substituents on the indium atoms. The synthesis and structure of **1** also suggest that the extrusion of part of the ligand array in simple clusters such as R_2MMR_2 (M = Ga, In) or $(InR)_n$ to give higher clusters that incorporate unsubstituted metal atoms may be a general phenomenon in these sterically crowded species. Another distinctive feature of the synthesis of **1** is that an In^I compound was employed as starting material. This already has a 1:1 metal:ligand ratio and is closer stoichiometrically to the more highly aggregated cluster product **1** than are the higher valent starting materials, which usually carry two substituents per metal atom. It now seems likely that further examples of these interesting species will be isolated not only for indium but also for the other Group 13 metals.

Experimental Section

Under anaerobic and anhydrous conditions, a pale yellow solution of LiC_6H_3-2,6-Mes_2 (1.60 g, 4.99 mmol) in THF (20 mL) was cooled to ca. −78 °C and added dropwise to a yellow suspension of InCl (0.82 g, 5.5 mmol) in THF (5 mL) at ca. −78 °C. The solution became dark orange-brown upon addition and was stirred for 30 min. The solution was warmed to −15 °C, and the THF was removed under reduced pressure. The orange-brown solid was extracted with hexanes (100 mL) and gravity filtered through a Celite pad. The volume of the orange-brown solution was reduced to 30 mL. Cooling to ca. 0 °C for 12 h produced dark brown crystals of **1** (0.55 g, 0.25 mmol, 36.8% yield based on InCl). M.p. 207–210 °C; ^{1}H NMR (399.77 MHz, C_6D_6, 25 °C, TMS): $\delta = 0.88$ (t, hexane), 1.22 (m, hexane), 1.88 (s, 24H, *p*-Me, Mes), 2.12 (br s, 24H, *o*-Me, Mes), 2.29 (br s, 24H, *o*-Me, Mes), 6.75 (d, ^3J (H, H) = 7.2 Hz, 8H, *m*-C_6H_3), 6.86 (s, *m*-Mes, 16H), 7.05 (t, ^3J(H, H) = 7.2 Hz, 4H, *p*-C_6H_3); ^{13}C{^{1}H} NMR (100.53 MHz, C_6D_6, 25 °C, TMS): $\delta = 21.29$ (*p*-Me, Mes), 21.65 (*o*-Me, Mes), 129.28 (*m*-Mes), 136.59 (*m*-C_6H_3), 137.13 (*o*-Mes), 137.23 (*p*-C_6H_3), 141.53 (*p*-Mes), 144.97 (*i*-Mes), 148.77 (*o*-C_6H_3), 189.88 (*i*-C_6H_3); UV/Vis (hexanes): λ_{max} (ε) = 305sh (1000).

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The Synthesis of a Novel Strained Diyneparacyclophane and Its Dimer by Metal-Mediated Coupling**

Shawn K. Collins, Glenn P. A. Yap, and Alex G. Fallis*

Diverse families of cyclophanes[1] and assorted cage compounds[2] with novel structures and properties continue to be topics of wide-spread interest.[3] Earlier, we reported the synthesis of a novel class of enediyne cyclophanes by sequential palladium- or copper-mediated coupling.[4] In contrast to normal [n.m]paracyclophanes, the rotation of the benzene ring in these molecules is not restricted by the bridging bonds. Consequently they were christened revolveneynes **1** as the aromatic rings rotate freely, with "skipping rope"-type properties, in which the bridging units and one aromatic ring may swing around each other. The unsaturated bonds in these bridges impart a helical twist to the structures. As a result, they possess helical chirality, a property that is shared with related D_2-symmetric olefinic paracyclophanes.[5] In a related area, we[6] and others[7] have attemped to extend these syntheses to multibridged systems in order to prepare potential precursors to fullerenes such as C_{60}, but with limited success. However, Vollhardt and co-workers[8] have demonstrated that **2** decomposed explosively to form carbon onions when heated, and cobalt alkyne complexes afforded carbon nanotubes.

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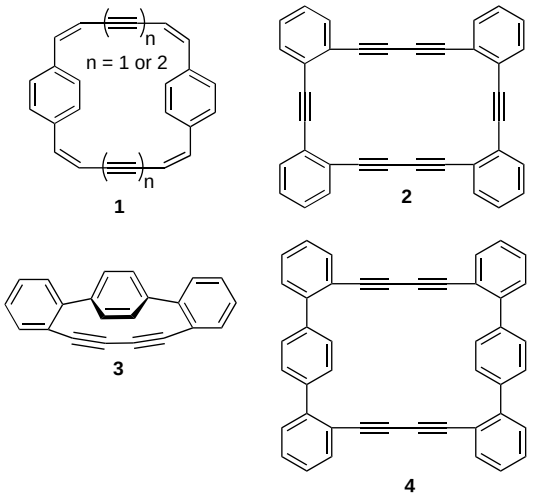
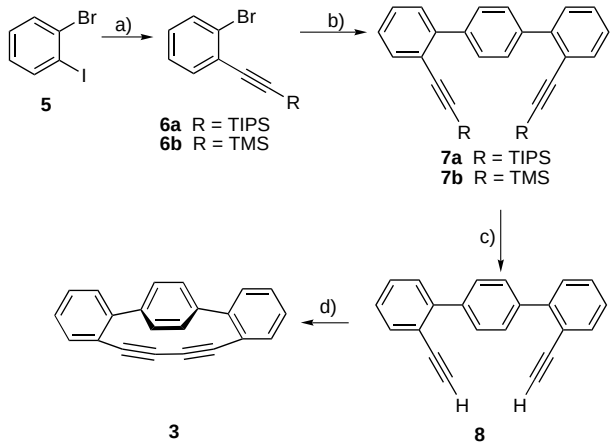


Herein we report an extension of our initial investigations which culminated in the synthesis of the strained diyne system **3** in 90% yield. Modification of the coupling conditions afforded the corresponding dimer **4** which is the benzenoid analogue of **1** for $n=2$. A variety of related bis-acetylene systems are also known[9] and the relevant bond angles are compared with those of **3** and **4**.

The synthesis of **3** is outlined in Scheme 1 and commenced with commercially available 1-bromo-2-iodobenzene (**5**).



Scheme 1. Synthesis of strained cyclophane **3**. a) TMSA (or TIPSA), $[Pd(PPh_3)_2Cl_2]$, CuI, THF, DEA, 55 °C, 15 h, 90% for R = TMS, 80% for R = TIPS; b) 1) *n*BuLi, THF, −78 °C, 30 min, 2) $ZnBr_2$, THF, 0 °C, 15 min, 3) $[Pd(PPh_3)_4]$, 1,4-dibromobenzene, THF, 65 °C, 15 h, 90% for R = TMS, 80% for R = TIPS; c) For R = TIPS: TBAF, THF, 3 h, 100%; for R = TMS: K_2CO_3, MeOH, THF, H_2O, 3 h, 100%; d) $Cu^{II}(OAc)_2$ (6 equiv), pyridine/diethyl ether 3/1, 90 °C, 3 h, 90%.

Selective reaction at the iodine center by palladium(0)-mediated coupling in the presence of copper iodide with triisopropylsilyl- or trimethylsilylacetylene provided the phenyl acetylenes **6a** and **6b**[10] in yields of 80 and 90%, respectively. The most efficient procedure for the coupling of **6a** with 1,4-dibromobenzene involved the use of an organozincate generated in situ by halogen–metal exchange with *n*BuLi followed by transmetalation with $ZnBr_2$. Subsequent addition of tetrakis(triphenylphosphane)palladium(0) and 1,4-dibromobenzene followed by a 15-hour reflux afforded the silyl-protected derivatives **7** (80–90% yield). This organozinc protocol[11] was superior to traditional tributyl- or trimethyltin coupling methods because it avoided the difficult chromatographic separations encountered from the co-elution of alkyltin byproducts and the phenylacetylenes. Removal of the triisopropylsilyl protecting groups was accomplished by treatment with tetra-*n*-butylammonium fluoride in THF, although traces of triisopropylsilyl fluoride complicated the separation. Removal of the trimethylsilyl groups was accomplished efficiently with K_2CO_3 in THF/MeOH/H_2O at 21 °C, thus protection using the trimethysilyl was preferred. The diacetylene **8**, was then subjected to oxidative coupling using $Cu^{II}(OAc)_2$[12] and by refluxing in pyridine/diethyl ether (3/1). A single product was isolated in 90% yield whose spectral features suggested it was the monomer **3**[17] and not the anticipated dimer **4** which would be formed from an intermolecular coupling. Thus the strained system **3** from the intramolecular coupling of the terminal acetylenes formed preferentially. In order to understand this preference various reaction conditions were examined, as summarized in Table 1.

Table 1. Effect of oxidative-coupling conditions on product ratios.

Coupling conditions[a]	Yields [%]	
	3	**4**
90 °C, 3 h	90	0
21 °C, 3 d	43–58	18–26
21 °C, 3 d (protected from light)	54	17–21

[a] $Cu^{II}(OAc)_2$, 6 equiv; pyridine/diethyl ether 3/1.

Variation of the reaction temperature afforded considerable control over the ratio of inter- versus intramolecular coupling. Reactions protected from light produced emerald green solutions, while in reactions left unprotected the solution remained the characteristic sapphire blue of the $Cu^{II}(OAc)_2$, although the total yields and product mixtures were similar. Cu^{I}/O_2 mediated couplings,[7, 13] in contrast, gave a complex "soup" of products with no trace of **3**, although a disappointing 10% yield of the dimer **4** was isolated.

Crystals of the dimer **4**[17] suitable for X-ray analysis were grown from a dichloromethane/methanol solution. It was anticipated that the unsaturated bonds in the bridges would impart a helical twist to the molecule as observed previously for the revolveneynes. Thus, the two central benzene rings were expected to be aligned in an overlapping manner, superimposed on each other but slightly offset. The crystal structure analysis revealed the dimer, which co-crystallized with dichloromethane in a 2:1 ratio, was indeed helical but the spacial arrangement of the "outer" rings created two "arms" (Figure 1).[14] This stereochemical relationship appears to result from a twisting of the molecule to facilitate through-space alignment between two of the "outer" benzene rings of the bridges. This creates a pincer-like structure,[15] with one molecule of dichloromethane within the cavity of every second molecule dispersed uniformly throughout the lattice of the crystal. The helical conformation of the dimer helps to relieve strain within the acetylene bonds. The bond angles at the four triple bonds are as follows: C(19)-C(20)-C(21) 177.7°, C(20)-C(21)-C(22) 177.1°, C(41)-C(42)-C(43) 175.9°, C(42)-C(43)-C(44) 178.7°.

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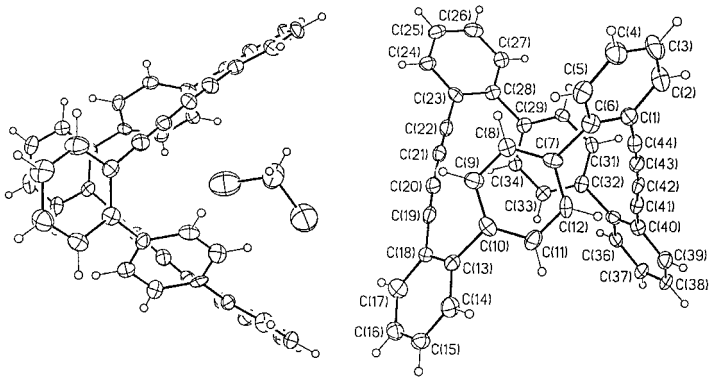
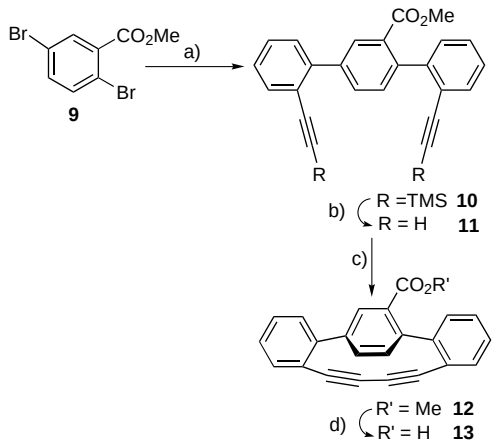


Figure 1. Structure of **4** in the crystal: view from the side with a co-crystallized molecule of dichloromethane (left), and from above without a molecule of dichloromethane (right).

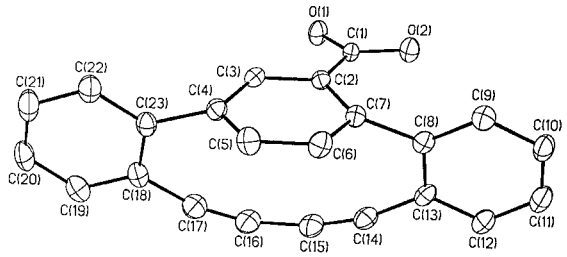
Several attempts to crystallize **3** were unsuccessful and resulted in the formation of a material assumed to be a polymer. In order to assign the structure of **3** unambiguously, a new analogue was synthesized containing a carboxylic acid group. This facilitated crystallization, allowed X-ray structural analysis of the crystal, and provided insight into the hydrogen bonding of the acid dimers in the crystal. The acid **13** was assembled using a parallel set of reactions (Scheme 2) to those



Scheme 2. Synthesis of the carboxylic acid cyclophane derivative **13**. a) 1) **6b**, *n*BuLi, THF, −78 °C, 30 min, 2) $ZnBr_2$, THF, 0 °C, 15 min, 3) [$Pd(PPh_3)_4$], methyl 2,5-dibromobenzoate, THF, 65 °C, 15 h, 80 %; b) K_2CO_3, MeOH, THF, H_2O, 3 h, 99 %; c) $Cu^{II}(OAc)_2$ (6 equiv), pyridine/diethyl ether 3/1, 90 °C, 3 h, 64 %; d) LiOH, H_2O, MeOH, 50 °C, 3 h, 25 %.

described above. The organozinc derivative of **6b** (Scheme 2) was prepared as previously and the solution treated with tetrakis(triphenylphosphane)palladium(0) and methyl 2,5-dibromobenzoate (reflux, 15 h) to afford **10**[17] in 80 % yield. Removal of the trimethylsilyl groups and oxidative coupling with $Cu^{II}(OAc)_2$ in refluxing pyridine/diethyl ether (3/1) gave **12**[17] in 64 % yield. Saponification of the methyl ester with lithium hydroxide required warming to reflux in methanol over 3 h to produce the carboxylic acid **13** in a modest 25 % yield. More vigorous conditions and alternative bases (KOH, NaOH) caused decomposition. The carboxylic acid crystallized from dichloromethane as monoclinic crystals for X-ray analysis.[14]

Figure 2 illustrates the influence of the free acid group which, as expected, forms hydrogen bonded dimers through intermolecular association. This clearly establishes the structure of both **3** and **13**.[15] The inherent strain in this unique ring



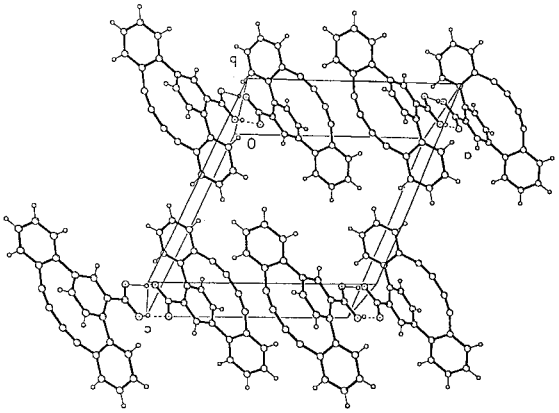


Figure 2. Structure of **13** in the crystal (top) and intermolecular hydrogen bonding within the lattice (bottom).

system is reflected in the deviation from planarity observed between the two outer benzene rings which lie perpendicular to the central ring and the connecting bonds. The bond between C(7)–C(8) is bent 17.8° out of the plane of the central ring, while the C(4)–C(23) bond is distorted by 18.7°. The acetylene bonds are also strained as the angles C(14)-C(15)-C(16) and C(15)-C(16)-C(17) are 163.7° and 163.5°, respectively. However, the carbon – carbon bond lengths fall within the normal range. The corresponding bond angles in a related [4.4]orthocyclophane bisdiyne system prepared by Zhou, Carroll, and Swager[9b] were 165.8° and 166.7°, respectively, while the [3.4]paracyclophane diynes synthesized by Ueda, Katayama, and Tanaka[9d] are also bowed, but the deformation is less, with bond angles of 172.8° and 173.9°, respectively.

In conclusion, this palladium-coupling sequence provided a rapid route to novel benzene – diyne bridged cyclophanes that possess interesting geometric features. It is anticipated that current investigations will lead to more highly functionalized systems with unique properties, capable of binding transition metals[16] and acting as multidentate ligands when heteroatoms are present. In addition, with appropriate functionality, these methods will provide access to novel liquid crystals.

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[15] For an example of "pincer"-shaped molecules, see R. Rathore, S. V. Lindeman, J. K. Kochi, *Angew. Chem.* **1998**, *110*, 1665 – 1667; *Angew. Chem. Int. Ed.* **1998**, *37*, 1585 – 1587.

[16] J. Schulz, F. Vögtle in ref. [1e], pp. 41 – 86.

[17] Physical data for the new compunds. **3**: White solid, m. p. 167 – 170 °C; ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.39$ (m, 9H), 7.72 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 84.1$, 98.1, 124.8, 126.4, 126.9, 127.4, 128.7, 129.8, 141.5, 150.9 ; IR ($CHCl_3$): $\tilde{\nu} = 2965$, 2921, 1508, 1457, 1260, 1099, 1019 cm^{-1}; MS (70 eV): *m*/*z* (%): 276 (100), 248 (6), 198 (1), 162 (10), 137 (14), 99 (2), 70 (2), 31 (6); HRMS for $C_{22}H_{12}$: calcd: 276.0940; found: 276.0938. **4**: Yellow solid, m. p. 257 – 260 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.27$ (m, 4H), 7.36 (m, 8H), 7.53 (s, 8H), 7.58 (d, $J = 7.4$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 76.7$, 81.3, 120.4, 127.1, 128.8, 129.2, 129.5, 133.7, 139.3, 145.2; IR ($CHCl_3$): $\tilde{\nu} = 3055$, 3029, 2924, 2854, 2216, 1468, 1439, 1220, 840 cm^{-1}; MS (FAB): *m*/*z* (%): 551 (3), 461 (1), 391 (1), 369 (1), 338 (1), 277 (5), 246 (5), 219 (3). **10**: Pale yellow solid, m. p. 113 – 116 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 0.02$ (s, 9H), 0.11 (s, 9H), 3.66 (s, 3H), 7.30 (m, 4H), 7.40 (m, 3H), 7.48 (dm, 1H), 7.58 (dm, 1H), 7.83 (dd, $J = 2.0$, 7.9 Hz, 1H), 8.20 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -0.40$, -0.32, 51.9, 97.6, 98.1, 103.8, 104.4, 121.5, 122.3, 126.9, 127.3, 128.4, 128.4, 128.9, 129.3, 130.3, 130.7, 130.8, 131.6, 132.4, 133.4, 139.6, 141.0, 143.0, 145.0, 167.5; IR ($CHCl_3$): $\tilde{\nu} = 3006$, 2957, 2156, 1722, 1474, 1437, 1312, 1248, 1208, 1118 cm^{-1}; MS (70 eV): *m*/*z* (%): 480 (23), 465 (25), 435 (23), 407 (6), 391 (10), 376 (32), 348 (54), 333 (30), 319 (13), 303 (20), 289 (30), 263 (16), 225 (10), 201 (7), 147 (7), 89 (43), 73 (100), 59 (36); HRMS for $C_{30}H_{34}O_2Si_2$: calcd: 480.1942; found: 480.1927; elemental analysis for $C_{30}H_{34}O_2Si_2$: calcd: C 74.95, H 6.71; found: C 75.05, H 6.65. **12**: Yellow solid, m. p. 143 – 146 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 3.66$ (s, 3H), 7.24 (m, 2H), 7.33 (m, 3H), 7.45 (m, 3H), 7.69 (d, $J = 6.8$ Hz, 1H), 7.73 (d, $J = 7.1$ Hz, 1H), 7.95 (d, $J = 1.7$ Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 51.8$, 83.3, 84.8, 97.9, 98.0, 123.1, 124.9, 126.4, 126.9, 127.0, 127.0, 127.2, 127.8, 128.6, 128.8, 130.9, 132.0, 132.3, 133.4, 142.1, 142.7, 149.4, 150.5, 166.4; IR ($CHCl_3$): $\tilde{\nu} = 2999$, 2954, 2858, 2169, 1720, 1436, 1308, 1213, 1140 cm^{-1}; MS (70 eV): *m*/*z* (%): 334 (35), 303 (4), 274 (41), 218 (1), 143 (30), 112 (12), 69 (100), 40 (16); HRMS for $C_{24}H_{14}O_2$: calcd: 334.0094; found: 334.1018.

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