An Alkyne Metathesis-Based Route to ortho-Dehydrobenzannulenes

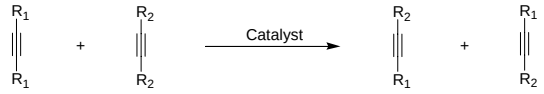
Ognjen Š. Miljanić, K. Peter C. Vollhardt,* Glenn D. Whitener

Center for New Directions in Organic Synthesis, Department of Chemistry, University of California at Berkeley, and the Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-1460, USA
Fax: ++1 510 643 5208; E-mail: kpcv@uclink.berkeley.edu
Received

Abstract: An application of alkyne metathesis to 1,2-di(prop-1-ynyl)arenes, producing dehydrobenzannulenes, is described. An efficient method for selective Sonogashira couplings of bromoiodoarenes under conditions of microwave irradiation is also reported.

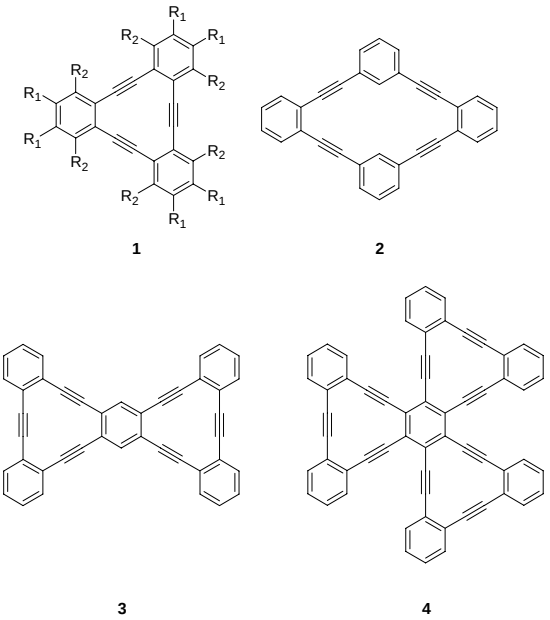
Keywords: alkyne metathesis, 1,2-di(prop-1-ynyl)arenes, dehydrobenzannulenes, microwave irradiation, Sonogashira coupling

Alkyne metathesis (Scheme 1) has not been used widely in organic syntheses until recently, even though the first reports of its homogeneous, catalytic version date back to as early as 1974 with results of Mortreux et al.[1] A resurgence of the field occurred in the 1990s, based on the work by the groups of Bunz[2] and Fürstner,[3] which includes examples of ring closures, one notably leading to a meta-dehydrobenz-annulene system.[2e]



Scheme 1

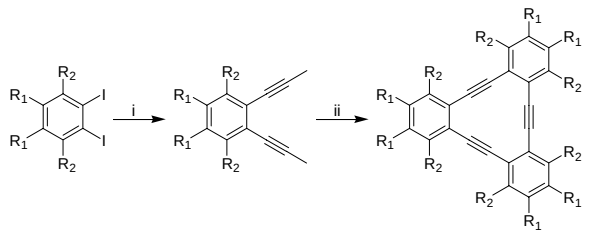
We report here the investigation of the potential of alkyne metathesis in the construction of dehydrobenzannulenes (Scheme 2).[4] This class of molecules is interesting in several respects – it provides attractive ligands to transition metal complexes,[5] models for subunits of graphyne, a novel allotrope of carbon,[6] precursors to ordered carbon nanostructures,[7] scaffolds for molecules on which to study supramolecular phenomena,[8] and materials with interesting photophysical properties.[9] Our need for an efficient synthetic entry into substituted derivatives stems from our quest for the first members of the circular phenylenes, such as antikekulene.[10] As representative targets, we directed our initial efforts to examples of tribenzocyclyne **1**, as in Scheme 3, and subsequently the more challenging tetrabenzocyclyne **2**, as well as the fused systems **3** and **4**. The parent **1a** and its derivatives have received considerable attention as synthetic targets,[4] whereas a substituted version of **2**[8f] and parent **3**[6c] have been prepared for the first time only recently, the latter two through relatively long sequences.



Scheme 2

Following the lead of the literature,[2,3] we chose 1-propynylarenes as the starting materials to be subjected to ring closure, because the second alkyne to be formed on metathesis, 2-butyne, is removed readily from the reaction mixture. The requisite diynes **6** were accessed by Sonogashira reaction of appropriately substituted iodoarenes (Scheme 3, Table 1).[11] The respective couplings of otherwise unsubstituted and of alkyl- or alkoxy-substituted iodoarenes proceeded cleanly, in good to excellent yields (entries 1-4, 7-9, 11 in Table 1).[12]

To retain the potential of subsequent introduction of further alkyne substituents,[10] tribenzocyclynes bearing bromine substituents were also of interest. Their preparation required the selective alkynylation of bromoiodoarenes (entries 5,6,10 in Table 1). While such is often achievable at room temperature,[13] we noticed significant overalkynylation in systems **5e**, **f**, and **j**. Monitoring the course of the reaction to the point of optimal conversion proved difficult, because of the use of closed systems under the positive pressure of propyne.



Scheme 3 Reagents and conditions: (i) propyne, $PdCl_2(PPh_3)_2$, CuI, NEt_3 (or NEt_3/DMF), Δ; (ii) $(Me_3CO)_3W{\equiv}CCMe_3$, toluene, 80 °C.

We therefore turned our attention to microwave-assisted Sonogashira couplings[14,15] executed in a Smith Synthesizer. Application of this technique allowed the dipropynylation of three isomers of dibromodiiodobenzene at 100-110 °C (entries 5,6,10 in Table 1) with excellent selectivity in less than 20 minutes.[16] Monitoring the change in pressure during the course of the reaction (Figure 1) provided a convenient gauge of its progress. The results of all propynylation reactions, both "classical" and microwave-assisted, are summarized in Table 1.

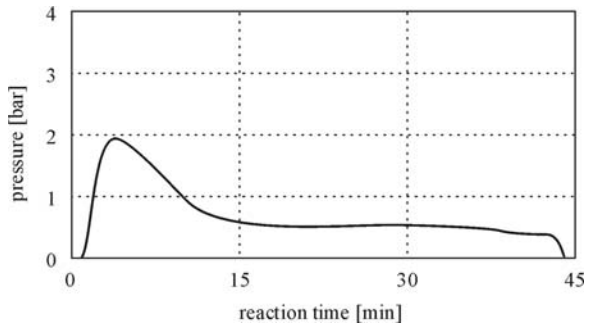
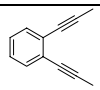
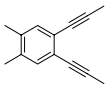
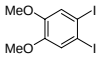
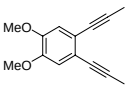
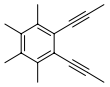
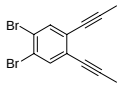
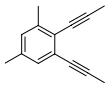
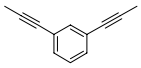
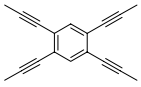
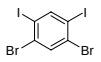
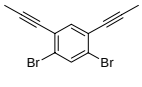
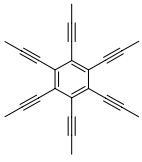


Figure 1 Pressure changes as a function of reaction time in Pd-catalyzed propynylations of **5** in a Smith Synthesizer. There is an initial pressure increase, as heating commences. The reaction starts at t ~ 5 min, causing the propyne pressure to drop, and ends at t ~ 15 min). The heater was turned off at t ~ 44 min.

With this route to *o*-dipropynylated arenes in hand, the feasibility of alkyne metathesis to tribenzocyclynes could be tested. Three catalytic systems are presently most popular: a) a mixture of $Mo(CO)_6$ and *p*-chlorophenol, typically used in *o*-dichlorobenzene at high temperatures (130-150 °C),[2,3b,3e] b) the better defined $(Me_3CO)_3W{\equiv}CCMe_3$ which is active at lower temperatures (80 °C in, e.g., toluene),[3b,d,e,g] and (c) a less-defined alternative based on Mo amido complexes.[3c,d,f] Due to the simplicity of a), this catalyst was used in our first experiments with **6a** as the substrate. Under a variety of conditions – performing the reaction at decreased pressure, under a constant stream of nitrogen (both of which served to remove 2-butyne formed), or with variable catalyst loading – not even trace amounts of **1a**

Table 1 Propynylation Reactions

Entry	Iodoarene[a]	Product	Conditions/Yield
1	 **5a**	 **6a**	25 °C / 22 h 95%
2	 **5b**	 **6b**	25 °C / 26 h 57%
3	 **5c**	 **6c**	25 °C / 48 h 81%
4	 **5d**	 **6d**	25 °C / 96 h 91%
5	 **5e**	 **6e**	110 °C / 3.75 min (microwave) 71%
6	 **5f**	 **6f**	110 °C / 20 min (microwave) 60%
7	 **5g**	 **6g**	25 °C / 44 h 76%
8	 **5h**	 **6h**	25 °C / 22 h 93%
9	 **5i**	 **6i**	90 °C / 36 h 77%
10	 **5j**	 **6j**	100 °C / 2 min (microwave) 64%
11[b]	 **5k**	 **6k**	90 °C / 60 h 28%

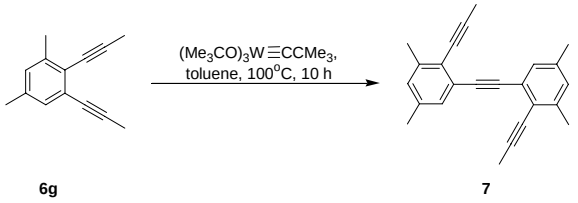
[a] Ref. 11. [b] Penta(prop-1-ynyl)benzene was obtained as a side product in 32% yield.

(GC/MS) were detectable. The only occasional product was a metathesis dimer, 1,1'-(1,2-ethynediyl)bis[2-(prop-1-ynyl)]benzene, generated in approximately 2% yield (by GC/MS analysis).

Gratifyingly, turning to catalyst b), the reaction proceeded cleanly to give **1a** in 54% yield as the only isolable product (entry 1 in Table 2). This preparation is superior in terms of yield and simplicity compared to other recently published approaches.[5,6c,17]

Encouraged by this result, scope and limitations were investigated, summarized in Table 2. A rather simple trend was observed – sterically more crowded bisorthosubstituted precursors did not undergo cyclization (entries 4,6 in Table 2), whereas bismetasubstituted ones did (entries 2,3,5 in Table 2). This outcome was not particularly dependent on electronic effects – both electron withdrawing (Br) and electron donating (OMe and Me) substituents were tolerated as long as they were located in meta positions; interestingly, substrates with resonance donors as substituents (Br and OMe) reacted more slowly (~2-4 times) than their unsubstituted or alkylsubstituted counterparts.

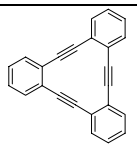
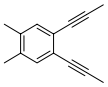
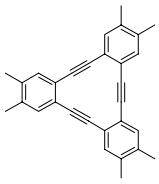
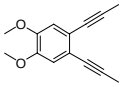
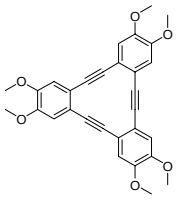
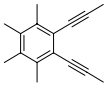
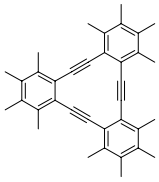
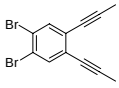
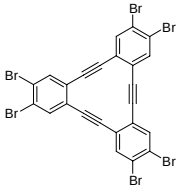
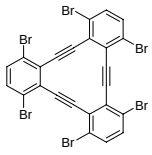
To provide an intramolecular test for the proposed steric trend, substrate **6g** was investigated, in which the two alkyne units are differentiated by bearing an ortho- and a meta-methyl group, respectively. It should react only once, to give the product of metathesis of the sterically less crowded triple bond. Indeed, the system produced solely **7** in 55% yield (Scheme 4).



Scheme 4

While the yields of the products depicted in Table 2 are modest, the simplicity and straightforward execution of the method would seem to make it that of choice for the rapid synthesis of specific derivatives, in particular when such are endowed with interesting novel topologies. As a consequence, and to explore the possibility of ring closure cross metathesis, we targeted the parent hydrocarbons **2**-**4**. To our delight, equimolar proportions of **6a** and **6h** converted directly to the new tetrabenzocyclyne **2** in 19% yield![19] Even more impressive was the finding that **6a** and **6i** (4:1) underwent six fold metathesis to furnish **3** in 6% yield. This compound, as previously reported,[10] was extremely insoluble in common organic solvents, probably to the detriment of the isolated yield. Finally, not unexpectedly in light of the results described above, hexapropynylbenzene **6k** was inert to metathesis with **6a** (on route to **4**) and even simple propynylbenzenes.

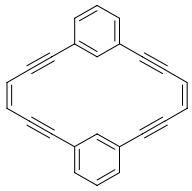
Table 2 Tribenzocyclynes by Alkyne Metatheses Catalyzed by $(Me_3CO)_3W{\equiv}CCMe_3$[a]

Entry	Starting material	Cyclyne	Conditions/ Yield
1[b]	 **6a**	 **1a**	80 °C, 8 h 20 mol% cat. 54%
2[c]	 **6b**	 **1b**	80 °C, 24 h 20 mol% cat. 27%
3[d]	 **6c**	 **1c**	80 °C, 140 h 20 mol% cat. 28%
4	 **6d**	 **1d**	80 °C, 96 h 20 mol% cat. no reaction
5	 **6e**	 **1e**	80 °C, 120 h 20 mol% cat. 12%
6	 **6f**	 **1f**	80 °C, 96 h 20 mol% cat. no reaction

[a] Ref. 19. [b] Ref. 20. [c] Ref. 21. [d] Ref. 4.

Cyclyne **2** constitutes the parent of a di-*tert*-butyl derivative synthesized as part of a series of phenylacetylene macrocycles adorned with solubilizing substituents.[8f] It is,

nonetheless, quite soluble in common organic solvents, exhibiting strong, green fluorescence. Its ^{1}H-NMR spectrum contains a characteristic peak due to the proton inside the macrocycle at δ = 8.05 ppm ($CDCl_3$). The less benzofused system **8** shows the analogous absorption at δ 7.82 ppm ($CDCl_3$),[22] possibly (but not necessarily) a reflection of increased dehydro[18]annulenoid diatropism. The aromaticity of cyclynes as measured by the ring current criterion is a topic of renewed current scrutiny.[23]



8

The X-ray crystal structure of **2**,[24] shown in Figure 2, is only slightly distorted from ideal planarity – the dihedral angle between the planes of the respective meta- and ortho-fused rings is 7.1°. The intraannular hydrogen-hydrogen distance is 2.29 Å; in comparison, in **8** this distance is 2.57 Å – a possible indication of the greater flexibility of the system.[22] The compound crystallizes in the *C2/c* space group, with four molecules of **2** in the unit cell.

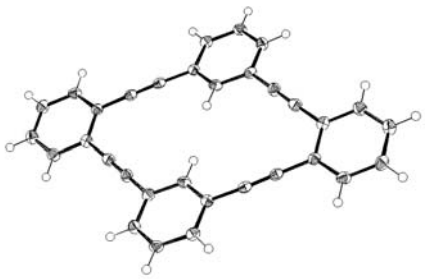


Figure 2 X-ray crystal structure of **2**

While **3** is known,[6c] its ^{1}H-NMR spectrum could not be obtained due to seemingly poor solubility. We have found **3** sufficiently soluble in $CDCl_3$ to allow for such a measurement. The molecule gives rise to an AA'BB' multiplet for the peripheral aromatic hydrogens at δ = 7.19 and 7.44 ppm, instead of the expected ABCD pattern, reflecting local symmetry, and a singlet at δ = 7.34 ppm for the protons on the central benzene ring. These appear shielded relative to the corresponding ring hydrogens in 1,2,4,5-tetraethynylbenzene, which resonate at δ 7.63 ppm ($CDCl_3$) – an indication of the effect of the two neighboring paratropic cyclyne moieties.[23]

In summary, we have shown that alkyne metathesis can be a potentially useful method for the construction of benzocyclynes. Although as yet the yields are only moderate, for certain targets, this drawback is compensated for by a synthetic approach that is short and straightforward. Current work is aimed at improving catalyst efficiency to render this strategy more broadly applicable.

Acknowledgements

This work was facilitated by the National Science Foundation (CHE-0071887) and the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy, under Contract DE-AC03-76SF00098. The Center for New Directions in Organic Synthesis is supported by Bristol-Myers Squibb as a Sponsoring Member and Novartis as a Supporting Member. We would like to thank Prof. Alois Fürstner and Mr. Günter Seidel (Max-Planck-Institut für Kohlenforschung, Mülheim/Ruhr, Germany) for catalyzing the initiation of this effort with a generous sample of $(Me_3CO)_3W{\equiv}CCMe_3$. We are also indebted to Personal Chemistry, Inc. for providing us with access to a Smith Synthesizer™, Prof. John Anthony (University of Kentucky) for communicating the experimental route to 1,4-dibromo-2,3-diiodobenzene, Prof. Sethuraman Sankamaran (Indian Institute of Technology, Madras) for helpful correspondence, and Prof. Uwe Bunz (University of South Carolina) for stimulating advice.

References

(1) Mortreux, A.; Blanchard, M. *J. Chem. Soc, Chem. Comm.* **1974**, 786.

(2) For recent references, see: (a) Brizius, G.; Bunz, U. H. F. *Org. Lett.* **2002**, *4*, 2829. (b) Brizius, G.; Kroth, S.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 5317. For reviews, see: (c) Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998. (d) Bunz, U. H. F.; Kloppenburg, L. *Angew. Chem. Int. Ed.* **1999**, *38*, 478. For a pertinent example, see: (e) Ge, P.-H.; Fu, W.; Herrmann, W. A.; Herdtweck, E.; Campana, C.; Adams, R. A.; Bunz, U. H. F. *Angew. Chem. Int. Ed.* **2000**, *39*, 3607.

(3) For selected references, see: (a) Fürstner, A.; Mathes, C.; Grela, K. *Chem. Commun.* **2002**, 1057. (b) Fürstner, A.; Stelzer, F.; Rumbo, A.; Krause, H. *Chem. Eur. J.* **2002**, *8*, 1856. (c) Fürstner, A.; Mathes, C.; Lehmann, C. W. *Chem. Eur. J.* **2001**, *7*, 5299. (d) Fürstner, A.; Grela, K.; Mathes, C.; Lehmann, C. W. *J. Am. Chem. Soc.* **2000**, *122*, 11799. (e) Fürstner, A.; Guth, O.; Rumbo, A.; Seidel, G. *J. Am. Chem. Soc.* **1999**, *121*, 11108. (f) Fürstner, A.; Mathes, C.; Lehmann, C. W. *J. Am. Chem. Soc.* **1999**, *121*, 9453. (g) Fürstner, A.; Seidel, G. *Angew. Chem. Int. Ed.* **1998**, *37*, 1734.

(4) For reviews, see: (a) Haley, M. M. *Synlett* **1998**, 557. (b) Haley, M. M.; Pak, J. J.; Brand, S. C. *Top. Curr. Chem.* **1999**, *202*, 81. (c) Haley, M. M.; Wan, W. B. In *Advances in Strained and Interesting Organic Molecules*, Vol. 8; Halton, B., Ed.; JAI Press: New York, **2000**, 1. (d) Kennedy, R. D.; Lloyd, D.; McNab, H. *J. Chem. Soc., Perkin Trans. 1* **2002**, 1601. (d) Balaban, A.T.; Banciu, M.; Ciorba, V. *Annulenes,*

Benzo-, Hetero-, Homo-Derivatives and Their Valence Isomers; CRC Press: Boca Raton, 1987; Vol. 2, p. 146.

(5) Youngs, W. J.; Tessier, C. A.; Bradshaw, J. D. *Chem. Rev.* **1999**, *99*, 3153.

(6) For a review, see: (a) Bunz, U. H. F.; Rubin, Y.; Tobe, Y. *Chem. Soc. Rev.* **1999**, *28*, 107. See also, inter alia: (b) Narita, N.; Nagai, S.; Suzuki, S. *Phys. Rev. B* **2002**, *64*, 245408. (c) Kehoe, J. M.; Kiley, J. H.; English, J. J.; Johnson, C. A.; Petersen, R. C.; Haley, M. M. *Org. Lett.* **2000**, *2*, 969. (d) Grima, J. N.; Evans, K. E. *Chem. Commun.* **2000**, 1531.

(7) (a) Boese, R.; Matzger, A. J.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1997**, *119,* 2052. (b) Dosa, P. I.; Erben, C.; Iyer, V. S.; Vollhardt, K. P. C.; Wasser, I. M. *J. Am. Chem. Soc.* **1999**, *121*, 10430.

(8) For selected recent references, see: (a) Pak, J. J.; Weakley, T. J. R.; Haley, M. M.; Lau, D. Y. K.; Stoddart, J. F. *Synthesis* **2002**, 1256. (b) Tobe, Y.; Utsumi, N.; Kawabata, K.; Nagano, A.; Adachi, K.; Araki, S.; Sonoda, M.; Hirose, K.; Naemura, K. *J. Am. Chem. Soc.* **2002**, *124*, 5350. (b) Hosokawa, Y.; Kawase, T.; Oda, M. *Chem. Commun.* **2001**, 1948. (c) Nakamura, K.; Okubo, H.; Yamaguchi, M. *Org. Lett.* **2001**, *3*, 1097. (d) Höger, S.; Enkelmann, V.; Bonrad, K.; Tschierske, C. *Angew. Chem. Int. Ed.* **2000**, *39*, 2268. See also: (e) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402. (f) Zhang, J.; Pesak, D. J.; Ludwick, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4227. (g) Pickholz, M.; Stafström, S. *Chem. Phys.* **2001**, *270*, 245.

(9) See, inter alia: (a) Sarkar, A.; Pak, J. J.; Rayfield, G. W.; Haley, M. M. *J. Mater. Chem.* **2001**, *11*, 2943. (b) Wan, W. B.; Haley, M. M. *J. Org. Chem.* **2001**, *66*, 3893.

(10) Eickmeier, C.; Junga, H.; Matzger, A. J.; Scherhag, F.; Shim, M.; Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2103.

(11) Most of the starting iodoarenes are either commercially available (**5a**, **5h**, **5k**) or have been described previously: e.g., **5b, 5d**: Kryska, A.; Skulski, L. *J. Chem. Res.(S)* **1999**, 590; **5c**: Lacour, J.; Monchaud, D.; Bernardinelli, G.; Favarger, F. *Org. Lett.* **2001**, *3,* 1407; **5g**: Nakayama, J.; Sakai, A.; Hoshino, M. *J. Org. Chem.* **1984**, *49*, 5084; **5i**: Mattern, D. L. *J. Org. Chem.* **1983**, *48*, 4772; **5j**: Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578.
1,2-Dibromo-4,5-diiodobenzene (**5e**) was prepared using the general procedure described for **5j**. **5e**: white needles (33%), mp 173-175 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 142.5, 125.4, 106.9. MS (EI, 70 eV): *m*/*z* (%) 488 (M^+, 100), 361 (32), 234 (17), 153 (8), 74 (20). IR (CS_2): $\tilde{\nu}$ = 2925, 1408, 1282, 1005, 877 cm^{-1}. HRMS: Calcd for $C_6H_2Br_2I_2$: 487.6592. Found 487.6596. Anal. Calcd for $C_6H_2Br_2I_2$: C, 14.78; H, 0.41. Found C, 14.55; H, 0.43.
1,4-Dibromo-2,3-diiodobenzene (**5f**): The first two steps followed the general procedure in: Garden, S. J.; Torres, J. C.; Ferreira, A. A.; Silva, R. B.; Pinto, A. C. *Tetrahedron Lett*. **1997**, *38*, 1501. Chloral hydrate (9.93 g, 60.0 mmol), 2,5-dibromoaniline (12.6 g, 50.0 mmol), hydroxylamine hydrochloride (5.21 g, 75.0 mmol), and sodium sulfate (60.0 g) were suspended in a mixture of water (300 mL) and ethanol (300 mL). The mixture was stirred and kept at reflux for 12 h. It was then concentrated by evaporation of the ethanol and poured onto crushed ice, which caused precipitation of a white solid. After 5 h at 0 °C, the suspension was filtered, and the crystals were air dried to yield 13.5 g (84%) of crude 2,5-dibromoisonitroso-acetanilide. This amount was then cyclized by heating at 100 °C in 86% sulfuric acid for 15 min. The resulting dark red suspension was poured onto crushed ice to yield 5.98 g (47 %) of 3,6-dibromoisatine as bright orange crystals, which were subsequently subjected to basic hydrolysis in aqueous hydrogen peroxide (Lisowski, V.; Robba, M.; Rault, S. *J. Org. Chem.* **2000**, *65*, 4193) to yield 2.72 g (47%) of off-white crystals of 3,6-dibromoanthranilic acid. Finally, 3,6-dibromoanthranilic acid was converted to 1,4-dibromo-2,3-diiodobenzene by employing the aprotic diazotization procedure in: Nakayama, J.; Sakai, A., Hoshino, M. *J. Org. Chem.* **1984**, *49*, 5084. After column chromatography (hexanes) the product was obtained as white crystals, 2.61 g (58%), mp 97-99 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 132.8, 127.8, 117.4. MS (EI, 70 eV): *m*/*z* (%) 488 (M^+, 100), 361 (29), 234 (21), 153 (18), 74 (24). IR ($CHCl_3$): $\tilde{\nu}$ = 2920, 1396, 1150, 1002, 810 cm^{-1}. HRMS: Calcd for $C_6H_2Br_2I_2$: 487.6592. Found 487.6596. Anal. Calcd for $C_6H_2Br_2I_2$: C, 14.78; H, 0.41. Found C, 14.74; H, 0.04.

(12) General procedure for propynylations: To a 150 mL Schlenk flask, equipped with a Teflon-coated magnetic stirring bar, were added the diiodoarene (1.67 mmol), $PdCl_2(PPh_3)_2$ (177 mg, 0.25 mmol), CuI (32 mg, 0.17 mmol), and triethylamine (7.50 mL). The flask was then evacuated and filled with propyne gas up to 1.5 atm (approx. 10 mmol, 3 eq) of pressure. Depending on the system, the reaction mixture was stirred for 22-96 h, at either room or elevated temperatures (Table 1). The reaction mixture was then diluted with ether, washed with two portions of aq. NH_4Cl, and dried over $MgSO_4$. Solvent was removed in vacuo and the resulting crude product purified by Kugelrohr distillation, sublimation, or chromatography.

(13) (a) Sonogashira, K. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: New York, **1998**, Chapter 5. (b) Sonogashira, K. In *Comprehensive Organic Synthesis*, Vol. 3; Trost, B. M., Ed.; Pergamon: New York, **1991**, Chapter 2.4.

(14) A somewhat related application of microwaves in Sonogashira reactions is described in: Erdelyi, M.; Gogoll, A. *J. Org. Chem.* **2001**, *66*, 4165.

(15) Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* **2001**, *57*, 9225.

(16) General procedure for microwave-assisted propynylations: A heavy-walled Smith process vial was charged with a magnetic stirring bar, triethylamine (0.9 mL), DMF (0.1 mL), $PdCl_2(PPh_3)_2$ (19.6 mg, 0.028 mmol), CuI (5.4 mg, 0.028 mmol), and the dibromodiiodobenzene (0.113 mmol). The vial was sealed, evacuated, and filled with propyne through a Teflon septum up to 2.5 atm pressure. It was then irradiated in a Smith Synthesizer single-mode microwave cavity, producing continuous radiation at 2450 MHz. The resulting solution was immediately filtered through a short plug of silica gel (hexanes/ethyl acetate) to remove the catalyst and the crude product further purified by column chromatography on silica gel (hexanes).

(17) (a) Iyoda, M.; Vorasingha, A.; Kuwatani, Y.; Yoshida, M. *Tetrahedron Lett.* **1998**, *39*, 4701. (b) Huynh, C.; Linstrumelle, G. *Tetrahedron* **1988**, *44*, 6337.

(18) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; Chapter 9, University Science Books: Mill Valley, **1987**.

(19) General procedure for $(Me_3CO)_3W{\equiv}CCMe_3$–mediated alkyne metathesis: A 25 mL Schlenk flask was charged, under the atmosphere of nitrogen, with the respective propynylated arene (0.20-0.35 mmol), $(Me_3CO)_3W{\equiv}CCMe_3$ (20-40 mol %), and toluene (20 mL). The solution was stirred at 80 °C for 8-96 h (Table 2). After the reaction was complete, solvent was removed in vacuo, and the residue was subjected to flash chromatography on silica, eluting with hexane/ethyl acetate. **1e**: brown crystals, showing green fluorescence, mp 292-300 °C (dec); 1H-NMR (400 MHz, $CDCl_3$): δ = 7.56 (s). MS (EI, 70 eV): *m*/*z* (%) 774 (M^+, 100), 695 (29), 614 (19). IR($CHCl_3$): $\tilde{\nu}$ = 2933, 2255, 1464, 1274, 1154 cm^{-1}. The compound decomposed upon standing for one week. **2**: pale yellow crystals, showing green fluorescence, mp 310-315 °C (dec). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.05 (br t, 2H, J = 1.5 Hz), 7.59 (dd, 4H, J_1 = 3.3 Hz, J_2 = 5.7 Hz), 7.54 (dd, 4H, J_1 = 1.6 Hz, J_2 = 7.9 Hz), 7.38 (t, 2H, J = 8.0 Hz), 7.32 (dd, 4H, J_1 = 3.4 Hz, J_2 = 5.8 Hz). MS (EI, 70 eV): *m*/*z* (%) 401 ($[M+H]^+$, 31), 400 (M^+, 100), 199 (11). HRMS: Calcd for $C_{32}H_{16}$: 400.1252. Found 400.1248. UV/Vis (CH_2Cl_2): λ_{max} (lg ε) 265 (4.03), 272 (4.05), 278 (4.11), 280 (4.10), 317 (3.62), 341 (3.26) nm. IR($CHCl_3$): $\tilde{\nu}$ = 2920, 2219, 1468, 1212, 892 cm^{-1}. Selected spectral data for **3**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.44 (AA' m, 8H), 7.34 (s, 2H), 7.19 (BB' m, 8H). MS (EI, 70 eV): *m*/*z* (%) 524 ($[M+2H]^+$, 10), 523 ($[M+H]^+$, 42), 522 (M^+, 100), 261 (25, M^{2+}). HRMS: Calcd for $C_{42}H_{18}$: 522.1408. Found 522.1428.

(20) The spectral data are in good agreement with those in: Staab, H. A.; Graf, F. *Chem. Ber.* **1970**, *103*, 1107.

(21) The spectral data are in good agreement with those in ref. 17a.

(22) Srinivasan, M.; Sankararaman, S.; Dix, I.; Jones, P. G. *Org. Lett.* **2000**, *2*, 3849.

(23) (a) Alkorta, I.; Rozas, I.; Elguero, J. *Tetrahedron* **2001**, *57*, 6043. (b) Jusélius, J.; Sundholm, D. *Phys.Chem. Chem.Phys.* **2001**, *3*, 2433. (c) Godard, C.; Lepetit, C.; Chauvin, R. *Chem. Commun.* **2000**, 1833. (d) Wan, W. B.; Kimball, D. B.; Haley, M. M. *Tetrahedron Lett.* **1998**, *39*, 6795. (e) Matzger, A. J.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1998**, *39*, 6791.

(24) Details of the crystal structure determination (deposition number CCDC 192630) may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Graphical abstract

An Alkyne Metathesis-Based Route to ortho-Dehydrobenzannulenes

Ognjen Š. Miljanić, K. Peter C. Vollhardt,* Glenn D. Whitener