Journal of Organometallic Chemistry, 382 (1990) 191–200
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20562

Tandem palladium-, cobalt-, and nickel-catalyzed syntheses of polycyclic π-systems containing cyclobutadiene, benzene, and cyclooctatetraene rings *

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(Received August 14th, 1989)

Abstract

A sequence is described in which Co^I serves as a catalyst in the co-cyclization of 1,2-diethynylarenes (in turn derived by Pd^{II}-catalyzed alkynylation of the corresponding haloaromatics) with alkynes to furnish substituted biphenylenes and Ni^0 is used to dimerize the latter to the corresponding tetrabenzocyclooctatetraenes. The strategy provides a novel synthetic entry into novel polycyclic π-systems of synthetic and theoretical interest.

Introduction

We have described recently how 1,2-diethynylated arenes, available through the Pd^{II}-catalyzed alkynylation of 1,2-dihaloaromatics, can be subjected to the cobalt-catalyzed co-cycloaddition with alkynes [1] to furnish biphenylenes and their higher benzocyclobutadienologs, termed [N]phenylenes [2–6]. The strain inherent in the cyclobutadienoid ring of these systems has given rise to varied products by ring opening [2,5,7–9]. Of particular interest in this connection appeared the dimerization of biphenylene (**1**) to tetrabenzocyclooctatetraene (**2**), a process that, in the absence of additives, has required synthetically prohibitive high temperatures [7], but had been shown to be catalyzed by transition metals, especially Rh and Ni, although even then necessitating relatively strenuous conditions [10–13]. On the other hand, mechanistic work with Ni had established that the presumed first step of this tranformation, oxidative addition to generate a dibenzonickelole intermediate, occurred at temperatures as low as 0 °C [14], thus indicating that mild dimerization conditions might be attainable.

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* Dedicated to Professor Dr. G. Wilke on the occasion of his 65th birthday.

0022-328X/90/$03.50

Achieving such a goal would have impact on a number of research efforts, including; (1) the possible use of biphenylene-based monomers [15] for the preparation of novel, potentially conducting polymers or, along related lines, such treatment of biphenylene-bearing polymers to undergo crosslinking to similar materials [10–13], (2) the construction of novel structures of theoretical [7,16,17] or bioorganic [18,19] importance, and (3) a more general access to substituted tetrabenzocyclooctatetraenes, recently shown to exhibit interesting properties [20,21]. The following account describes the successful execution of experiments that utilize the specific catalytic power of the three title metals to assemble complex polycyclic π-systems.

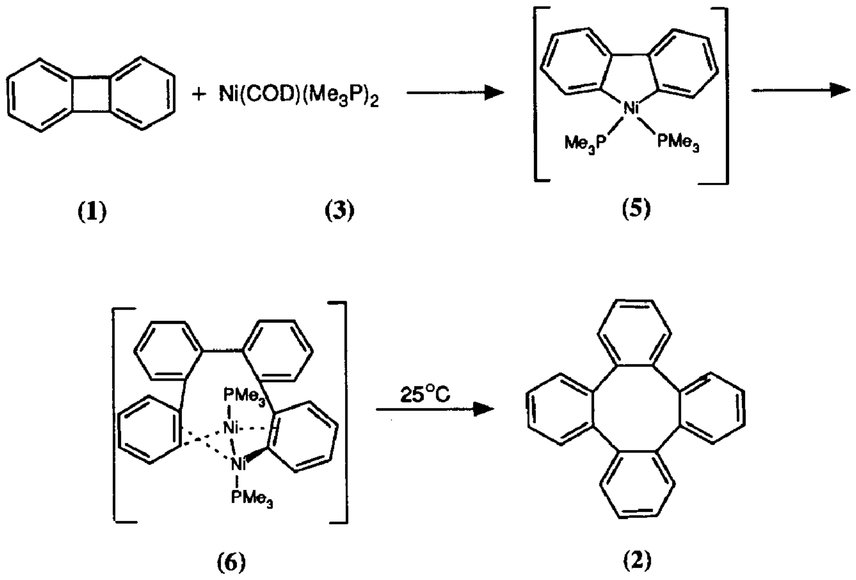
Results and discussion

To complement the results of Eisch et al. [14], the metal systems (1,5-cyclooctadiene)bis(trimethylphospine)nickel, $Ni(COD)(Me_3P)_2$ (**3**), and bis(1,5-cyclooctadiene)nickel, $Ni(COD)_2$ (**4**), were selected at potential catalysts for the prototype conversion of **1** to **2** and initial screening performed by ^1H NMR spectroscopy in THF-d_8 (Table 1).

The spectroscopic data indicate that the reaction of **1** with **3** appears to proceed by a similar mechanism (eq. 1) to the one suggested [14] when using tetrakis(triethylphosphine)nickel, although there are some quantitative differences. Thus, the triethylphosphine complex undergoes facile insertion at 0 °C to furnish a dibenzonickelole analog of **5**, followed by a rearrangement to a dimer analogous to **6** at 25 °C without the formation of **2**. In contrast, we observe very little conversion at 0 °C and at 25 °C, **2** was already the major component of the mixture. The (tentative) insertion product **5** was present in only very small amounts over the entire reaction period. Its ^1H NMR spectrum exhibited a characteristic ABCD pattern (δ 7.6 (br d), 7.4 (br t), 7.0 (br t), 6.8 (m)) for the aromatic protons. During the early stages of the reaction, low intensity signals were detected in the aromatic region with a very similar appearance to those exhibited by the triethylphosphine analog of **6** [14], making it tempting to invoke the intermediacy of **6** in eq. 1. The resonances for **2** give rise to a diagnostic AA′BB′-pattern centered at δ 7.17 ppm.

Significantly, biphenylene (**1**) was converted into **2** by **3** catalytically on raising the temperature above 70 °C. For example, a quantitative transformation was recorded with 10% catalyst at 100 °C over 3 h. Further heating decomposed the nickel complexes, the final products being **2**, free 1,5-cyclooctadiene, $Ni(PMe_3)_4$, and a small amount of an unknown compound exhibiting a doublet signal at δ 0.54 ppm (PMe_3). As expected [14], **1** was inert to $Ni(COD)_2$ (**4**), even at temperatures as high as 110 °C, more vigorous conditions generating free ligand and a black precipitate of, presumably, Ni powder, while the substrate remained intact.

The relatively mild conditions of the above experiments prompted an investigation of their scope by varying the structure of the substrates to include substituted biphenylenes. In particular, we were curious to what extent the differing steric and electronic properties of the substituents would affect reactivity. To this end, similar ^1H NMR measurements were carried out with 2,3-bis(trimethylsilyl)biphenylene (**7**), 2,3-diphenylbiphenylene (**8**), and 2,3-diethylbiphenylene (**9**). The spectroscopic profile of their conversions in the presence of **3** were all similar to that observed with **1**, the only differences being their relative reactivities (Table 1). Qualitative rate measurements indicated the latter to increase along the series **1**, **9**, **8**, and **7**.



(1)

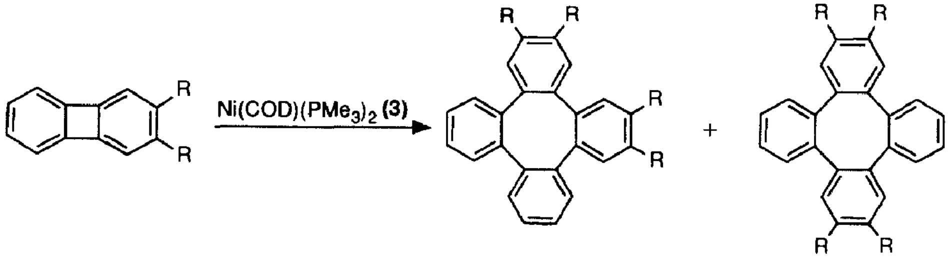
Consistent with these findings, both **8** and **9** gave the corresponding dimers even when Ni(COD)$_2$ (**4**) was employed, although the metal complex had to be present in two-fold excess to achieve reasonable reaction rates at 100 ° C. Compound **7**, on the other hand, did so under catalytic conditions (10% Ni complex). In all cases, the resulting tetrabenzocyclooctatetraenes formed as an equimolar mixture of the two possible isomers. On a preparative scale (1–10 mmole of substrate), **7**, **8**, and **9** led to the desired products (separated by column chromatography) in 86, 93, and 68% yield, respectively.

Although more complicated factors may be responsible for the observed rate differences, the previous work by Eisch et al., suggesting that the liberation of dimer from complexes of the type **6** may be rate-determining, prompts us to invoke steric activation of this intermediate by the substituent R as the rationale. Inspection of the X-ray structure of the analogous triethylphosphine derivative reveals steric interference between the phosphine substituents and the *meta*-positions on the aromatic rings [14]. The lack of regioselectivity is more difficult to explain and necessitates a precursor to substituted **6** in which such interference is absent.

With these results in hand, more complex extensions of the methodology were sought. In this vein, eq. 2 was executed starting from the symmetrical **11**, using a well-established sequence [1–6], and culminating in the novel 36π-electron polycycle **20**, containing fused cyclobutadiene, benzene, and cyclooctatetraene rings. Perhaps most noteworthy about this assembly is the ^{1}H NMR chemical shift of the internal biphenylene hydrogens at δ 6.45 ppm, quite shielded relative to the corresponding positions in tetrabenzocyclooctatetraene itself. A related, linearly biphenylene-fused monobenzocyclooctatetraene is known [22]. It is amusing to note that the construction of **20** involves 22 metal-catalyzed bond formations and two such disconnections, 20 bonds and seven rings being assembled by the presence of Pd, Co, and Ni in various steps.

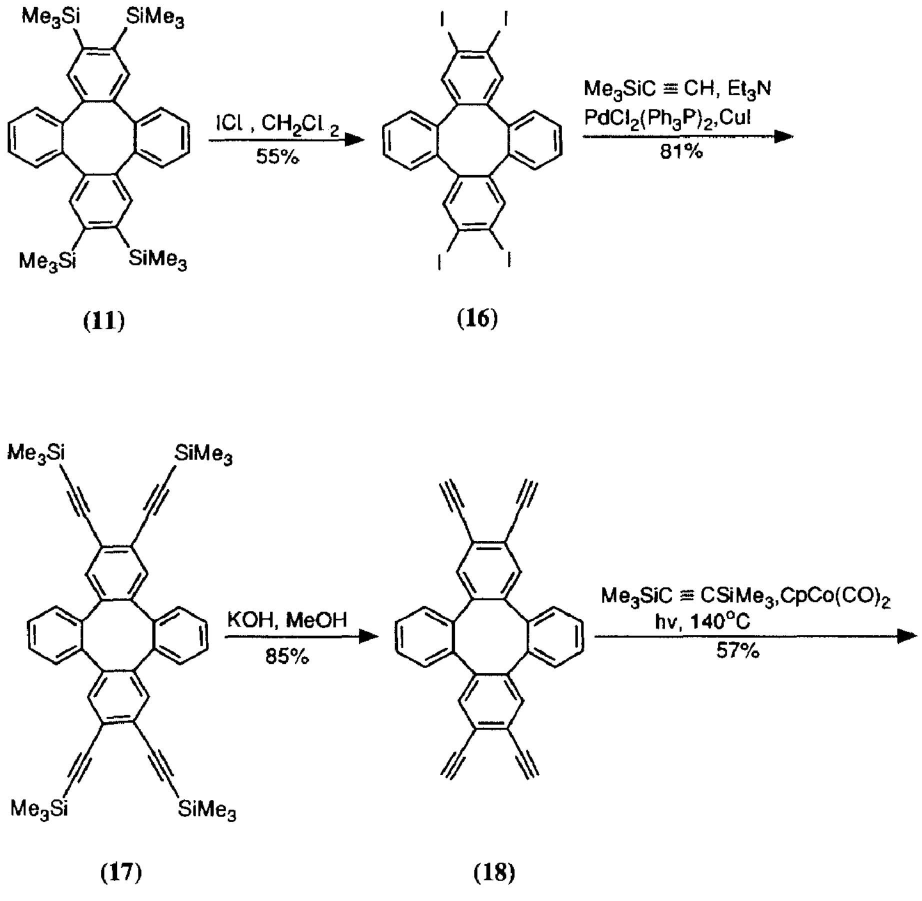
To add further variability to this strategy and to enter additional synthetic avenues, it was deemed attractive to effect the Ni-catalyzed biphenylene dimeriza-

Table 1
Qualitative ^1H NMR spectroscopic results of the reaction of **1**, **7**, **8**, and **9** and **3**

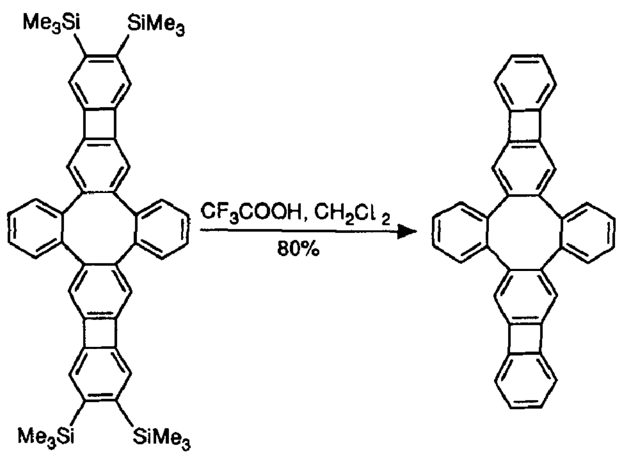


A **B** **C**

A	R	*T* (°C)	*t* (h)	% **3**	% conversion	B	C
1	H	100	3	8	50	**2**	
7	$SiMe_3$	75	4	8	100	**10**	**11**
8	Ph	100	1	20	100	**12**	**13**
9	Et	100	1	20	100	**14**	**15**



(2)



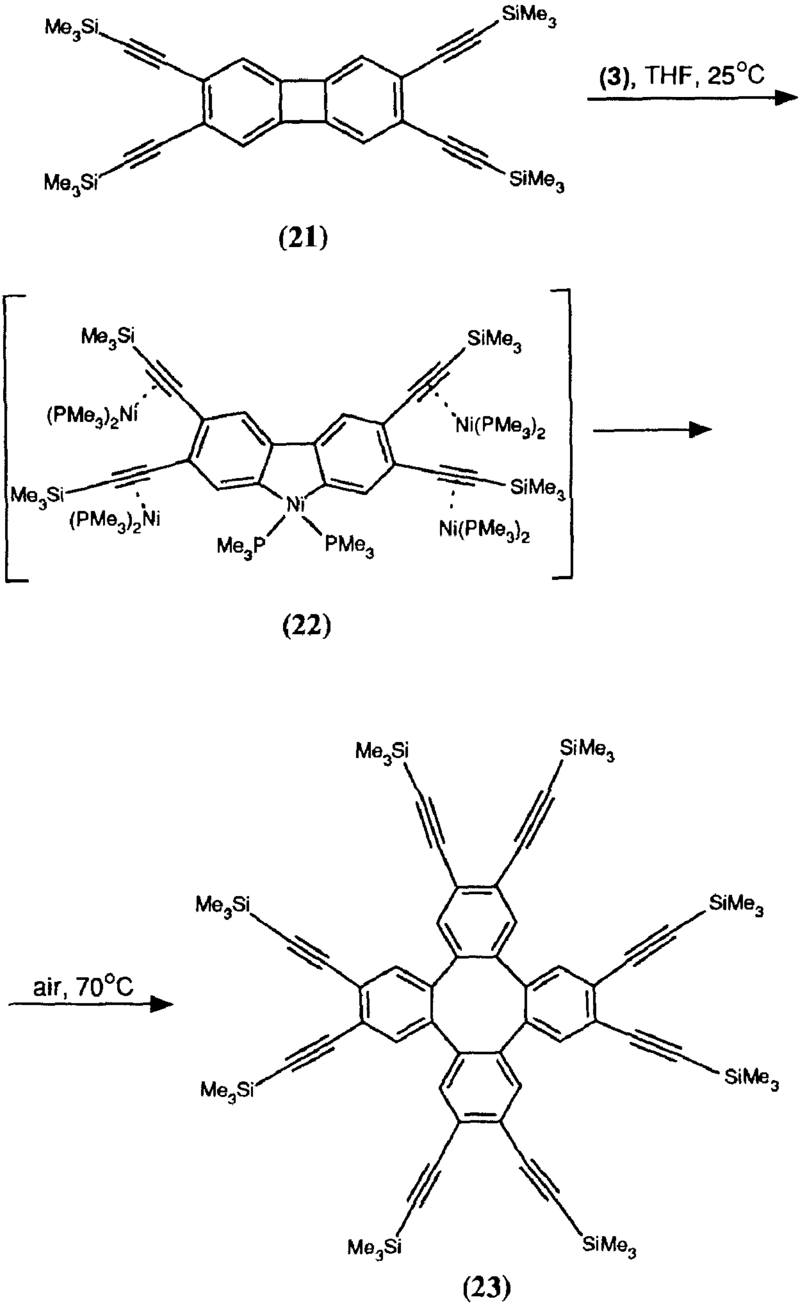
(19) **(20)**

tion step in the presence of (protected) alkynyl substituents. In a series of preliminary experiments, substrate **21** [4] was subjected to increasing quantities of **3** (eq. 3). After six equivalents had been added at 25 ° C, ^{1}H NMR spectroscopy in THF-d_8 revealed the presence of **3**, free 1,5-cyclooctadiene, Ni(PMe$_3$)$_4$, and a new compound giving rise to a remarkably simple spectrum: two equally integrating singlets in the aromatic region at δ 6.70 and 6.85 ppm (1H each), two singlet lines assigned to the trimethylsilyl hydrogens (9H each), and three absorptions for trimethylphosphine groups at δ 0.84, 1.39, and 1.44 ppm. A ^{31}P {^{1}H} spectrum consisted of two multiplets centered at δ −15.5 and −17.0 ppm. These data are consistent with the generation of **22** or a system of similar symmetry. While isolation was not attempted at this stage, it appears feasible, as solutions are stable to 60 ° C, decomposition setitng in beyond that temperature. Alkyne complexation by NiL$_2$ under these conditions is not surprising [23,24] and, in the case of **21**, appears to hinder dimerization. Interestingly, however, and boding well for future experiments, exposing solutions containing putative **22** to air at 70 ° C did furnish the desired **23**, albeit in low yield.

Experimental

General comments

Infrared spectra were recorded on a Perkin Elmer model 681 infrared spectrophotometer. ^{1}H, ^{13}C, and ^{31}P{H} NMR spectra were obtained at 300 MHz with a Nicolet model 1280 data collecting system. ^{1}H NMR chemical shifts are reported in ppm downfield from TMS, referenced to the residual proton peaks of the deuterated solvents CDCl$_3$, 7.24 ppm, and THF-d_7, 3.58 ppm. ^{13}C NMR peaks are quoted in ppm downfield from TMS, referenced to the central peaks of CDCl$_3$ at 76.9 ppm. ^{31}P{^{1}H} NMR data are referenced to external phosphoric acid. UV spectra were measured on a Hewlett–Packard 8450 A diode array spectrophotometer. Mass spectra were obtained with a Finnigan 4000 mass spectrometer and appear in the form of as m/z (rel intensity) values at 70 eV. Elemental analyses were provided by



(21)

(22)

(23)

(3)

the UC Berkeley Microanalytical Laboratory. $Ni(COD)(Me_3P)_2$ (**3**) was prepared from $Ni(COD)_2$ (**4**) by the addition of PMe_3 at −78°C [25].

2,3-Diethylbiphenylene (9)

Degassed 1,2-diethynylbenzene (250 mg, 2 mmol), 3-hexyne (600 mg, 7 mmol), and $CpCo(CO)_2$ (40 μl, 0.3 mmol) in benzene (10 ml) were added via syringe pump over 6 h to boiling benzene (25 ml) under N_2 while being irradiated with a slide projector lamp. Column chromatography (silica gel/hexane) afforded as the first fraction **9** (85 mg, 22%): off-white crystals, m.p. 54–55 °C (from EtOH/ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.67 (m, 2H, AA′), 6.55 (m, 2H, BB′), 6.47 (s, 2H), 2.44 (q, 4H, J 3 Hz), 1.13 (t, 6H, J 3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.9, 149.1, 141.4, 128.1, 118.9, 117.1, 26.4, 15.9; UV (hexane): λ_{max} (logϵ) 245 (4.37), 254 (4.63), 346 (3.46), 3.50 (3.42), 356 (3.28), 366 (3.67) nm; MS: m/z (rel. intensity) 208 (M^+, 100), 193 (68), 178 (48), 165 (12), 152 (10); HRMS calcd. for $C_{16}H_{16}$ 208.1252, found 208.1246. Anal. Found: C, 92.36; H, 7.75. $C_{16}H_{16}$ calcd.: C, 92.26; H, 7.74 %.

General procedure for the dimerization of biphenylenes with $(Me_3P)_2Ni(COD)$ (3)

In a glove box, the respective biphenylene (1 mmol) was dissolved in dry THF (20 ml) in a thick-wall glass bomb fitted with a Teflon stopcock. A solution of $(Me_3P)_2Ni(COD)$ (**3**) (0.1 mmol) in dry THF (20 ml) was added and the bomb closed tightly. The green mixture was heated for 2 h at 60 °C and another 2 h at 100 °C. The brown-red suspension was exposed to air and the precipitated Ni filtered off. The solution was concentrated and the residue subjected to column chromatography. The unsymmetrical dimer was eluted first in all cases.

Dimerization of biphenylene (1)

This reaction gave 1,2,3,4,5,6,7,8-tetrabenzocyclooctatetraene (92%): colorless crystals, m.p. 229–231° C (lit. [26] m.p. 232–233° C); MS: 304 (M^+, 100).

Dimerization of 2,3-bis(trimethylsilyl)biphenylene (7)

Treatment of **7** according to the above general procedure gave an equimolar mixture of **10** and **11** (86%), separated by column chromatography (neutral alumina, activity III, pentane) to furnish first 2,3,6,7-tetrakis(trimethylsilyl)tetrabenzo[*a*,*c*,*e*,*g*]cyclooctatetraene (**10**): colorless crystals, m.p. 307–310 °C (from EtOH/ether); ^{1}H NMR (300 MHz, $CDCl_3$); δ 7.42 (s, 2H), 7.40 (s, 2H), 7.31–7.28 (m, 4H), 7.20–7.13 (m, 4H), 0.33 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.2, 145.1, 142.2, 142.1, 140.9, 140.8, 137.1, 136.1, 130.2, 130.1, 127.6, 127.5, 2.42, 2.40; UV (hexane): λ_{max} (logϵ) 223 (4.84), 245 (4.72) nm; MS: m/z (rel. intensity) 592 (M^+, 50), 579 (16), 578 (32), 577 (63), 563 (13), 562 (20), 561 (29), 489 (10), 265 (11), 145 (11), 73 (100); HRMS calcd. for $C_{36}H_{48}Si_4$: 592.2833, found 592.2833. Anal. Found: C, 73.32; H, 8.20. $C_{36}H_{48}Si_4$ calcd.: C, 72.90; H, 8.16%. Next eluted 2,3,10,11-tetrakis(trimethylsilyl)tetrabenzo[*a,c,e,g*]cyclooctatetrane (**11**): colorless plates, m.p. 256–257 °C (from EtOH/ether); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (s, 4H), 7.27 (m, 4H, AA′), 7.12–7.11 (m, 4H, BB′), 0.35 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$): 145.1, 142.0, 141.0, 137.0, 130.2, 127.7, 2.5; UV (hexane): λ_{max} (logϵ) 223 (4.92), 240 sh (4.75) nm; MS: m/z (rel. intensity) 592 (M^+, 94), 580 (11), 579 (32), 578 (33), 577 (100), 563 (12), 562 (12), 547 (12), 546 (18), 545 (31), 490 (23), 489 (46), 473 (21), 73 (49); HRMS calcd. for $C_{36}H_{48}Si_4$: 592.2833, found 592.2813. Anal. Found: C, 73.04; H, 7.97. $C_{36}H_{48}Si_4$ calcd.: C, 72.90; H, 8.16%.

Dimerization of 2,3-diphenylbiphenylene (8)

Reaction of **8** gave **12** and **13** (1/1, 93%), separated by column chromatography (neutral alumina, activity III, hexane/CH_2Cl_2, 6/1) to give first 2,3,6,7-tetraphenyltetrabenzo[*a,c,e,g*]cyclooctatetraene (**12**): colorless powder, m.p. 313–315 °C (from CH_2Cl_2/EtOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.26 (m, 12H), 7.21–7.08

(m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.0, 141.4, 141.21, 141.16, 141.11, 140.5, 139.70, 139.68, 132.14, 132.07, 132.05, 130.2, 130.0, 128.26, 128.23, 128.14, 127.75, 127.65, 126.81, 126.79; UV (hexane): λ_{max} (logϵ) 253 (4.69) nm; MS: m/z (rel intensity) 608 (M^+, 100) 607 (7), 593 (4), 595 (6), 439 (4); Anal. Found: C, 94.63; H, 5.20. $C_{48}H_{32}$ calcd.: C, 94.70; H, 5.30%. The second compound to elute was 2,3,10,11-tetraphenyltetrabenzo[*a,c,e,g*]cyclooctatetraene (**13**): colorless powder, m.p. 328–330 °C (from EtOH/benzene); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.29 (m, 12H), 7.20–7.15 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) 141.4, 141.2, 141.1, 139.6, 132.1, 130.3, 129.9, 128.2, 127.8, 126.8; UV (hexane): λ_{max} (logϵ) 245 (4.89) n; MS: m/z (rel intenstiy) 608 (M^+, 100) 607 (7), 593 (5), 207 (4); HRMS calcd. for $C_{48}H_{32}$: 608.2504, found 608.2515; Anal. Found: C, 94.78; H, 5.28. $C_{48}H_{32}$ calcd.: C, 94.70; H, 5.30%.

Dimerization of 2,3-diethylbiphenylene (9)

Transformation of **9** gave the two isomers **14** and **15** (68%) along with 15% of starting material. Column chromatography (neutral alumina activity III, hexane/CH_2Cl_2, 99/1) resulted in the elution of first **14** contaminated with **9**. Trituration with hexane at 0 °C furnished pure 2,3,6,7-tetraethyltetrabenzo[*a,c,e,g*]cyclooctatetraene (**14**): colorless crystals, m.p. 259–260 °C (from EtOH/ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 4H), 7.14 (m, 4H), 6.94 (s, 2H), 6.92 (s, 2H), 2.59 (m, 8H), 1.19 (m, 12H); UV (hexane) λ_{max} (logϵ) large end absorption, 235 sh (4.45) nm; MS m/z (rel. intensity) 416 (M^+, 100), 402 (11), 401 (32), 387 (16), 343 (12), 329 (12), 327 (10); HRMS calcd. for $C_{32}H_{32}$ 416.2504, found 416.2497. Anal. Found C, 92.06; H, 7.83. $C_{32}H_{32}$ calcd.: C, 92.26; H, 7.74%. The next compound off the column was 2,3,10,11-tetraethyltetrabenzo[*a,c,e,g*]cyclooctatetraene (**15**): colorless crystals, m.p. 219–221 °C (from EtOH/ether); ^{1}H NMR (MHz, $CDCl_3$): δ 7.22 (m, 4H, AA′), 7.13 (m, 4H, BB′), 6.94 (s, 4H), 2.60 (m, 8H), 1.20 (t, 12H, J 3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$); 142.2, 140.7, 139.5, 129.8, 129.3, 127.2, 25.4, 15.2; UV (hexane): λ_{max} (logϵ) large end absorption, 235 sh (4.37) nm; MS: m/z (rel intensity) 416 (M^+, 100), 402 (13), 401 (36), 387 (21), 343 (13), 293 (13), 328 (10), 327 (10); HRMS calcd. for $C_{32}H_{32}$ 416.2504, found 416.2500. Anal. Found C, 92.13; H, 7.86. $C_{32}H_{32}$ calcd.: C, 92.26; H, 7.74%.

2,3,10,11-Tetraiodotetrabenzo[a,c,e,g]cyclooctatetraene (16)

The silylated derivative **11** (200 mg, 0.34 mmol) was dissolved in CH_2Cl_2 (30 ml) and ICl (350 mg, 1.8 mmol) in CH_2Cl_2 (10 ml) added dropwise. A white precipitate appeared after 10 min, removed by filtration after stirring the mixture for an additional h at 23 °C. The filtrate was subjected to aqueous work-up and concentrated to a volume of 5 ml resulting in a second crop of solid material. The combined solids were washed with small amounts of CH_2Cl_2 to result in **16** (160 mg, 55%): colorless powder, m.p. 330 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (s, 4H), 7.27 (m, 4H, AA′), 7.08 (m, 4H, BB′); MS m/z (rel intensity) 808 (M^+, 100), 554 (30), 301 (25), 300 (94), 299 (29), 298 (55), 217 (13), 150 (28), 149 (37).

2,3,10,11-Tetrakis[(trimethylsilyl)ethynyl]tetrabenzo[a,c,e,g]cyclooctatetraene (17) and 2,3,10,11-tetraethynyltetrabenzo[a,c,e,g]cyclooctatetraene (18)

Tetraiodo compound **16** (50 mg, 0.06 mmol) was suspended in a mixture of piperidine (30 ml) to which were added triethylamine (30 ml) and $PdCl_2(Ph_3P)_2$ (20 mg, 0.03 mmol) and CuI (5 mg, 0.025 mmol). After degassing with argon at 0 °C, trimethylsilylacetylene (0.3 ml, 2.2 mmol) was injected by syringe. The suspension was stirred at 23 °C for 24 h and then heated to reflux for 2 h. Acidic aqueous work-up, followed by column chromatography (silica gel, hexane/CH_2Cl_2 4/1) gave **17** (35 mg, 81%): off-white crystals, m.p. 320 °C dec (from hexane/ether), ^1H NMR (300 MHz, $CDCl_3$): δ 7.24 (m, 4H, AA′), 7.22 (s, 4H), 7.09 (m, 4H, BB′), 0.22 (s, 36H); MS: m/z (rel. intensity) 688 (M^+, 45), 73 (100); HRMS calcd. for $C_{44}H_{48}Si_4$ 688.2833, found 688.2836. Anal. Found C, 77.03; H, 7.02. $C_{44}H_{48}Si_4$ calcd.: C, 76.68; H, 7.02%.

Crude **17** (35 mg) was desilylated with KOH/MeOH in ether to furnish 2,3,10,11-tetraethynyltetrabenzo[*a,c,e,g*]cyclooctatetraene (**18**) (17 mg, 85%): colorless plates, subjected immediately to the subsequent cyclization.

Cobalt-catalyzed cyclization to 19

Alkyne **18** (17 mg, 0.04 mmol) and $CoCp(CO)_2$ (50 μl, 0.4 mmol) in THF (20 ml) were degassed and added over 8 h to boiling bis(trimethylsilyl)acetylene while being irradiated with a slide projector lamp (25 ml). After an additional 2 h, the volatiles were removed by vacuum transfer and the residue subjected to column chromatography (silica gel, hexane/CH_2Cl_2, 6/1) to result in **19** (17 mg, 57%): pale yellow crystals, m.p. 330 °C (from EtOH/ether); ^1H NMR (300 MHz, $CDCl_3$); δ 7.18 (m, 4H, AA′), 7.08 (m, 4H, BB′), 6.90 (s, 4H), 6.45 (s, 4H), 0.28 (s, 36H); ^{13}C NMR (75 MHz, $CDCl_3$); δ 151.5, 150.1, 148.3, 141.8, 141.0, 128.5, 127.5, 123.6, 118.9, 2.5; UV (hexane); λ_{max} (logϵ) 264 (5.21), 279 (5.18), 355 (4.33), 374 (4.51) nm; MS; m/z (rel intensity) 740 (M^+, 65), 129 (12), 73 (100); HRMS calcd. for $C_{48}H_{52}Si_4$ 740.3146, found 740.3151. Anal. Found C, 77.78; H, 7.37. $C_{48}H_{52}Si_4$ calcd.: C, 77.77; H, 7.07%.

1,2,5,6-Bis(biphenyleno[b])-3,4,7,8-dibenzocyclooctatetraene (20)

Polycycle **19** (10 mg, 0.014 mmol) was dissolved in CH_2Cl_2 (10 ml) and CF_3COOH (1 ml) added. After 2 h at 23 °C and basic work-up, the residue was filtered through alumina (neutral, activity III, hexane/CH_2Cl_2, 3/1) to give **20** (5 mg, 80%): off-white crystals, m.p. 330 °C (from EtOH/EtOEt); ^1H NMR (300 MHz, $CDCl_3$): δ 7.18 (m, 4H, AA′), 7.08 (m, 4H, BB′), 6.70 (m, 4H, C,C′), 6.59 (m, 4H, D,D′), 6.45 (s, 4H); UV (hexane): λ_{max} (logϵ) 265 (4.46), 267 (4.44), 348 (3.65), 369 (3.82) nm; MS m/z (rel. intensity) 452 (M^+, 100), 451 (25), 450 (44), 449 (15), 448 (19), 226 (13), 225 (26), 224 (21); HRMS calcd for $C_{36}H_{20}$ 452.1565, found 452.1573.

Reaction of 2,3,6,7-tetrakis[(trimethylsilyl)ethynyl]biphenylene (21) with Ni(COD)$(Me_3P)_2$ (3)

Alkyne **21** (110 mg, 0.20 mmol) was dissolved in THF (20 ml) and **3** (400 mg, 1.25 mmol) in THF (20 ml) added in a glove box. The initially green solution was heated to 70 °C for 24 h, whereupon it turned red-brown. Exposure to air for 24 h produced a green precipitate which was removed by filtration. Addition of hexane resulted in the appearance of white needles of $Ni(Me_3P)_4$ (100 mg). The filtrate was chromatographed on a column (silica gel, hexane/CH_2Cl_2, 19/1) to provide 2,3,6,7,10,11,14,15-octakis[(trimethylsilyl)ethynyl]tetrabenzo[*a,c,e,g*]cyclooctatetraene (**23**) (4 mg, 3.5%): pale yellow crystals, m.p. 293–295 °C (from EtOH); ^1H

NMR (300 MHz, $CDCl_3$) δ 7.18 (s, 8H), 0.22 (s, 72H); UV (hexane) λ_{max} (logϵ): 254 (4.52), 272 (4.55), 285 (4.56) nm; MS: m/z (rel. intensity) 1072 (M^+, 30), 309 (30), 307 (17), 207 (11), 83 (11), 73 (100); HRMS calcd. for $C_{64}H_{80}Si_8$ 1072.4414, found 1072.4454.

Acknowledgment

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy (Contract No. DE-AC03-76 SF 00098). H.S. was the recipient of an Otto-Hahn fellowship and a Max-Planck Institute of Coal Research (Mülheim) fellowship (1986–1987). S.S. acknowledges a sabbatical leave fellowship (1986–1987) from the University of Thessaloniki, Greece.

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