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REACTION OF 1,5-CYCLOUNDECADIYNE AND 1,6-CYCLOUNDECADIYNE WITH $CpCo(CO)_2$

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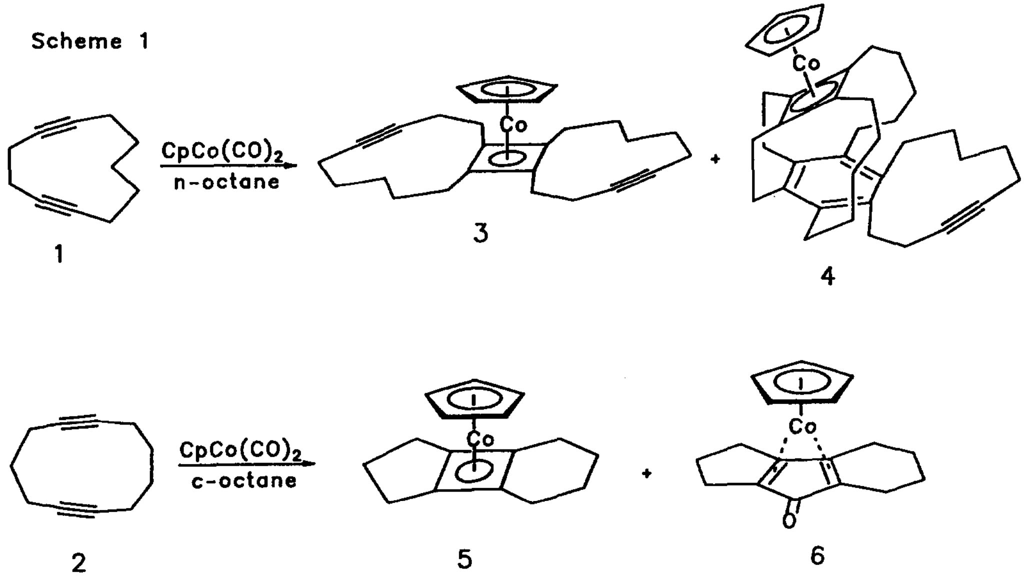
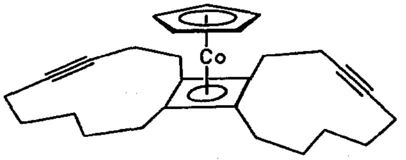
The reaction of 1,5-cycloundecadiyne with $CpCo(CO)_2$ leads to <u>inter</u>molecular products while 1,6-cycloundecadiyne reacts in an <u>intra</u>molecular fashion.

Recently we showed that 1,6-cyclodecadiyne reacts with $CpCo(CO)_2$ mainly in an intermolecular fashion[1]. To test the reactivity of other cyclic diacetylenes we prepared 1,5-cycloundecadiyne (**1**) and 1,6-cycloundecadiyne (**2**)[2]. The results of the reaction of **1** and **2** with $CpCo(CO)_2$ are summarized in Scheme 1. In the case of **1** we find an intermolecular reaction to **3** (7%). The other possible isomer, **7**,

Scheme 1





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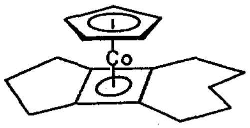

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could not be detected. As a side product (3%) we isolated a compound whose spectroscopic data are compatible with structure **4** (see Table 1). The less strained compound **2** reacts intramolecularly to yield **5** (32%) and **6** (2.5%). Similarly 1,6-cyclododecadiyne yields **8** in 75% yield. The results summarized in Scheme 1 demonstrate a strong influence of the chain length on the reactivity. The same holds for the intermolecular formed cyclic products. The X-ray investigation on single crystals of **3** shows that the two triple bonds are separated considerably (see Figure 1)[3]. They are not aligned parallel to each other, so that a second dimerization to an unsymmetrical superphane seems unlikely. Furthermore, a superphane of this type would exhibit extreme sterical crowding. Semiempirical calculations (AM1)[4] on a model with a square planar cyclobutadiene ring without a CpCo unit reproduce the geometry of the carbon skeleton of **3** rather accurately. Our calculations (on a model) for the non-isolated intermediate **7** predict, however, a conformation which is suited for the

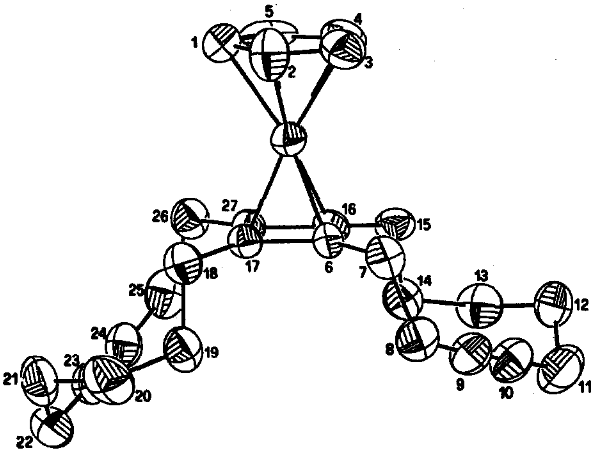

Fig.1 Structure of **3** according to an X-ray investigation. The most relevant bond(Å)lengths are:

C(6)-C(17) = 1.46; C(6)-C(16) = 1.46; C(16)-C(27) = 1.45; C(17)-C(27) = 1.44; C(9)-C(10) = 1.16; C(23)-C(24) = 1.17; C(9)-C(24) = 6.42; C(9)-C(23) = 6.75; C(10)-C(23) = 7.31; C(10)-C(24) = 6.90.

reaction with a further triple-bond in a [2+2+2] fashion. This would rationalize the side-product **4** and the absence of **7**.

Our studies on medium sized diacetylenes[1,5] indicate that the intramolecular reaction to a tricyclic CpCo-stabilized cyclobutadiene is preferred if $n \geq 3$ in both - $(CH_2)_n$ - chains. This is in line with the observation that **2** and cyclic diacetylenes of larger ring-size[6] yield the intramolecular cyclobutadienes in large amounts with $CpCo(CO)_2$. Once $n < 3$ (e.g. as in **1**) a cyclobutene annelated cyclobutadiene would result, a structure which has not been observed to date[7]. If the total ring size is twelve or larger the yield of the intramolecular complex is substantial[6] while for smaller rings the bifunctionality of the diacetylene mainly leads to undefined products next to small amounts of the discussed complexes (see Scheme 1).

Table 1: Most relevant analytical data of **3-6** and **8**.

3: mp. = 133°C; **^{1}H-NMR** (300 MHz, C_6D_6): δ = 4.62 (s, 5H), 2.45 (t, $^3J(H,H)$ = 10Hz, 2H), 2.14-2.30 (m, 8H), 1.83-2.08 (m, 10H), 1.54-1.67 (4H), 1.33-1.45 (4H), 1.33-1.45 (4H); **^{13}C-NMR** (50.32 MHz, C_6D_6): δ = 18.55 (CH_2), 20.33 (CH_2), 24.54 (CH_2), 24.78 (CH_2), 27.67 (CH_2), 28.50 (CH_2), 28.75 (CH_2), 77.61 (C), 79.99 (C), 81.28 (CH), 81.56 (C), 82.26 (C); MS (EI): m/z 416 (M^+, 12.2%), 350 (M^+-C_5H_6, 2.2), 291 (M^+-CoC_5H_6, 3.1), 189 ($Co(C_5H_5)_2^+$, 11.6), 124 (CoC_5H_5, 80), 91 (48), 59 (Co, 100); MS (CI): m/z 416 (M^+), 417 (M^++H), 445 (M^++C_2H_5); **IR** ($CDCl_3$): ν [cm^{-1}] = 2924 (CH_2), 2238 (C=C), 1448, 1432, 802; **UV/VIS** (CH_2Cl_2): λ_{max}[nm] (lgϵ) = 264 (4.35), 290 (3.23), 365 (2.8).

4: mp. = 98°C; **^{1}H-NMR** (300 MHz, C_6D_6): δ = 4.56 (s, 5H), 3.46 (m, 2H), 2.30-3.15 (m, 16H), 1.80-2.20 (m, 12H), 1.25-1.60 (12H); **^{13}C-NMR** (50.32 MHz, C_6D_6): δ = 18.65 (CH_2), 21.26 (CH_2), 22.39 (CH_2), 23.53 (CH_2), 24.27 (CH_2), 24.54 (CH_2), 24.81 (CH_2), 25.94 (CH_2), 25.98 (CH_2), 26.14 (CH_2), 26.55 (CH_2), 26.91 (CH_2), 27.11 (CH_2), 27.31 (CH_2), 28.14 (CH_2), 28.18 (CH_2), 28.68 (CH_2), 29.45 (CH_2), 30.08 (CH_2), 30.15 (CH_2), 31.11 (CH_2), 77.31 (C), 77.76 (C), 78.17 (C), 78.62 (C), 80.35 (CH), 82.60 (C), 83.87 (C), 136.37 (C), 136.80 (C), 138.10 (C), 138.30 (C), 139.01 (C), 139.40 (C); MS (EI): m/z 562 (M^+, 89.7%), 355 (10.3), 278 (33.3), 255 (33.3), 189 ($Co(C_5H_5)_2^+$, 25.6), 124 (CoC_5H_5, 82.1), 91 (59), 59 (Co, 38.5), 41 (100); **IR** ($CDCl_3$): ν [cm^{-1}] = 2918 (CH_2), 1483, 1455, 1268, 800; **UV/VIS** (n-pentane): λ_{max}[nm] (lgϵ) = 212 (3.51), 268 (3.31), 300 (2.09), 370 (1.05).

5: mp. = 64°C; **^{1}H-NMR** (300 MHz, C_6D_6): δ = 4.59 (s, 5H), 2.25 (m, 2H), 1.62-2.12 (m, 12H); **^{13}C-NMR** (75.46 MHz, C_6D_6): δ = 23.78 (CH_2), 24.68 (CH_2), 26.98 (CH_2), 29.17 (CH_2), 70.18 (C), 80.69 (CH), 81.42 (C); **MS** (EI): m/z 270 (M^+, 63%), 265 (73), 200 (70), 189 ($Co(C_5H_5)_2^+$, 92), 141 (34), 124 (CoC_5H_5, 85), 91 (30), 59 (Co, 100); **IR** (KBr): ν [cm^{-1}] = 2969 (CH_2), 2830 (CH_2), 1445, 1435, 801; **UV/VIS** (n-pentane): λ_{max}[nm] (lgϵ) = 205 (3.08), 267 (3.13), 300 (2.73), 375 (1.80).

6: **^{1}H-NMR** ($CDCl_3$, 300 MHz): δ = 4.73 (s, 5H), 1.92-2.56 (m, 14H); **^{13}C-NMR** (75.47 MHz, $CDCl_3$): δ = 21.98 (CH_2), 22.27 (CH_2), 22.75 (CH_2), 23.29 (CH_2), 24.33 (CH_2), 24.50 (CH_2), 28.09 (CH_2), 82.99 (CH), 85.32 (C=C), 85.80 (C=C), 86.69 (C=C), 98.04 (C=C), 149.91 (C=0); **MS** (EI): m/z 298

(M^+, 41%), 269 (M^+-COH, 10), 265 (28), 200 (34), 189 ($Co(C_5H_5)_2^+$, 49), 141 (35), 124 (CoC_5H_5, 88), 115 (33), 91 (24), 59 (Co, 100), 44 (13); **IR** ($CDCl_3$): ν [cm^{-1}] = 2954 (CH_2), 2204, 1559 ($C=O$), 1548 ($C=O$), 1432, 1258, 818; **UV/VIS** (CH_2Cl_2): λ_{max}[nm] (lgϵ) = 222 (4.04), 284 (4.22), 364 (3.30), 415 (3.01).
8: mp. = 91°C; **^{1}H-NMR** (300 MHz, C_6D_6): δ = 4.68 (s, 5H), 1.84-2.14 (m, 4H), 1.82-1.92 (m, 4H), 1.49-1.80 (m, 8H); **^{13}C-NMR** (75.46 MHz, C_6D_6): δ = 27.19 (CH_2), 28.83 (CH_2), 29.98 (CH_2), 31.00 (CH_2), 31.17 (CH_2), 74.86 (C), 79.72 (CH), 81.83 (C); **GC-MS** (EI): m/z 284 (M^+, 69.7%), 255 (M^+-C_2H_5, 12.8), 189 ($Co(C_5H_5)_2^+$, 100), 124 (CoC_5H_5, 31.4), 91 (13.2), 59 (Co, 32.6); **IR** (CH_2Cl_2): ν [cm^{-1}] = 2916 (CH_2), 2836 (CH_2), 1443 (CH_2), 804; **UV/VIS** (n-pentane): λ_{max}[nm] (lgϵ) = 205 (4.07), 265 (4.09), 295 (2.87), 380 (2.5).

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3 Unit cell constants for **3**: a = 9.799(6) Å, b = 13,815(8) Å, c = 16.535(8) Å; V = 2238.39 Å^3, Z = 4. Space group $D_2^4P2_1,2_1,2_1$ (19). Data were collected on a SYNTEX R3 diffractometer using a crystal of dimensions 0.4x0.5x0.7 mm^2. Ω-scan ($3^\circ < 2\theta < 60^\circ$) $MO_{K\alpha}$ radiation; 2336 reflexions of which 2285 were judged to be independent ($I > 2.50\ \sigma$ (I)). All crystallographic calculations used the SHELXTL program package 5.1 (December 1985). Empirical absorption correction (6 reflections, $5.0 < 2\theta < 30^\circ$). Relative range of transmissions factors 0.92 - 1.00 (μ = 7.72 cm^{-1}). Least-squares refinement with ($w = 1/\sigma^2$ (F)). The structure was solved by direct methods (SOLVE, SHELXTL). The hydrogen atoms were located by the option HFIX of the SHELXTL program; R = 0.061, R_w=0.054. Complete structural data have been submitted to the **Cambridge University Crystallographic Center.**
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