

## From superphanes to beltenes\*

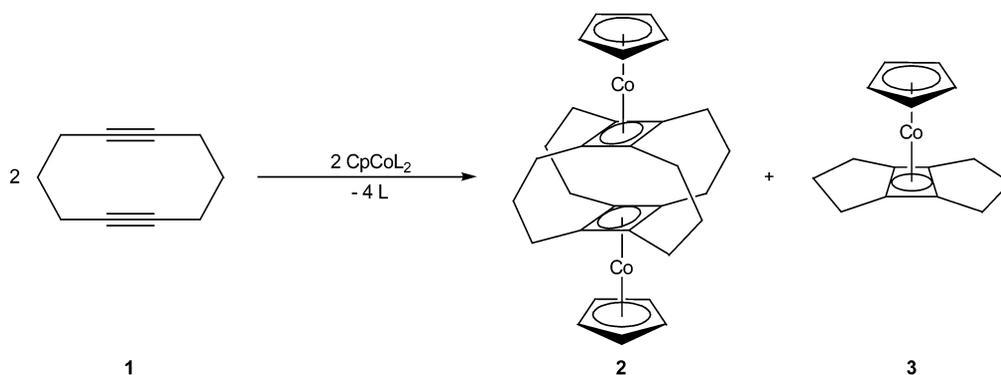
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**Abstract:** This short review describes paths to superphanes with metal-stabilized cyclobutadiene and cyclopentadienone rings in a one-pot and stepwise fashion. The stepwise synthesis also led to a new class of belt-like systems with large rings composed of CpCo-stabilized cyclobutadiene rings connected with propane chains. Finally, our research yielded the first beltenes composed of alternating four- and eight-membered conjugated rings.

**Keywords:** superphanes; cyclacenes; cyclobutadiene; cobalt; beltenes.

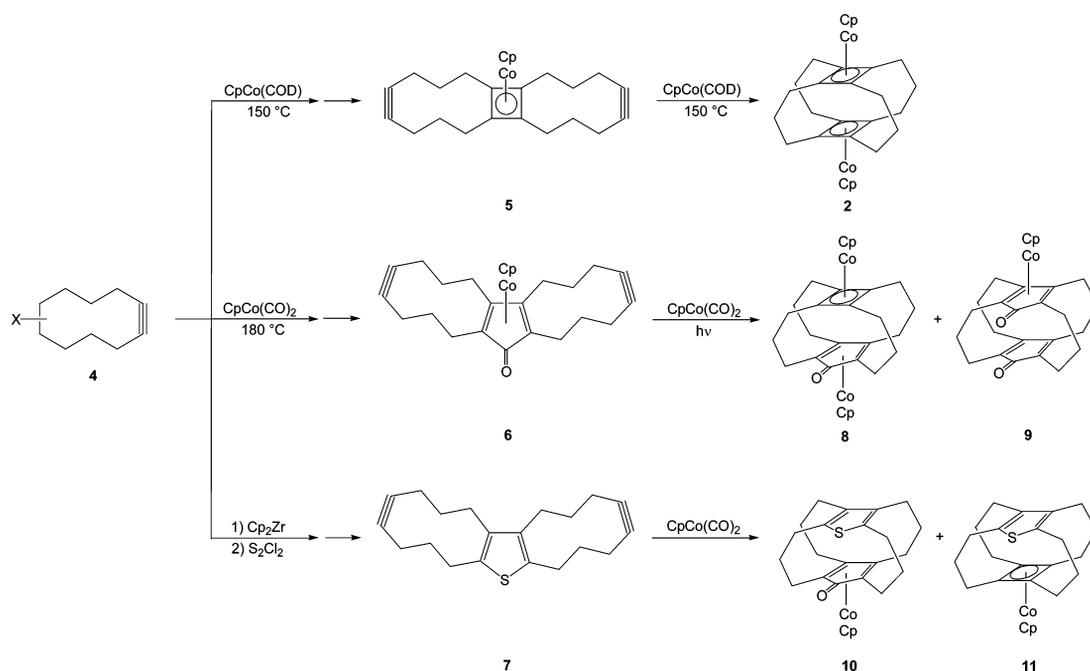
A superphane is a phane in which all hydrogen atoms of the cyclic conjugated rings are tethered by bridges. This definition goes back to Boekelheide and Hopf [1]. So far, a number of superphanes with benzene rings, heterocycles, and metal-stabilized  $\pi$ -systems have been prepared [2]. Our affair with superphanes started with the reaction of cyclodeca-1,6-diyne **1** with  $\text{CpCoL}_2$ , which afforded in a one-pot reaction the superphane **2** (Scheme 1) [3]. This reaction was first extended to other cyclic alkynes such as cyclotetradeca-1,8-diyne [4] and cyclooctadeca-1,10-diyne [5]. The superphanes proved to be excellent starting materials for bridged cage hydrocarbons [6] and model compounds to study the interactions between two metal centers separated by chains of different lengths [7]. This encouraged us to design also a path for a stepwise synthesis of superphanes with four- and five-membered [8–10] rings as summarized in Scheme 2. The resulting superphanes are stable at room temperature, and their molecular structures were investigated. The intermediates **5–7**, which were cyclized in an intramolecular reaction to **2** and **8–11**, stimulated us to look for higher oligomers.



Scheme 1

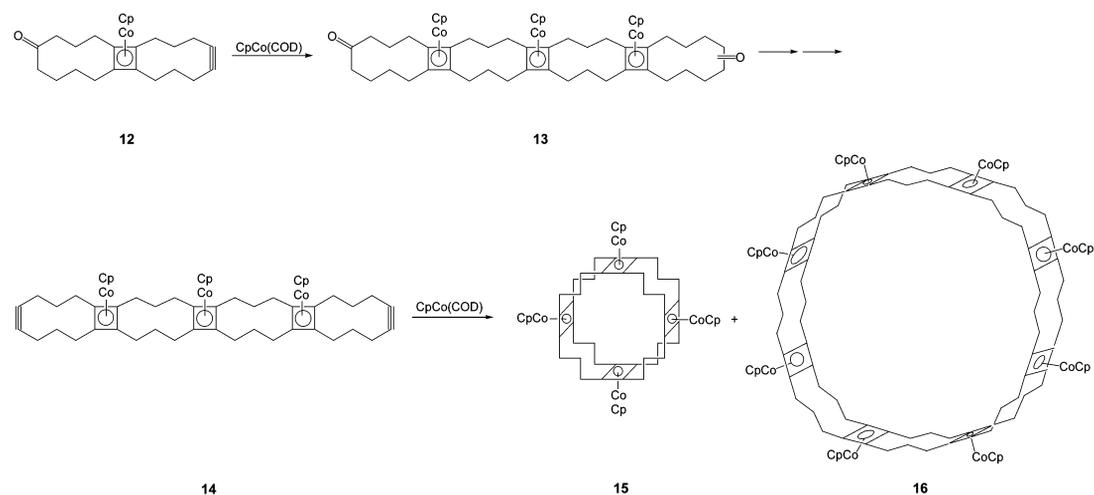
\*Paper based on a presentation at the 11<sup>th</sup> International Symposium on Novel Aromatic Compounds (ISNA-11), St. John's, Newfoundland, Canada, 14–18 August 2005. Other presentations are published in this issue, pp. 685–888.

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Scheme 2

To achieve this goal, we dimerized the tricyclic species **12** to **13** [11]. The *syn*-isomer of **13** could be isolated in 25 % yield. From **13**, it was possible to introduce the terminal triple bonds in **14** (Scheme 3). X-ray investigations on this species revealed a distance of 10.5 Å between triple bonds [11]. The twist boat conformation of the 10-membered rings is indicative for a higher flexibility of the rings. Cyclization of **14** yielded the belt-like systems with four and eight CpCo(cyclobutadiene) units, **15** and **16** [11].



Scheme 3

The generation of the radical cation of **2** by means of cyclic voltammetry and its investigation by IR and UV/vis spectroscopy [7] led us to conclude that the radical cation of **2** is almost delocalized and therefore belongs to class II according to the classification of Robin and Day [12]. This finding initiated efforts either to shorten the bridges in **2** or to introduce conjugation between the  $\pi$ -systems. The latter brought us to look first at cyclacenes, which are annelated benzene rings as shown below in Chart 1 [13]. If we just consider the most likely valence structure of the linear annelated cyclacenes (**17**) we come to the conclusion that **17** should have olefinic character because it is composed of *o*-quinoid structural units only. Another possibility, the cyclophenacene **18**, can be described as a  $\pi$ -system with a central *p*-polyphenylene skeleton with additional double bonds. This view led one to assume that the latter systems are more stable than the former. This qualitative judgement is supported by calculations using various levels of sophistication [14,15]. These results indicate also that the synthesis of the linear cyclacene **17** should be difficult due to its olefinic character and small singlet–triplet gap, especially for an even number of six-membered rings.

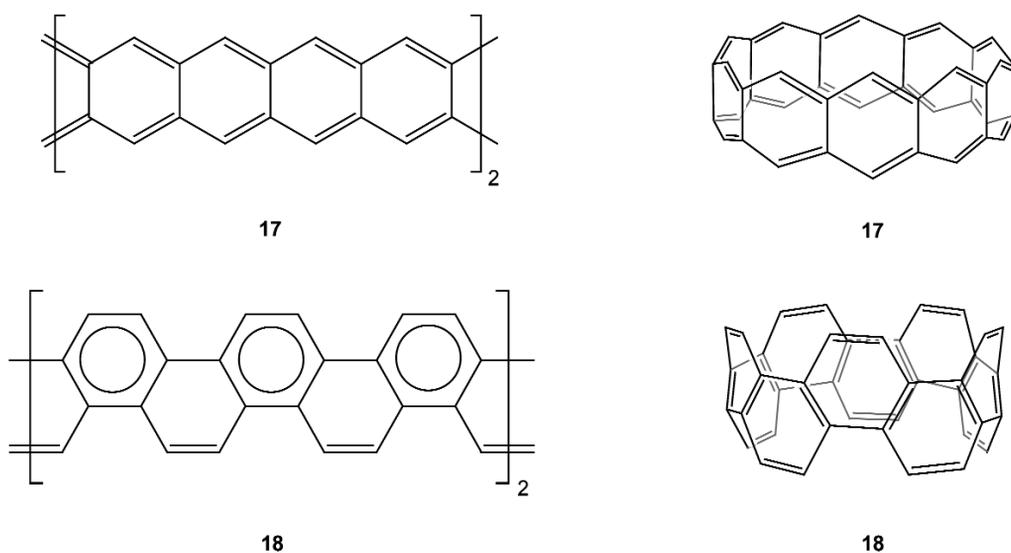
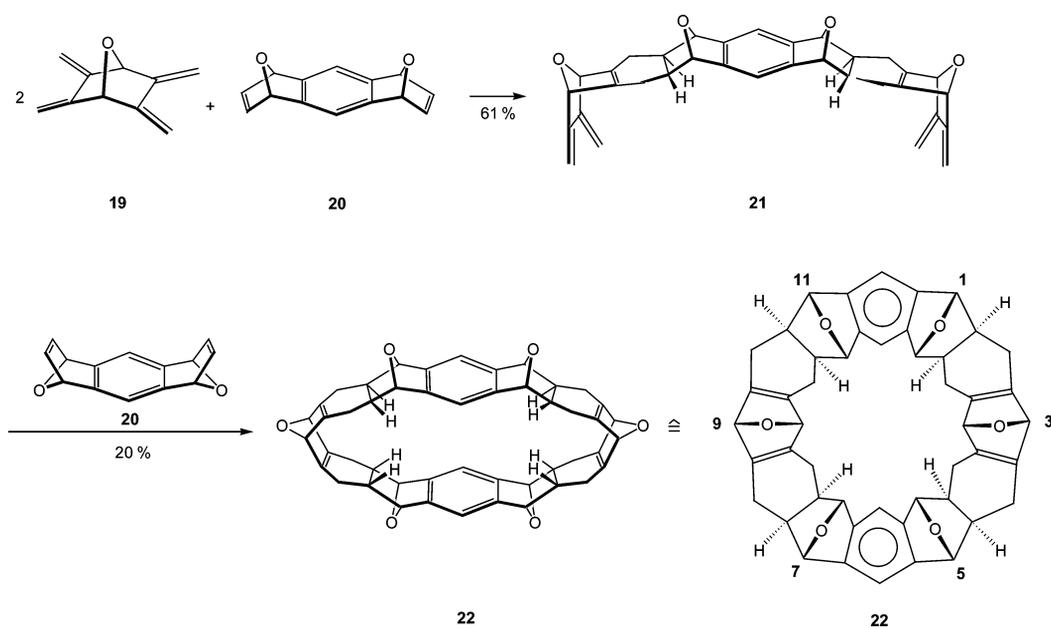


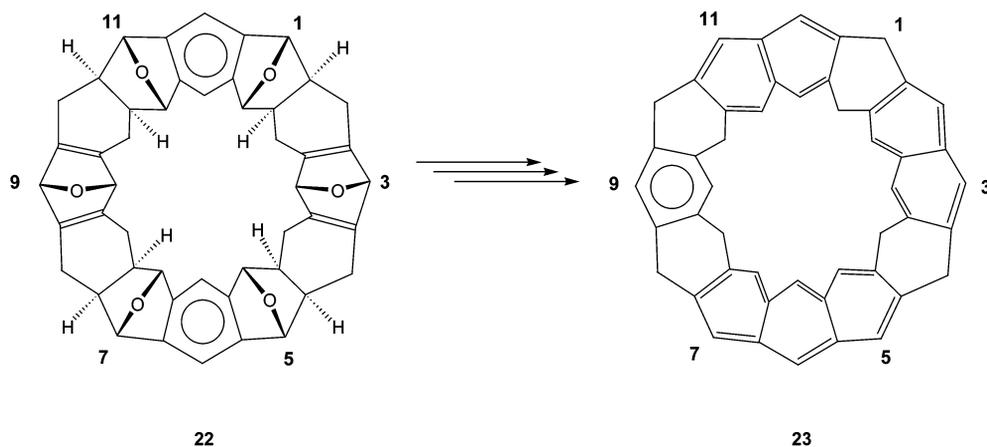
Chart 1

A first effort to synthesize the linear annelated [12]cyclacene was reported by Stoddart, Kohnke et al. [16]. They started off with a Diels–Alder reaction between 2,3,5,6-tetramethylidene-7-oxabicyclo[2.2.1]heptane (**19**) and the dienophile **20** (Scheme 4). A second Diels–Alder reaction between **21** and **20** yielded **22** in which 12 six-membered rings are assembled in a cycle. The bending to a cyclic structure was achieved by using six oxabicyclo[2.2.1]heptane units as building blocks.



Scheme 4

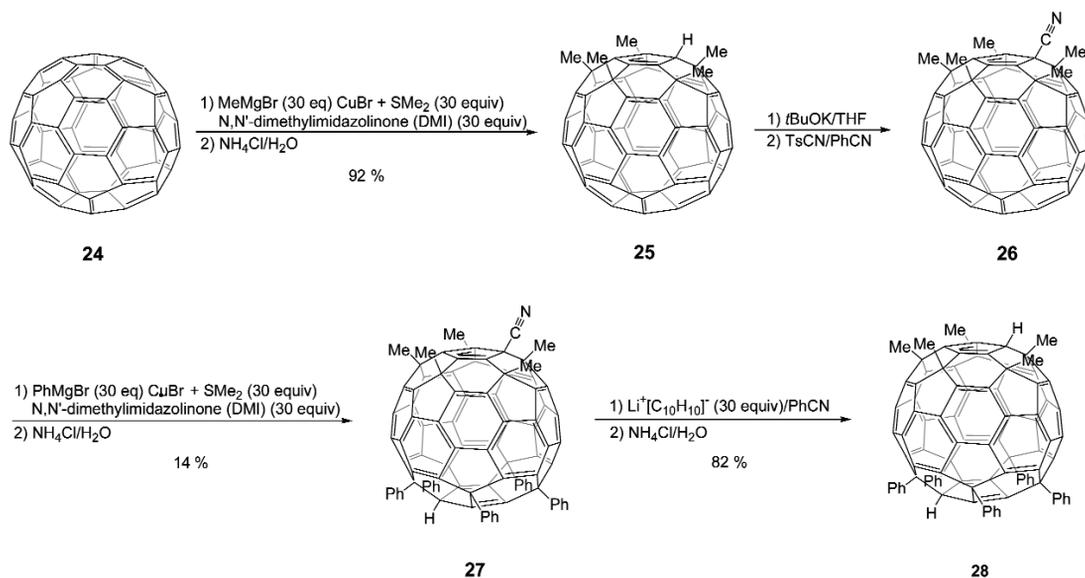
In the final steps, the task was to remove the oxygen atoms from rings 1, 3, 5, 7, 9, and 11 of **22**. This was only partially achieved by reduction with  $\text{LiAlH}_4$  followed by treatment with  $\text{Ac}_2\text{O}$ . The final product was **23** with four saturated ring systems (Scheme 5) [16]. The unsuccessful transformation of **23** into the desired [12]cyclacene is probably also due to the predicted low stability of a singlet [12]cyclacene [15].



Scheme 5

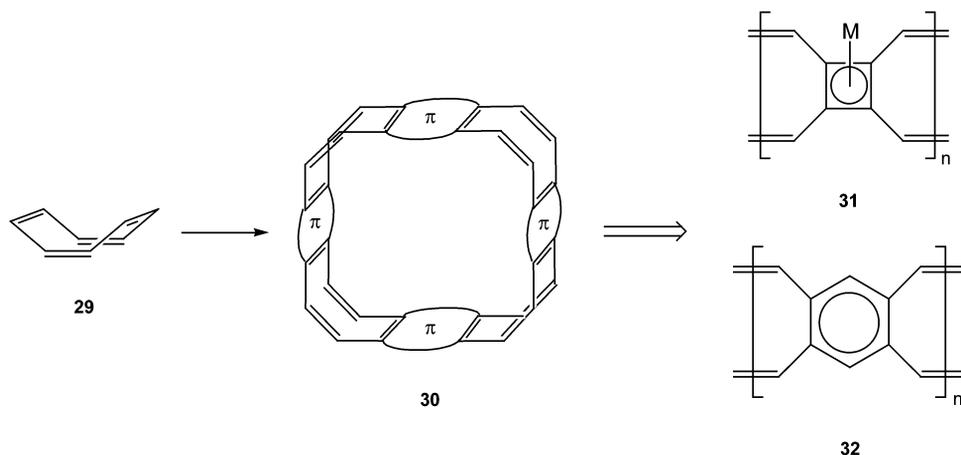
Alternative pathways are either by starting from a cage which has already an angular annelated cyclacene skeleton or switching to more flexible conjugated rings. The first approach was used by Nakamura et al. [17], who started from  $\text{C}_{60}$  by reducing the north- and south-polar region (Scheme 6). The partial reduction was achieved first by using a methylcopper reagent to yield **25**. After protection

of the acidic proton in **25** by a cyano group, the stage was set to reduce the lower part of **26** by a phenyl-copper reagent. This reaction afforded **27**, which was transferred to the [10]cyclophenacene **28**.



**Scheme 6**

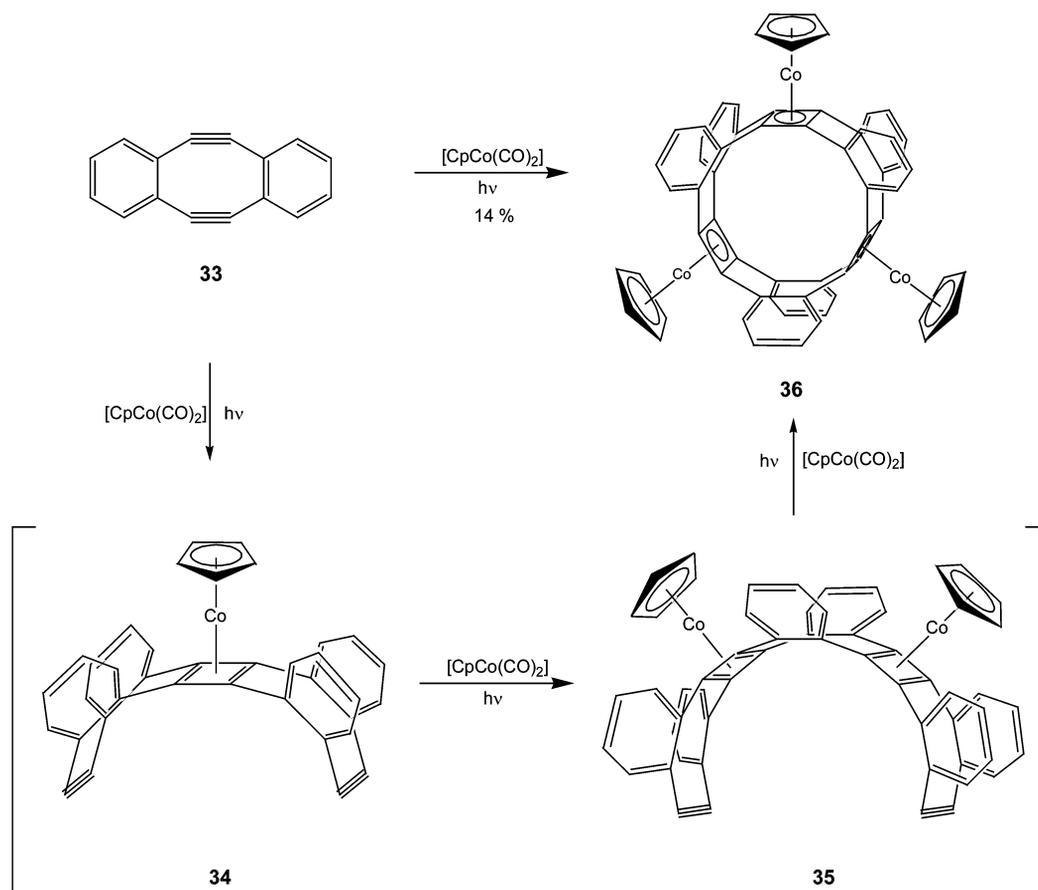
Our concept uses eight-membered rings as one building unit (Scheme 7). The boat conformation of cyclooctatetraene provides excellent conditions for bending annelated conjugated  $\pi$ -systems to a ring such as **30** and even allows (reduced) conjugation. This brings us immediately to the [4.8] or [6.8]beltene **31** and **32**.\*



**Scheme 7**

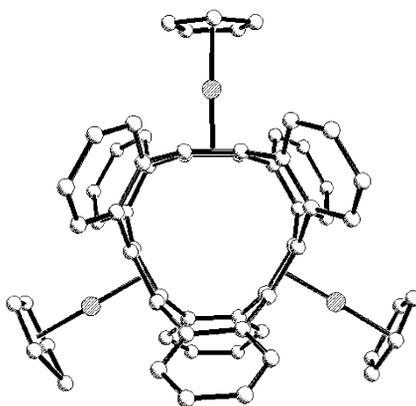
\*We suggest reserving the name “cyclacene” for annelated benzenes such as **17** and **18** and using “beltene” for the other congeners shown in Scheme 7.

Our first approach to prepare a congener of **31** was again a one-pot synthesis using tetrahydrodibenzo[*a,e*]cyclooctene (**33**) as starting material (Scheme 8).



**Scheme 8**

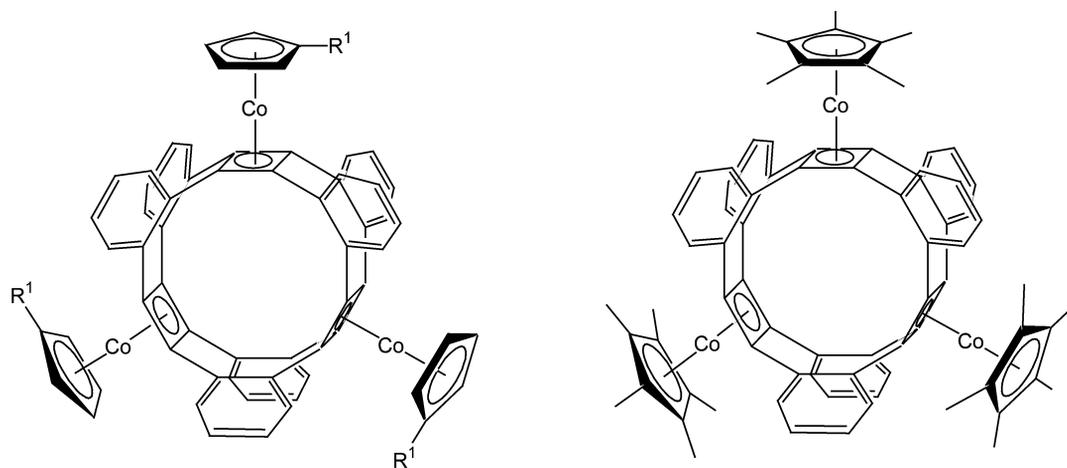
A recent improved synthesis of this compound by Otera et al. made it available for reactions [18]. Irradiation of **33** with CpCo(CO)<sub>2</sub> afforded the [4.8]<sub>3</sub>beltene **36** [19]. Mass spectrometric investigations of the crude reaction products of **36** and the congeners with Cp\*, CpCO<sub>2</sub>Me, and CpSiMe<sub>3</sub> ligands by mass spectrometry (HRMS) led us to postulate that intermediates such as **34** and **35** are formed. The synthesis summarized in Scheme 8 provides the first example of a *de novo* synthesis of a beltene. We were able to grow single crystals of the [4.8]<sub>3</sub>beltene **36** and three further congeners [19]. The X-ray investigation of **36** shows an inner diameter of the ring of 4.18 Å (Fig. 1).



**Fig. 1** Molecular structure of **36**. The cobalt centers are hatched, and the hydrogens are omitted for the sake of clarity.

The distance between the center of the Cp rings and the metal amounts to 1.69 Å, that between the cyclobutadiene rings and cobalt to 1.68 Å. The *ortho*-phenylene units are twisted by about 60° out of plane of the cyclobutadiene rings.

We varied the substituents on the Cp-rings of **36** to learn more about steric and perhaps electronic effects on the yield of the beltene resulting from the one-pot reaction shown in Scheme 8. The isolated products together with their yields are listed in Chart 2. It is found that a sterically more demanding ligand as the cyclopentadienyl ligand, such as the pentamethylcyclopentadienyl ring, produces unexpectedly higher yields of **40**.



R<sup>1</sup> = H(**36**) (14 %), Si(CH<sub>3</sub>)<sub>3</sub>(**37**) (8 %),  
COOCH<sub>3</sub>(**38**) (13 %), COCH<sub>3</sub>(**39**) (17 %)

**40** (43 %)

#### Chart 2

In our tour from superphanes to beltene we encountered a large number of new superphanes with conjugated four- and five-membered rings. On this route we also found a stepwise synthesis of belt-like

systems, and finally we synthesized the first members of the [8.4]<sub>3</sub> beltanes. Our future work will focus on the design of stepwise paths to larger rings of the [8.3]<sub>n</sub> and [8.6]<sub>n</sub> beltanes **31** and **32**.

## ACKNOWLEDGMENT

We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the State of Baden-Württemberg for financial support. We thank Mrs. P. Krämer for her help in preparing the manuscript.

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