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A ONE STEP SYNTHESIS OF A PENTAMETHYLENE–BRIDGED SUPERPHANE OF A CpCo-STABILIZED CYCLOBUTADIENE COMPLEX[1]

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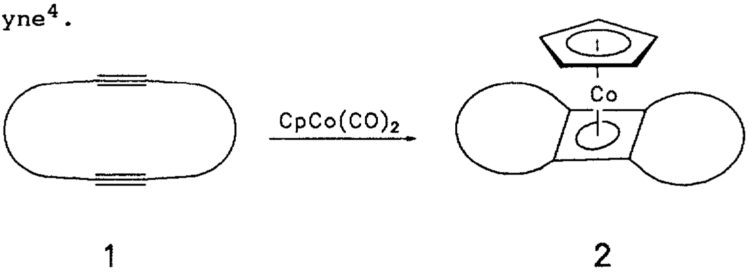
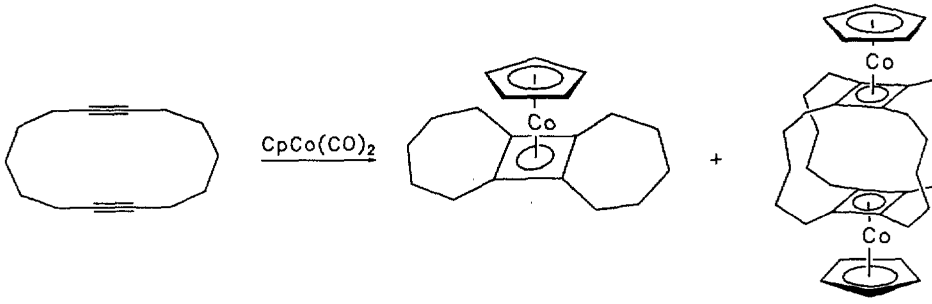
Heating 1,8-cyclotetradecadiyne with dicarbonyl(η^5-cyclopentadienyl)cobalt(CpCo(CO)$_2$) gives in 2-7% yield the [5_4]-(1,2,3,4)cyclobutadienophane complexed with two (C_5H_5)Co units in one step.

For the thermal reaction of cyclic nonconjugated diynes **1** with dicarbonyl(η^5-cyclopentadienyl)cobalt (CpCo(CO)$_2$) or the corresponding complex with 1,4-cyclooctadiene (cod), CpCo(cod), the intramolecular reaction yielding a tricyclic cyclobutadiene complex **2** is the rule[2-4]. Exceptions are found in the case of 1,6-cyclodecadiyne[3] and 1,5-cycloundecadiyne[4].



A comparison of the yields obtained for the intramolecular complexes of 1,6-cyclodecadiyne (6%)[3], 1,6-cycloundecadiyne (32%)[4], 1,7-cyclododecadiyne (86%)[2] and 1,7-cyclotridecadiyne (65%)[1] suggests that the less strained cyclodiynes should give good yields of the intramolecular products **2**. The low yields reported by King et al.[2] for 1,8-

cyclotetradecadiyne(**3**)(2-10% yield)^5 led us to reinvestigate the reaction of **3** with CpCo(CO)$_2$. We are not only able to confirm the



3 4 5

relatively low yield reported for **4** in n-octane (16-18% with CpCo(CO)$_2$, 29% with CpCo(cod)), but we were also able to isolate the intermolecular cycloaddition product **5**, the $[5_4]$(1,2,3,4)cyclobutadienophane complexed with two CpCo units in 2-7% yield. By carrying out the reaction in decalin at 180^o, we obtained **4** in 70% yield, while the yield of **5** remains on the order of 5-7%. To our knowledge this is the first CpCo-capped cyclobutadiene superphane with chains which are longer than three carbon atoms. So far, superphanes of metal complexed cyclobutadiene have been reported with trimethylene chains containing two CpCo-units, one CpCo and one Cp*Co unit or one Fe(CO)$_3$ unit, respectively^{3,6}.

The structural assignment of **5** reveals two crystallographically independent molecules^7 in the unit cell whose long axes are inclined to each other by 75.3^o. The pentamethylene bridges in both molecules adopt a zig-zag arrangement (Fig.1a) leading to a bend pin-wheel conformation. In one case this conformation is more rigid than in the other (Fig.1b). The distances between the cyclobutadiene units in **5** are found to be 5.34 Å and 5.37 Å, respectively. A similar zig-zag conformation has been found in 7,10,18,21-tetramethoxy[5.5]paracyclophane where both benzene rings are separated by 5.1 Å^8.

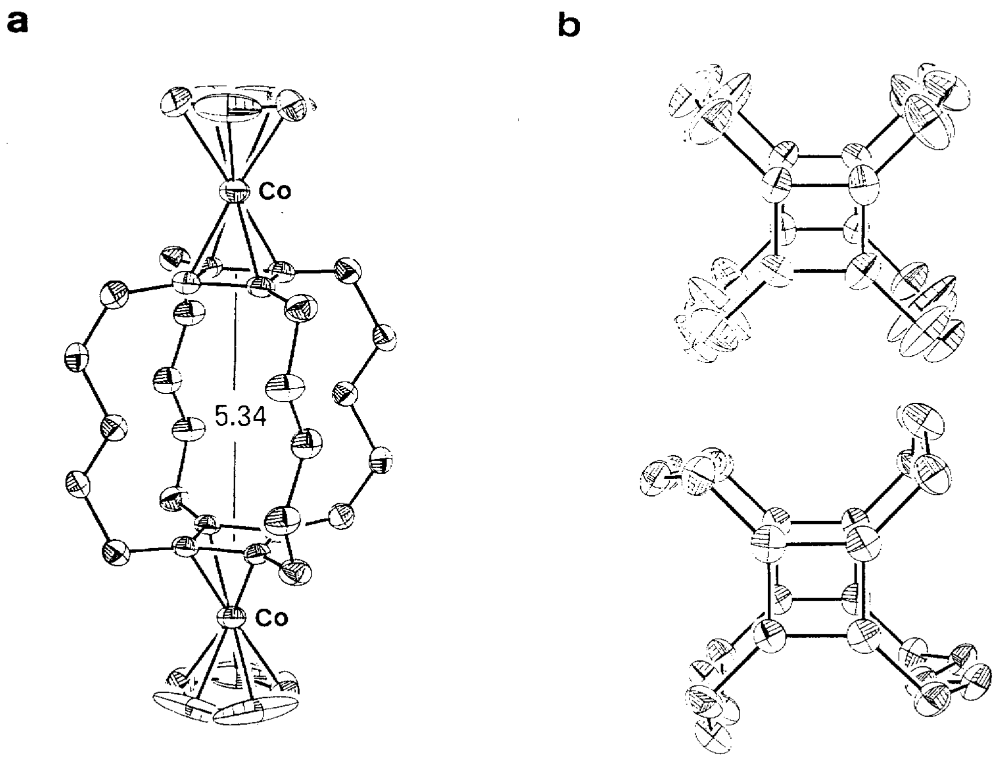


Figure 1

a) Side view of the molecular structure of **5**.

b) Thermal ellipsoids (40% probability) of the cyclobutadienophane skeletons of the two independent molecules of **5** in the unit cell. In both cases the hydrogens are omitted for clarity.

Table 1 Most relevant spectroscopic data of **4** and **5**.

4: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ=4.8 (s,5H), 2.1-1.9 (m,10H), 1.7-1.5 (m,8H), 1.0-0.8 (m,2H); ^{13}C-NMR ($CDCl_3$, 300 MHz): δ=79.6, 78.8, 30.5, 27.9, 26.7.

5: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ=4.4 (s,10H), 2.28 (s,br,16H), 1.27 (s,br,24H); ^{13}C-NMR ($CDCl_3$,200 MHz): δ=80.7, 80.0, 30.0, 27.2, 26.3; IR ($CDCl_3$):ν[cm^{-1}]= 2924, 2848, 1429, 1310, 1261; UV/VIS (pentane):λ_{max}[nm](lg ϵ)=197(4.27), 225 sh(4.13), 266(4.43), 380(2.70).HRMS: calc. 624.2564; found 624.2576.

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[1] Dedicated to Professor Klaus Weinges on the occasion of his 65th birthday.

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[5] With CpCo(CO)$_2$ and CpCo(cod) the yields of **4** reported are 2-4% and 10%, respectively[2].

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[7] Unit cell constants for **5**: a= 8.903(5)Å, b=9.520(6)Å, c=20.98(2)Å, α= 99.78(6), β=92.98(6), γ=113.57(4), V=1591.9 Å^3, Z=2. Space group P$\bar{1}$. Data were collected on a SYNTEX R3 diffractometer using a crystal of dimensions 0.04x0.35x0.5 mm^3. Ω-scan ($3.0<2\theta<52.5^\circ$), MoK$_\alpha$ radiation; 5973 reflexions of which 3290 were judged to be independent ($I>2.5\sigma(I)$). All crystallographic calculations used the SHELXTL PLUS program package (January 1989). Empirical absorption corrections (6 reflexions, $8.0<2\theta<40^\circ$). Relative range of transmissions factors 0.84-1.00 (μ=11 cm^{-1}). Least squares refinement with ($w=1/\sigma^2(F)$). The structure was solved by direct methods (TREF, SHELXTL PLUS). The hydrogen atoms were located by option HFIX of the SHELXTL PLUS program; R=0.064, R_w=0.055. Complete structural data have been submitted to the **Cambridge University Crystallographic Center.**

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