JOC The Journal of Organic Chemistry

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# Synthesis of 1,8,9,16-Tetrakis(trimethylsilyl)tetra-*cata*-tetrabenzoquadrannulene

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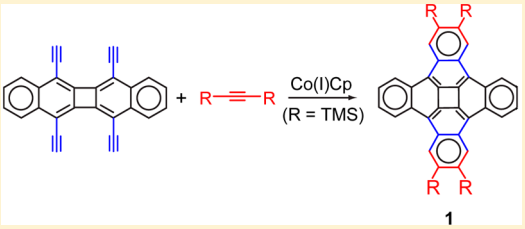
Supporting Information

**ABSTRACT:** The synthetic efforts that yielded the first stable [4]-circulene, 1,8,9,16-tetrakis(trimethylsilyl)tetra-*cata*-tetrabenzoquadrannulene ($TMS_4$-TBQ, **1**), are reported. The synthesis and characterization of different intermediates are described. The cyclotrimerization of the key precursor tetraalkyne was explored using Rh(I), Ni(0), and Co(I) catalysts. The ultimate product **1** was isolated only after oxidative demetalation of cobalt complexes.




## INTRODUCTION

Fullerenes contain five-membered rings, which induce curvature in an otherwise planar hexagonal graphitic lattice.[1] For example, 12 pentagons surrounded by 20 hexagons make up $C_{60}$. Pentagon−heptagon pairs and other large rings are found in carbon nanotubes.[1,2] Indeed, all known fullerenes contain five-membered rings. Four-membered rings can, in principle, also induce curvature in fullerenes.[3] Such fullerenes, the nonclassical fullerenes, have never been observed. The closest known structure, prepared by Rubin, contained a partially saturated four-membered ring.[4]

[*n*]Circulenes, with a central *n*-sided polygon surrounded by *n*-fused benzenoid rings, are fragments of graphitic structures. The smallest known circulene before our synthesis was [5]circulene, trivially known as corannulene (**2**). This bowl-shaped molecule was first synthesized by Lawton and Barth in 1966 (Figure 1).[5−7] Scott and co-workers improved its synthesis in 1991.[8] Since then, numerous improvements have been made in corannulene synthesis.[9,10]

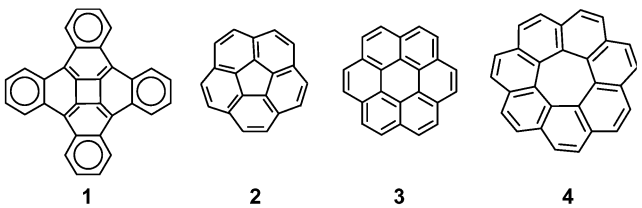


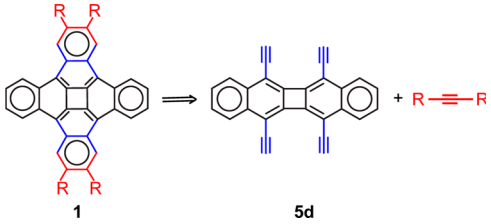

**Figure 1.** Known circulenes.

[6]Circulene, or coronene (**3**), consists of all hexagons and is planar. It was first synthesized by Scholl in 1936 and naturally occurs in the mineral carpathite.[11] Saddle-shaped [7]circulene (**4**) was first synthesized by Yamamoto and co-workers in 1983.[12,13]

A few unsuccessful attempts to prepare [4]circulene were reported,[14−17] and in 2010 we described the synthesis of a [4]circulene derivative, 1,8,9,16-tetrakis(trimethylsilyl)tetra-*cata*-tetrabenzoquadrannulene ($TMS_4$-TBQ).[18] The present paper provides a full account of its synthesis and complements our initial communication.[18]

Our approach relies on the intermolecular cyclotrimerization of precursor tetraalkyne **5d** as the key step (Scheme 1). We reasoned that formation of aromatic rings in the cyclotrimerization step would be sufficiently exothermic to bend the molecule into the necessary cup shape. This assertion was supported computationally.[18] Benzannelation should also prevent the target molecule from undergoing unwanted reactions, and thus stabilize the [4]circulene core. Cyclotrimerization has been successfully used to synthesize strained helicenes,[19] biphenylenes,[20] and indenocorannulenes.[21] The reaction can be intra- or intermolecular.

**Scheme 1. Key Cyclotrimerization Step in TBQ (1) Synthesis**



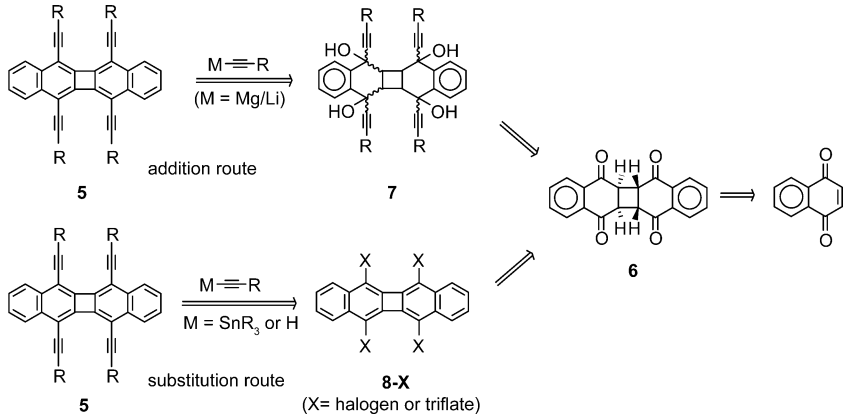

## RESULTS AND DISCUSSION

The precursor tetraalkyne **5** was itself a synthetic challenge. Two strategies were explored to synthesize **5**. The addition approach (Scheme 2) involved the nucleophilic addition of metal alkynes to quinone **6** and subsequent elimination. The substitution approach (scheme 2) involved palladium-catalyzed coupling (Stille or Sonogashira) of alkynes with tetrahalo or

**Received:** August 22, 2012
**Published:** November 28, 2012

**Scheme 2. Synthetic Approaches to Tetraalkyne 5**

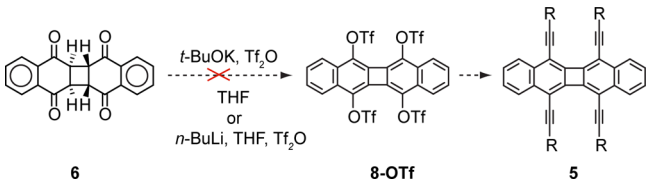



tetratriflate substituted derivatives **8-X**. Both approaches start with the naphthoquinone dimer **6**, which could be prepared on gram scale by photodimerization of commercially available 1,4-naphthoquinone.[22]

The direct addition of organometallic nucleophiles, such as Grignard reagents, to the carbonyl groups of **6** was reported to provide tetramethyl- and tetraphenyl-substituted dibenzobiphenylenes after acid-catalyzed dehydration.[23] All attempts (LiCCTMS, NaCCTMS, BrMgCCTMS, etc.) to synthesize tetraalkynes **5** using the conventional additions failed. Indeed, we could not reproduce the original procedures reported.[23] While partial alkynylation was observed by mass spectrometry, the desired 4-fold addition compounds were never detected. The conventional addition did not work, and we reconsidered our approach.

It was evident that dimer **6** readily enolizes under basic conditions,[24] and this enolization interferes with the addition of basic metal alkynyls. We decided to take advantage of enolization to prepare tetratriflate **8-OTf**, which would permit a Stille or Sonogashira coupling to prepare the required tetraalkyne intermediate (scheme 2). Trapping the enol of **6** with $Tf_2O$ should provide the tetratriflate **8-OTf**.[25,26] All attempts to prepare triflate **8-OTf** failed, giving black solutions, and no detectable products were observed (scheme 3).

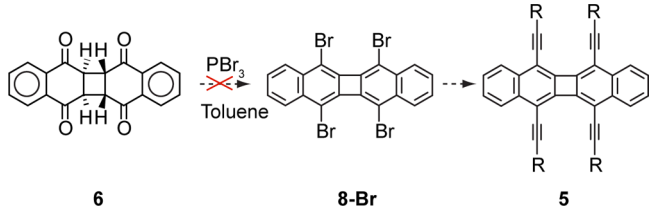
**Scheme 3. Attempted Synthesis of Tetraalkynes 5**




However, the tetraanion of dimer **6** could be trapped in 50% yield using trimethylsilyl chloride (scheme 4) to give TMS ether **9**, which was crystallographically characterized (see the Supporting Information). The synthesis of the TMS ether **9** by addition of base followed by TMSCl shows that the tetraanion was generated. The conversion of TMS ether **9** to triflate **8-OTf**[27−29] was unsuccessful, presumably because triflate **8-OTf** was unstable (scheme 4). Few PAHs bearing multiple triflate groups are known.

We also explored preparing **8-Br** as an intermediate (Scheme 5) in the substitution route (Scheme 2). The analogous

**Scheme 5. Attempted Synthesis of 8-Br**



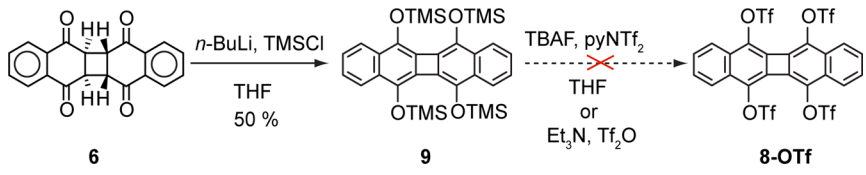

preparation of bromonaphthalenes from tetralone and $\alpha$-methyltetralone was reported.[30] Unfortunately, all attempts to synthesize tetrabromodibenzobiphenylene **8-Br** failed, and only the starting material was recovered.

These failures presented a quandary. We could not add alkynes to **6** because of enolization, and we could not prepare tetrakistriflate or tetrakisbromo coupling intermediates, **8-OTf** or **8-Br**, via the enol.

One avenue remained open, however: suppressing enolization. Organocerium reagents are known to enhance nucleophilicity and decrease the basicity of organolithium and Grignard reagents.[31] The organocerium reagents promote 1,2-addition to carbonyls and suppress enolization in many reactions.[32−35] This methodology worked, providing the tetraols **7**.[18]

The alkynyl cerium species were prepared by adding LiCCR to a solution of carefully dried[36] $CeCl_3$ in THF. Quinone **6** was added to this solution, giving tetraols **7** as a mixture of

**Scheme 4. Attempted Synthesis of Triflate 8-OTf**





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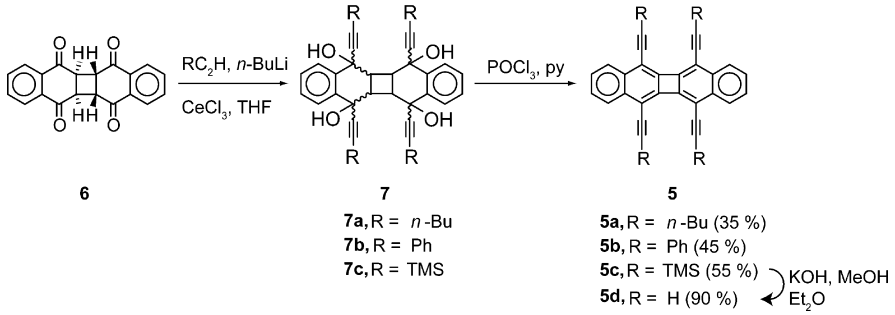
**Scheme 6. Synthesis of Tetraalkynes 5**




stereoisomers. Tetraols **7a** (R = *n*-Bu) and **7b** (R = Ph) were taken through the elimination step as a mixture of stereoisomers. A single isomer of tetraol **7c** (R = TMS, Scheme 6) precipitated from solution during workup in 50% yield.[18] Its single-crystal X-ray diffraction analysis revealed that the acetylides added to the exo face of **6** (Figure 2). The single stereoisomer of **7c** was used for subsequent reactions.

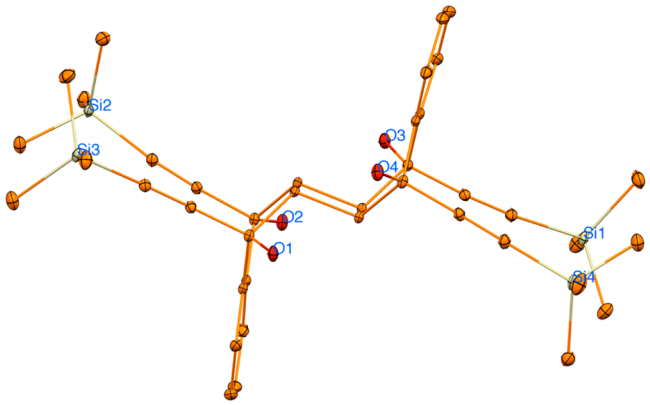
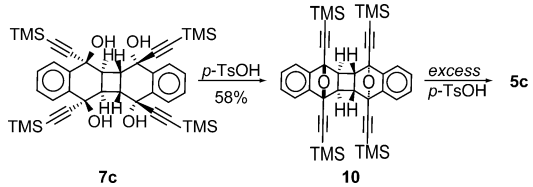



**Figure 2.** Crystal structure of tetraol **7c** (solvent and hydrogen atoms are omitted).

The dehydration of tetraols **7** using *p*-TsOH[37] gave the corresponding tetraalkynes **5** in moderate yields (35−55%), but the reactions often failed. One of the major products in the dehydration of **7c** was the oxy-bridged tetraalkyne **10** (Scheme 7), which could be converted to **5c** by a second treatment with

**Scheme 7. Acid-Catalyzed Dehydration**




*p*-TsOH under forcing conditions in moderate yields (20−40%). This reaction was not preparatively useful because yields were variable.

The crystal structure of **10** (Figure 3) retains the carbon-skeleton configuration of **7c**. This suggests that cyclization reaction proceeds by an $S_N1$ mechanism where $H_2O$ is lost, giving a benzylic carbocation that is intercepted by the remaining transannular hydroxide group.

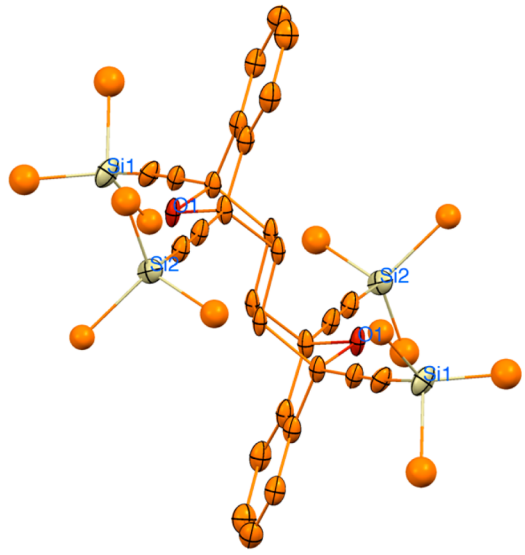



**Figure 3.** Crystal structure of **10** (hydrogen and disordered atoms are omitted).

The dehydration of tetraols **7** could be achieved using phosphorus oxychloride in pyridine,[33] giving TMS-protected tetraalkyne **5c** in acceptable yield (55%). The tetraalkyne **5c** was then deprotected with KOH to give **5d** in good yield (>90%).[18]

Because the crystal packing of related structures is important for material applications,[38,39] we determined the X-ray crystal structures of tetraalkynes **5a**, **5b**, and **5c** (Figure 4). The dihedral angle formed by the four carbon atoms of the alkynes on the same side were 4.0° (**5a**), 7.7° (**5b**), and 2.8° (**5c**). Compounds **5b** and **5c** pack in a herringbone pattern. Compound **5a** packs in a slipped $\pi$-stack with the distance between dibenzobiphenylene planes of 3.71 Å (Figure 5). Two columnar stacks form an angle of 35.6° for **5b** (Figure 6) and 54.8° for **5c** (Figure 7). For both structures, the $\pi$-stacked molecules are in van der Waals contact (**5b**, 3.29 Å; **5c**, 3.32 Å).

With the tetraalkynes **5a−d** in hand, we turned our attention to the key cyclotrimerization reactions. The cyclotrimerization of **5a**, which bears butyl chains on the alkynes, was first attempted using Wilkinson's catalyst and 3-hexyne as the external alkyne. This reaction yielded only starting material, even after increased reaction time and temperature or use of microwave irradiation. Other catalysts ($RhCl(PPh_3)_3$, $Rh_2(COD)_2Cl_2$, $Ni(PPh_3)_2(CO)_2$) also failed. Their failure can be explained by consideration of strain in the final product. Substituents at the bay positions will collide in the bowl-shaped product. This was supported by calculations (Scheme 8). A


dx.doi.org/10.1021/jo3015648 | J. Org. Chem. 2012, 77, 10617−10622

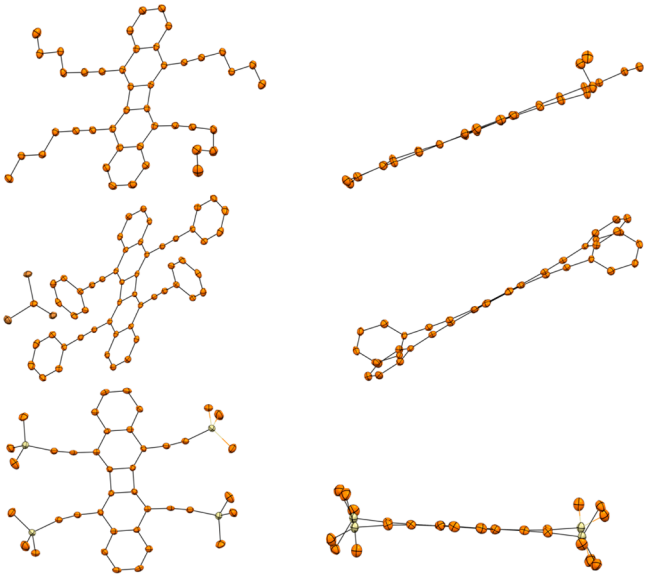


**Figure 4.** Crystal structures of tetraalkynes **5a**, **5b** (bromoform solvate) and **5c** (front and side view) (hydrogens are omitted).

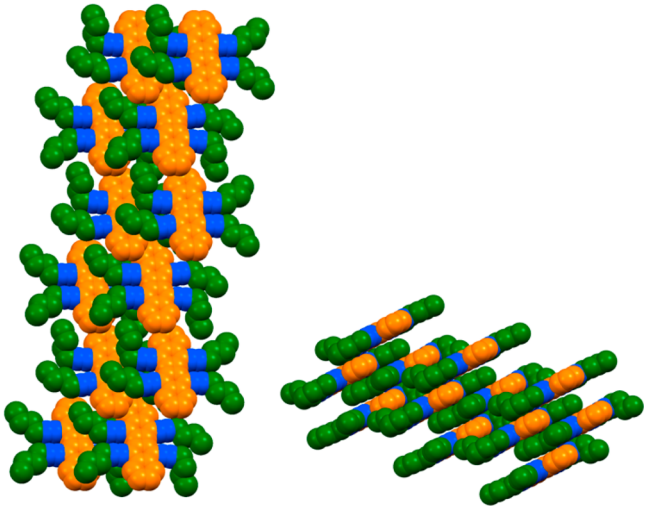


**Figure 5.** Crystal packing of **5a** (top and side view).

homodesmotic reaction shows that the presence of alkyl substituents in these bay positions will increase strain by at least 22 kcal/mol.

It follows that **5d** should be a better precursor for cyclotrimerization because the final product will not have any substituents at sterically crowded bay positions (Scheme 9). We therefore used only the parent tetraalkyne **5d** for the subsequent cyclotrimerization reactions.

Wilkinson's catalyst using norbornadiene as an acetylene equivalent gave a complex mixture. An ion corresponding to the half-reacted product with one bridge formed could be detected by mass spectrometry, but the desired product was not observed. $[RhCl(COD)]_2$ and $Ni(COD)_2$ were also ineffective. Bis(triphenylphosphine)dicarbonylnickel(0) was better, with the mass spectrum showing a peak corresponding to the desired product (Supporting Information). The reaction, however, failed to provide **1** in isolable quantities (Table 1).

The stepwise control offered by Negishi's reagent in the preparation of substituted benzenes via alkyne cyclotrimerization was appealing. These zirconocene-mediated cyclotrimerizations have been used to synthesize substituted anthracenes and pentacenes.[40] When **5d** was treated with Negishi's reagent, followed by addition of nickel or copper catalyst and external alkyne, starting material and various unidentified products were observed in NMR. No trimerization products were observed.

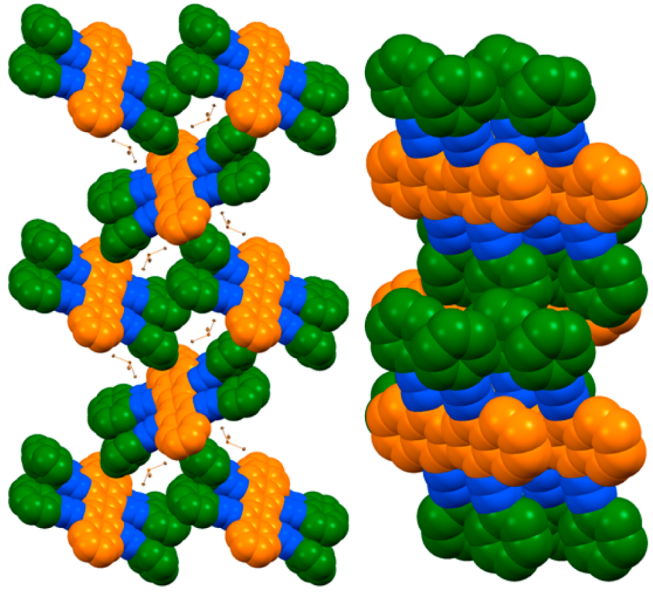


**Figure 6.** Crystal packing of bromoform solavate of **5b** (top and side view).

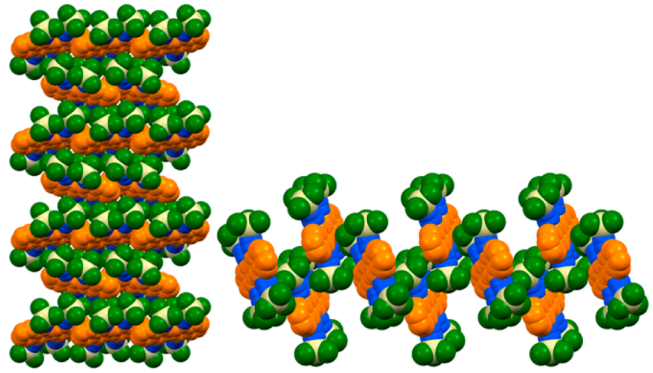
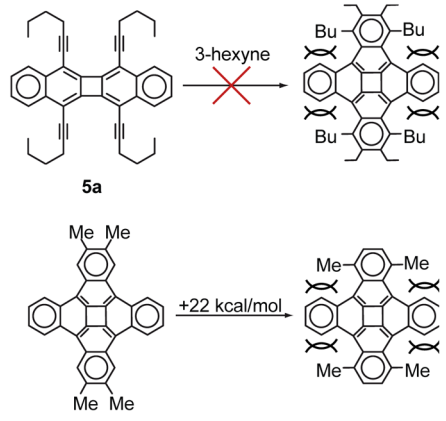


**Figure 7.** Crystal packing of **5c**.

**Scheme 8. Estimated Strain Energy of Methyl-Substituted TBQ**





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**Scheme 9. Attempted Cyclotrimerizations**

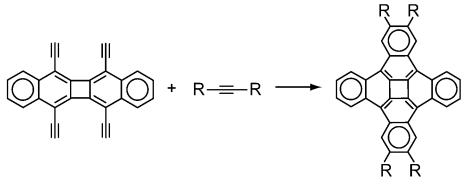


**Table 1. Summary of Different Catalysts Used for Cyclotrimerizations**

| catalyst | external alkyne or equivalent | product (by MS) | R |
|---|---|---|---|
| $RhCl(PPh_3)_3$ | NBD | half reacted | H |
| $[RhCl(COD)]_2$ | 3-hexyne | **1** + half reacted | Et |
| $Ni(COD)_2$ | 3-hexyne | no reaction | Et |
| $Ni(CO)_2(PPh_3)_2$ | 3-hexyne | **1** + half reacted | Et |
| $ZrCp_2Cl_2$/*n*-BuLi | 3-hexyne | no reaction | Et |
| $CoCp_2(C_2H_4)_2$/ oxidant | BTMSA | **1** | TMS |

Cobalt-based catalysts are among the most useful for cyclotrimerizations to give biphenylenes.[41] A noteworthy example is the formation of multiple four-membered rings in one step.[41] $CoCp(CO)_2$ and Jonas catalyst, $[CpCo(C_2H_4)_2]$, are common precatalysts. We prepared Jonas catalyst $[CpCo(C_2H_4)_2]$ using Vollhardt's improved protocol[42] of its original synthesis.[43]

The optimization of the Co-catalyzed cyclotrimerization was complicated by the complexation of CoCp to the various products in the reaction mixture. The CoCp complexation is often observed in these CoCp-catalyzed cyclotrimerizations, and products are normally decomplexed in an oxidative workup, usually employing ferric nitrate or other strong oxidants.[44] In our cyclotrimerizations, we frequently observed peaks in the mass spectrum corresponding to the **1**·$(CoCp)_n$, where $n$ = 1, 2, 3 (Supporting Information). We found that oxidative workup using ferrocenium hexafluorophosphate permitted the isolation of **1**, albeit in low yield.

The reason for the low yield remains unclear, but we suspect that the oxidant used in workup could destroy the product **1**. Indeed, **1** is destroyed by treatment with ferrocenium hexafluorophosphate in chloroform. This hypothesis is supported by the observation that when the stronger oxidant ferric nitrate is used, no product can be isolated. Alternatively, the cyclotrimerization itself might proceed in low yield. The formation of CoCp–cyclobutadienyl complexes[45,46] is a likely side reaction, and these have the same mass as **1**·CoCp and **1**·$(CoCp)_2$ and would be indistinguishable by mass spectrometry (Figure 8). The cyclobutadienyl units liberated by oxidation would polymerize.

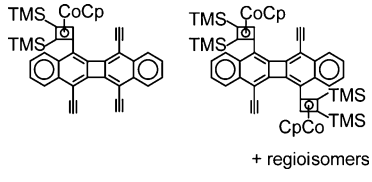


**Figure 8.** Some of the possible CoCp–cyclobutadienyl complexes.

## CONCLUSIONS

Our synthesis of **1** is short, requiring only five steps, and takes advantage of symmetry, building 18 C–C bonds in those five steps. The main shortcoming in the synthesis is the low yield in the key cyclotrimerization step. We hope that advances in cyclotrimerization methodology will allow us to overcome the low yield in this final step.

## EXPERIMENTAL SECTION

All reactions were run under $N_2$. THF, DME, and $Et_2O$ were distilled from Na and benzophenone. Dimer **6**,[22] tetraol **7c**,[18] tetraalkyne **5d**,[18] and $TMS_4$–TBQ **1**[18] were synthesized using literature procedures. The identity of known compounds was established by melting points and NMR spectroscopy. $^1H$ NMR spectra were recorded on 400 and 500 MHz spectrometers and $^{13}C$ NMR were recorded on 100 and 125 MHz spectrometers. IR spectra were recorded using a total internal reflectance module having a spectral range 4000–600 $cm^{-1}$. Mass spectra were recorded using an atmospheric pressure photoionization (APPI) source on a time-of-flight (TOF) instrument in the positive mode.

**Synthesis of 5,6,11,12-Tetrakis(trimethylsiloxy)dibenzo[*b*,*h*]biphenylene (9).** Dimer **6** (0.50 g, 1.5 mmol) and THF (100 mL) were added to a Schlenk flask. To the resulting suspension was added 1.6 M *n*-BuLi (9.6 mL, 6.0 mmol) dropwise at −78 °C. This mixture was stirred for 1 h and then warmed to room temperature. The trimethylsilyl chloride (5.0 mL, 55 mmol) was added, and the mixture was stirred for an additional 1 h. The solvents were evaporated, and the residue was passed through a silica plug with $CHCl_3$/hexane (3:7). The solvents were evaporated to give clean **9** (0.481 g, 50%): mp 243–246 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 7.82–7.80 (m, 4H, ArH), 7.30–7.28 (m, 4H, ArH), 0.27 (s, 36H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 136.4, 133.3, 129.1, 125.5, 123.7, 0.0; IR (ATR) ($cm^{-1}$) 2955, 1629, 1578, 1508, 1344, 1252, 1158, 1090, 1062, 932, 875, 828, 764, 688; UV–vis $\lambda_{max}$/nm (THF) (log $\varepsilon$) 416 (3.11), 391 (2.88), 368 (2.99), 342 (4.13), 303 (5.01), 290 (4.69), 257 (3.91); HRMS (APPI-TOF) calcd for $C_{32}H_{44}O_4Si_4$ 604.2317, found 604.2302.

**Synthesis of 10.** In a round-bottomed flask (250 mL) equipped with a Dean–Stark trap was added *p*-TsOH (0.02 g, 0.10 mmol) to a solution of **7c** (0.50 g, 0.71 mmol) dissolved in toluene (100 mL). Molecular sieves (4 Å, 8–10 beads) were added, and the solution was refluxed for 8 h with continuous removal of water. The crude reaction became orange-red. The reaction mixture was passed through a silica plug (~10 g of $SiO_2$). The organic solvents were evaporated, and oxy-bridged **10** was purified by column chromatography using hexane/chloroform (8:2) (0.25 g, 58%): mp >400 °C (darkens 290 °C); $^1H$ NMR (400 MHz, $CDCl_3$) 7.40–7.37 (m, 4H, ArH), 7.29–7.27 (m, 4H, ArH), 2.53 (s, 4H), 0.23 (s, 36H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 143.7, 127.9, 119.3, 97.7, 95.7, 81.5, 47.1, 0.0; IR (ATR) ($cm^{-1}$) 2962, 2183, 1458, 1245, 1131, 1065, 1008, 960, 831, 752, 650; UV–vis $\lambda_{max}$/nm (THF) (log $\varepsilon$) 460 (2.63), 352 (3.97), 334 (4.01), 252 (4.34); HRMS (APPI-TOF) calcd for $C_{40}H_{48}O_2Si_4$ 672.2731, found 672.2764.

**Improved Synthesis of 5c.** In a round-bottomed flask (250 mL) were added tetraol **7c** (0.60 g, 0.85 mmol), pyridine (60 mL), and phosphorus oxychloride (2.0 mL, 17 mmol). The reaction was refluxed for 16 h. The crude reaction became dark brown. The solvents were distilled under high vacuum, and solids were passed though a silica plug (~10 g $SiO_2$) using chloroform (200 mL) as solvent. The yellow band was collected, and the organic solvents were evaporated to give clean **5c** (0.24 g, 55%).[18]

**Synthesis of 5,6,11,12-Tetrakis(butylethynyl)dibenzo[*b*,*h*]biphenylene (5a).** Compound **5a** was synthesized following the same procedure as **5c** (0.170 g, yield = 35%): mp 168–170 °C; $^1H$ NMR (500 MHz, $CDCl_3$) $\delta$ 8.14–8.12 (m, 4H, ArH), 7.42–7.40 (m, 4H, ArH), 2.61–2.59 (t, $J$ = 7.2 Hz, 8H), 1.75–1.72 (dt, $J$ = 14.9, 7.4 Hz, 8H), 1.57–1.55 (dd, $J$ = 14.9, 7.4 Hz, 8H), 1.00–0.98 (t, $J$ = 7.3 Hz, 12H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ 146.5, 135.5, 127.3, 112.1, 105.2, 100.8, 76.1, 31.3, 22.6, 20.3, 13.9; IR (ATR) ($cm^{-1}$) 2953, 2924,


dx.doi.org/10.1021/jo3015648 | J. Org. Chem. 2012, 77, 10617–10622

2865, 2219, 1583, 1510, 1463, 1451, 1350, 1085, 758, 734, 628; UV–vis $\lambda_{max}$/nm (THF) (log $\varepsilon$) 451 (3.78), 427 (3.41), 420 (3.56), 383 (3.69), 353 (3.95), 331 (4.48), 318 (sh, 4.25), 280 (3.94), 251 (3.94); HRMS (APPI-TOF) calcd for $C_{44}H_{44}$ 572.3443, found: 572.3415.

**Synthesis of 5,6,11,12-Tetrakis(phenylethynyl)dibenzo[*b*,*h*]-biphenylene (5b).** Compound **5b** was synthesized following the same procedure as **5c** (0.25 g, yield = 45%): mp >400 °C (darkens 315 °C); $^1$H NMR (500 MHz, $CDBr_3$) $\delta$ 8.26–8.21 (m, 4H, ArH), 7.52–7.46 (m, 4H, ArH), 7.40–7.34 (m, 8H, ArH), 7.24–7.19 (m, 4H), 7.13–7.06 (m, 8H, ArH); $^{13}$C NMR (125 MHz, $CDBr_3$) $\delta$ 145.1, 133.7, 130.6, 127.2, 126.5, 126.1, 121.5, 110.6, 98.6, 83.7; IR (ATR) (cm$^{-1}$) 3053, 1485, 1439, 1362, 1125, 1065, 1022, 913, 752, 688, 629; UV–vis $\lambda_{max}$/nm (THF) (log $\varepsilon$) 464 (4.29), 432 (4.27), 353 (4.91), 308 (4.86), 277 (5.45), 252 (4.80); HRMS (APPI-TOF) calcd for $C_{52}H_{28}$ 652.2191, found: 652.2170.

**Cyclotrimerization Using Rh(I) or Ni(0) Catalyst.** In an oven-dried microwave tube were added **5d** (15 mg, 0.04 mmol), 3-hexyne (0.05 mL, 0.04 mmol), and chloro(1,5-cyclooctadiene)rhodium(I) dimer (0.002 g, 0.005 mmol) or bis(triphenylphosphine)-dicarbonylnickel (0) (0.003 mg, 0.005 mmol). Toluene (5 mL) was added to the microwave tube, and it was closed under nitrogen. The reaction mixture was irradiated (150 °C, 250 W) using CEM Discover (model no. 908005) microwave reactor for 30 min. The reaction was monitored by mass spectrometry (APPI-MS).

## ■ ASSOCIATED CONTENT

### Supporting Information

Crystallographic information files for **5a–c**, **7c**, **9**, and **10** (CIF) and NMR, IR, UV–vis, and mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (CHE-0957702).

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