3,7-diyne (**1**),[4] 1,1-dimethyl-1-silacyclonona-3,7-diyne (**2**),[4] and cyclonona-1,5-diyne (**3**)[4] with bis(ethylene)(1,5-pentamethylcyclo-pentadienyl)cobalt (**4**), (η^4-cyclooctadiene-1,5)(η^5-cyclopentadienyl)cobalt (**5**), and (η^4-cyclooctadiene-1,5)(η^5-(methoxycarbonyl)(cyclopentadienyl)cobalt (**6**) (Scheme 1).

The reaction of **1**–**3** with **4** at 60 °C afforded the corresponding superphanes **10**–**12**. All three superphanes belong to the point group C_{2v}. The configurations of **10** and **12** have been confirmed by X-ray structural analyses.[5] The preference of the structures with C_{2v} symmetry can be rationalized by assuming that the rate-determining step is the formation of a tricyclic metallacycle.[1, 3] The yields of the superphanes **10**–**12** are relatively low (**10**: 12 %, **11**: 10 %, **12**: 3 %)[6] if we compare them to those obtained by reaction of **4** with 1,1,2,2-tetramethyl-1,2-disilacycloundeca-3,10-diyne and 1,1,2,2-tetramethyl-1,2-disilacyclododeca-3,11-diyne (50–60 %).[3] We ascribe the low yields to the fact that in the intermediate tricyclic systems (**7**–**9**) the short bridges tend to favor a conformation in which the triple bonds are nearly coplanar to the cyclobutadiene ring. Only the relatively large "cap" of the Cp* ring induces a conformation in which both alkyne units of **7**–**9** are forced in relatively close proximity in the half-space below the cyclobutadiene ring.



Scheme 1.

In order to detect higher oligomers we reduced the steric bulk of the ligand and replaced the Cp* cap by a Cp cap; that is we replaced **4** by **5** and **6**. Indeed, the reaction of **1** with **5** and **6** does not give detectable amounts of the corresponding superphanes but rather yields the trimers **13** (20 %) and **14** (35 %). In **13**[6] and **14**[6] formally three diynes have reacted with three CpCo fragments. The structural assignments of the resulting trimers are based on their spectroscopic data[5] and an X-ray structural analysis of **13** (Figure 1).[7, 8] This reveals that in the resulting trimer the silyl bridges lie on one side of the ring and the ethano bridges on the opposite side. Therefore the tube formed by the three units has a conical shape. The widest diameter in the tube is found to be 6.9 Å, the narrowest one is 4.5 Å. In the case of the reaction of **1** with **6** we were also able to isolate the tetramer **16** in 8–10 % yield. The structural assignment of **16** is based on its spectroscopic data.[6] As in the case of **13** and **14** the NMR data suggest that the silyl and ethano bridges are on opposite sides of the ring.



13, R = H
14, R = CO_2Me • = $SiMe_2$ **16**, R = CO_2Me

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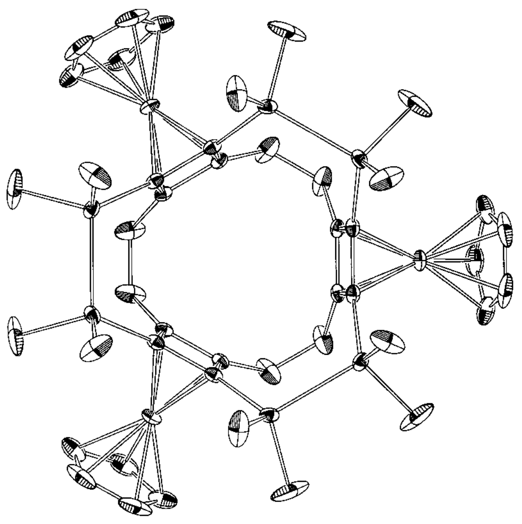

Figure 1. Molecular structure of **13**.

This gives rise to a conical shape of the ring for which we calculated (AM1[10]) the widest and narrowest diameter to be 8.4 Å and 5.5 Å, respectively. The species **13**, **14**, and **16** belong to the class of beltlike hydrocarbons[11] which have been investigated recently very intensively and for which several routes have been described.[11–14]

The reaction of **3** with $[Cp^*Co(C_2H_4)_2]$ at 60 °C also yields a species (**15**) which we assign to a trimer based on the high-resolution mass spectrum and ^1H NMR spectroscopic data.[6] The results obtained for **1** and **3** demonstrate that higher oligomers of cyclic diynes are amenable at elevated temperatures.

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[6] Selected spectroscopic data of **10**–**16**. **10**: ^1H NMR (300 MHz, C_6D_6): $\delta = 0.35$ (s, 12H), 0.38 (s, 12H), 1.9 (m, 8H), 2.1 (s, 30H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = -2.7$ (q), -1.5 (q), 11.8 (q), 23.6 (t), 65.0 (s), 86.6 (s), 88.6 (s); HR-MS (positive-ion FAB): *m/z*: calcd: 772.2593; found: 772.2629. **11**: ^1H NMR (300 MHz, C_6D_6): $\delta = 0.2$ (s, 12H), 1.29 (d, 4H), 1.34 (d, 4H), 1.9 (m, 8H), 2.0 (s, 30H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 0.6$ (q), 1.0 (q), 9.8 (q), 13.0 (t), 20.9 (t), 71.3 (s), 72.8 (s), 87.1 (s); HR-MS (Positiv-Ionen-FAB): *m/z*: calcd: 712.2741; found: 712.2733. **12**: ^1H NMR (500 MHz, C_6D_6): $\delta = 1.8$ (m, 20H), 1.9 (s, 30H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 11.1$ (q), 21.6 (t), 25.0 (t), 28.2 (t), 73.8 (s), 75.2 (s), 88.3 (s); HR-MS (positive-ion FAB): *m/z* calcd: 624.2576; found: 624.2587. **13**: ^1H NMR (300 MHz, C_6D_6, 60 °C): $\delta =$ 0.2 (s, 18H), 0.4 (s, 18H), 2.1–2.3 (m, 12H), 4.7 (s, 15H); HR-MS (positive-ion FAB): *m/z*: calcd.: 948.1541; found: 948.1528. The low solubility of **13** in the usual solvents prevented the recording of a ^{13}C NMR spectrum. **14**: ^1H NMR (300 MHz, C_6D_6): $\delta = 0.2$ (s, 18H), 0.3 (s, 18H), 2.0–2.3 (m, 12H), 3.6 (s, 9H), 4.9 (t, 6H), 5.4 (t, 6H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = -1.0$ (q), 2.8 (q), 27.0 (t), 51.5 (q), 69.5 (s), 83.0 (d), 83.1 (d), 86.4 (s), 92.7 (s), 167.9 (s); HR-MS (positive-ion FAB): *m/z*: calcd: 1122.1706; found: 1122.1708. **15**: ^1H NMR (500 MHz, C_6D_6): $\delta = 1.6$–2.2 (m, 30H), 1.8 (s, 45H); HR MS (positive-ion FAB): *m/z*: calcd: 936.3865; found: 936.3867. The small quantity of **15** prevented the recording of a ^{13}C NMR spectrum. **16**: ^1H NMR (300 MHz, C_6D_6): $\delta = 0.2$ (s, 24H), 0.4 (s, 24H), 2.2 (s, 16H), 3.6 (s, 12H), 5.0 (s, 8H), 5.5 (s, 8H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = -0.1$ (q), 2.4 (q), 27.4 (t), 51.7 (q), 68.1 (s), 82.9 (d), 83.0 (d), 86.5 (s), 93.4 (s), 168.0 (s); HR-MS (positive-ion FAB): *m/z*: calcd.: 1496.2274; found: 1496.2233.

[7] About 30% of the silylene units in the single crystals of **13** are disordered. In this fraction the $Si_2(CH_3)_4$ groups adopt a δ and λ conformation, respectively, instead of a conformation with a plane of symmetry.

[8] X-ray structure of **13**: $C_{45}H_{63}Co_3Si_6$, $M_r = 949.28$, rhombohedral, space group $R3m$, crystal dimensions: $0.45 \times 0.09 \times 0.08$ mm^3, $a = 21.024(1)$, $c = 9.031(1)$ Å, hexagonal axes, $V = 3456.9(2)$ Å^3, $F(000) = 1494$, $Z = 3$, $\rho_{calcd} = 1.37$ g cm^{-3}, $\mu = 1.25$ mm^{-1}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å. X-ray data were collected with a Siemens CCD diffractometer at 200(2) K; 8557 reflections were collected. Of 1470 unique reflections measured, 1360 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods by using the program SHELXTL.[9] Refinement of the non-hydrogen atoms was carried out anisotropically according to a full-matrix least-squares technique (F^2). $R1 = 0.035$, $wR2 = 0.081$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-102941. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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