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

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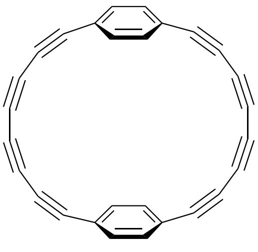
Use of a palladium/cobalt/copper alkyne reaction strategy provides the cobalt-stabilized complex of a highly strained cyclophane.

The recent discovery of the fullerenes[1] and related carbon nanotubes[2] 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 paraphenylenes[6] 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 macrocycles[10] 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 cyclophyne.[11]



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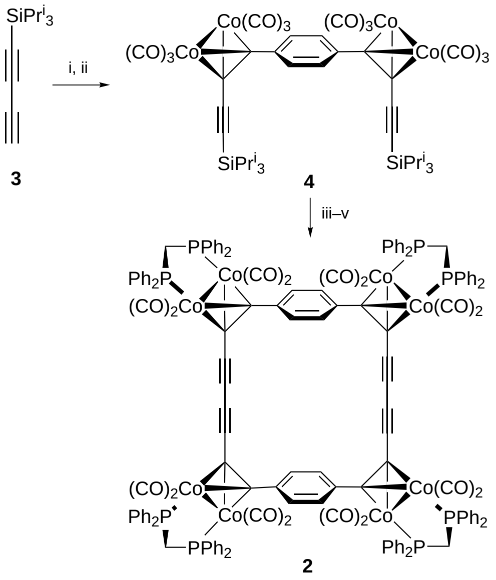
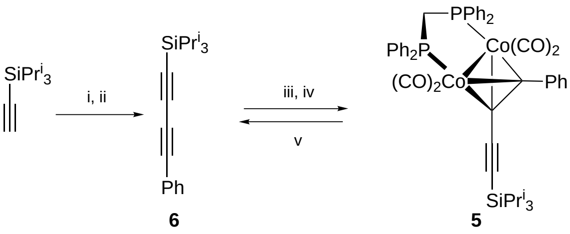
An octacobalt complex such as **2** was envisioned for the immediate precursor to the target macrocycle as: (*i*) the carbon skeleton could be assembled quickly and efficiently using known methodology, and (*ii*) the alkyne C≡C–C angles in this type of (μ-acetylene)dicobalt hexacarbonyl complex are reduced 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 alkynylation 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 coupling[13] 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 monoyne[8,15] and diyne[16] derivatives are known. The cyclocarbons represent the ultimate bent polyyne macrocycles; C_{18} is predicted to exhibit C≡C–C bond angles near 160°, leading to a strain energy of around 72 kcal mol^{-1}.[5b] Cyclophyne **1** should be similarly strained as the triple bond angles are calculated to



Scheme 1 *Reagents and conditions*: i, 1,4-diiodobenzene, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 73%; ii, $Co_2(CO)_8$, Et_2O, 66%; iii, dppm, toluene, 85%; iv, Bu_4NF, THF, > 95%; v, $Cu(OAc)_2 \cdot H_2O$, py, 47%



Scheme 2 *Reagents and conditions*: i, CBr_4, PPh_3, CH_2Cl_2, 85%; ii, phenylacetylene, CuCl, $NH_2OH \cdot HCl$, $PrNH_2$, MeOH, H_2O, 82%; iii, $Co_2(CO)_8$, Et_2O, 76%; iv, dppm, toluene, 87%; v, I_2, THF, 85%

be between 161.7 and 163.6°.[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 polyynes distorted on one or more edge.[18] These results will be reported in due course.

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Footnotes

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† *Selected spectral data* (^{1}H NMR: 300.13 MHz, ^{13}C NMR: 75.5 MHz). For **2** δ_H (CD_2Cl_2) 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 (CD_2Cl_2) 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 ($CDCl_3$) 7.65 (4 H, s), 1.14 (42 H, s); δ_C ($CDCl_3$) 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 (CD_2Cl_2) 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 (CD_2Cl_2) 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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