

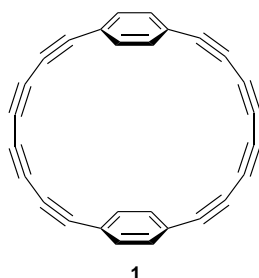
Cyclophynes chemistry: synthesis and study of an octacobalt complex of [8.8]paracyclophaneoctayne

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Use of a palladium/cobalt/copper alkyne reaction strategy provides the cobalt-stabilized complex of a highly strained cyclophane.

The recent discovery of the fullerenes¹ and related carbon nanotubes² has prompted a flurry of activity directed toward the synthesis and study of curved, fully conjugated π -systems.³ In a similar regard, there have been numerous attempts to prepare related belt-shaped molecules possessing conjugated π -electron circuits; the various belt- and hoop-shaped compounds studied include cyclacenes,⁴ $[n]$ cyclocarbons,⁵ cyclic paraphenylenes⁶ and others.⁷ Recently, two groups reported the successful preparation of fully conjugated, belt-shaped compounds. Oda and co-workers produced cyclic paraphenylacetylenes containing six and eight subunits.⁸ Herges and co-workers isolated a 'picotube' based on four anthracene units.⁹ Our recent work on polyacetylenic macrocycles¹⁰ spurred an interest in systems possessing the cyclic π -orbital motif. We report herein our work toward the synthesis of [8.8]paracyclophaneoctayne **1**, a cyclophane-cyclocarbon hybrid nicknamed a cyclophynne.¹¹

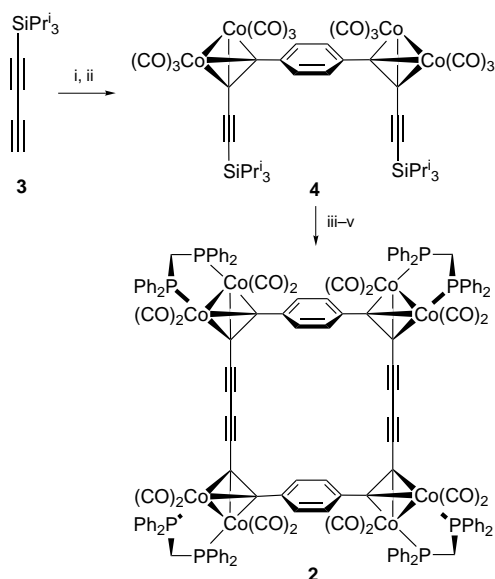


An octacobalt complex such as **2** was envisioned for the immediate precursor to the target macrocycle as: (i) the carbon skeleton could be assembled quickly and efficiently using known methodology, and (ii) the alkyne $\text{C}\equiv\text{C}$ angles in this type of (μ -acetylene)dicobalt hexacarbonyl complex are reduced to *ca.* 140° , thus allowing the complex to participate in reactions that might be difficult or otherwise impossible for the rigid, unbound molecule to undergo. The synthesis of **2** is depicted in Scheme 1. Palladium-catalysed alkylation of 1,4-diiodobenzene with excess triisopropylsilylbutadiyne **3**¹² furnished a pale yellow tetrayne, which in turn reacted with 2 equiv. of octacarbonyldicobalt to provide the sterically favoured tetracobalt complex **4**.[†] Attempted desilylation with tetrabutylammonium fluoride led to complete decomposition of **4**. Ligand exchange^{5a} with bis(diphenylphosphino)methane (dppm) afforded a bridged complex (85% yield) stable to fluoride ion; desilylation now proceeded in high yield (> 95%). Eglinton coupling¹³ of the terminal acetylenes provided fine, deep maroon crystals of **2**[†] in 47% yield. Spectroscopic data supported formation of the strain-free dimeric structure.

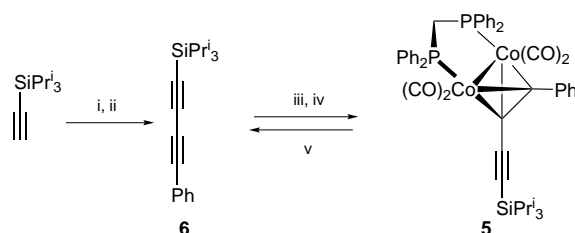
In their work with the hexacobalt complex of [18]cyclocarbon, Diederich *et al.* were unable to free C_{18} of the protecting groups by mild oxidation.^{5a,14} With this problem in mind, we prepared model complex **5**[†] (Scheme 2) in order to investigate various methods to remove the cobalts. Of the numerous

reagents and conditions explored, only oxidation by molecular iodine was found to regenerate butadiyne **6** cleanly and in excellent yield.

Application of the iodine-promoted decomplexation method to **2** provided dppm as the sole organic-soluble component along with a copious amount of insoluble material. Analysis of an aliquot of the crude reaction mixture by ¹H NMR showed a broad signal at δ 7.6 attributable to the phosphine ligand; no other aromatic peaks were observed. Although disappointing, this result is not wholly unexpected. A survey of the current literature reveals that, despite significant efforts on the part of several research groups, systems containing contiguous, bent triynes and higher polyynes have proven elusive.⁵ Only strained monoynes^{8,15} and diyne¹⁶ derivatives are known. The cyclocarbons represent the ultimate bent polyyne macrocycles; C_{18} is predicted to exhibit $\text{C}\equiv\text{C}$ bond angles near 160° , leading to a strain energy of around 72 kcal mol^{-1} .^{5b} Cyclophynne **1** should be similarly strained as the triple bond angles are calculated to



Scheme 1 Reagents and conditions: i, 1,4-diiodobenzene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , Et_3N , 73%; ii, $\text{Co}_2(\text{CO})_8$, Et_2O , 66%; iii, dppm, toluene, 85%; iv, Bu_4NF , THF, > 95%; v, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, py, 47%



Scheme 2 Reagents and conditions: i, CBr_4 , PPh_3 , CH_2Cl_2 , 85%; ii, phenylacetylene, CuCl , $\text{NH}_2\text{OH} \cdot \text{HCl}$, PrNH_2 , MeOH , H_2O , 82%; iii, $\text{Co}_2(\text{CO})_8$, Et_2O , 76%; iv, dppm, toluene, 87%; v, I_2 , THF, 85%

be between 161.7 and 163.6^o.¹⁷ Whether the failure to prepare these two classes of macrocycles is due to the extreme reactivity of the distorted polyyne moiety or to the lack of a viable synthetic route is not certain. Thus isolation and characterization of smaller bent hexatriyne- and octatetrayne-containing systems should help answer these questions. To this end, we are currently studying dehydrobenzoannulenes possessing higher polynes distorted on one or more edge.¹⁸ These results will be reported in due course.

We acknowledge the donors of The Petroleum Research Fund, administered by the American Chemical Society, and the University of Oregon for generous support of this research.

Footnotes

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† *Selected spectral data* (¹H NMR: 300.13 MHz, ¹³C NMR: 75.5 MHz). For **2** δ_H (CD₂Cl₂) 7.93 (8 H, s), 7.53 (16 H, m), 7.45–7.12 (64 H, m), 3.72 (4 H, dt), 3.39 (4 H, dt); δ_C (CD₂Cl₂) 206.61, 201.59, 142.67, 137.32, 135.03, 132.85, 131.78, 130.45, 130.03, 129.56, 128.89, 128.72, 100.11, 87.19, 83.50, 65.60, 37.73; ν_{max} (KBr)/cm⁻¹ 3033, 2154, 2089, 2055, 2023 For **4** δ_H (CDCl₃) 7.65 (4 H, s), 1.14 (42 H, s); δ_C (CDCl₃) 138.36, 129.77, 105.30, 104.03, 88.93, 69.59, 18.65, 11.37; ν_{max} (KBr)/cm⁻¹ 3069, 3056, 2130, 2092, 2038, 2006, 1976. For **5** δ_H (CD₂Cl₂) 7.87 (2 H, d), 7.51 (4 H, m), 7.42–7.16 (19 H, m), 3.66 (1 H, dt), 3.36 (1 H, dt), 1.12 (21 H, s); δ_C (CD₂Cl₂) 207.25, 201.38, 143.91, 139.00, 133.44, 131.37, 130.64, 129.87, 129.39, 128.97 (2), 128.94, 128.64, 127.11, 110.33, 99.04, 96.89, 65.36, 34.80, 19.21, 12.16; ν_{max} (KBr)/cm⁻¹ 3056, 2102, 2062, 2027, 2004, 1975.

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- We have recently prepared the first examples of triyne- and tetrayne-linked dehydrobenzoannulenes. These systems, however, are relatively strain-free: M. M. Haley, M. L. Bell and D. B. Kimball, unpublished work.

Received in Corvallis, OR, USA, 10th March 1997; Com. 7/01712J