It Takes Alkynes to Make a World – New Methods for Dehydrobenzoannulene Synthesis

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Abstract: Recent advances in the assembly of dehydrobenzoannulenes (DBAs) are the subject of this account. Using *in situ* generated acetylenic intermediates, novel α , ω -polyynes can be easily constructed using Pd-catalyzed alkynylation methodology. Subsequent cyclization via intra- and intermolecular Cu-mediated reactions can provide a wide variety of DBAs, including heretofore inaccessible topologies, systems with an unprecedented number of acetylenic linkages, structures with derivatized aromatic rings, and unusual organometallic species.

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1. An Introduction to DBAs

It was early April 1990, and I was under the gun. Every graduate student in the chemistry program at Rice University had to write and defend an original research proposal during the spring semester of their third year. The problem was that I was 3000 miles away working in Professor Roland Boese's laboratory in Essen, Germany. I was there as part of a collaborative program between the Boese group and my Ph.D. mentor's group (W. E. Billups), obtaining X-ray structural data on a variety of cyclopropenes and cycloproparenes.¹ Although the work was progressing well, I was having a hard time with the proposal. Like most graduate students, I had never written a research proposal and had no idea where to begin. Needing inspiration, Roland allowed me to look through his reprints. It was there I found the spark that I needed. In 1986, Vollhardt and co-workers, in collaboration with Boese, reported the synthesis and crystal structure of hexaethynylbenzene.² I was immediately taken by the beauty of the high symmetry and by the ease of preparation of the molecule. Later that same day I came across a paper by Michael Wright where he had successfully prepared phenylacetylene polymers via Stille-like coupling.³ What if it were possible to combine the results in these two articles? I began to doodle and soon filled up a page with a hybrid all-carbon network comprised of acetylenes and benzenes. Upon doing a search of the literature, I was surprised to find that a group of theoreticians had proposed the same idea.⁴ Ray Baughman and his co-workers had published a detailed article describing structure-property predictions for a new planar form of carbon containing equal numbers of sp and sp^2 atoms, which they nicknamed graphyne (1). In addition, they had included calculations on some model dehydrobenzoannulene (DBA) subunits of the larger polymeric network (e.g., 2). This was just exactly what I was looking for! Although I knew next to nothing about acetylene chemistry, I wrote the proposal describing the synthesis of graphyne and four DBA subunits using Stille chemistry⁵ and defended it shortly after I returned to Houston in mid-May. I passed the exam and soon tried to put the "unpleasant" experience behind me. Little did I know that this did not represent the end, but just the beginning of my odyssey with dehydrobenzoannulenes.....



2. Setting the Stage

The 1960s and 1970s saw a tremendous explosion in the area of dehydrobenzoannulene chemistry.⁶ The groups of Nakagawa, Staab, and Sondheimer, the principal protagonists of this era, prepared an impressive array of DBA structures. Molecules **3–5** are representative examples from each group, respectively.⁷ The main factor driving this research was the dominating question of ring currents in the DBA macrocycles. How diatropic, paratropic, or atropic were each of these systems? While there were and still are an infinite number of DBA topologies that could be synthesized, after awhile it became apparent that there needed to be additional impetus for this research; thus, interest waned and the area languished in the 1980s.



The renaissance for DBA chemistry began in the early 1990s. Two key events made this resurgence possible: (1) the isolation and characterization of the fullerenes;⁸ and (2) the extensive development of palladium-catalyzed cross-coupling reactions using alkynes.⁹ Fullerene chemistry has single-handedly made research on all-carbon and carbon-rich molecular and polymeric systems, of which DBAs are a prime

example, in vogue once more. Many of these molecules, including DBAs, can potentially serve as precursors for a variety of technologically important materials, such as novel allotropes of carbon, molecular scaffolds, and ladder polymers.^{8b,c,10-12} Palladium-catalyzed alkynylation has revolutionized the way DBAs are constructed (*vide infra*). Not only have new topologies now become accessible, but also the number of steps to known macrocycles has been shortened and overall yields dramatically increased in some cases. For example, Staab's original synthesis of DBA **4** required six steps (8% yield) starting from *o*-tolane, itself the product of a four-step reaction sequence.^{7b} Conversely, using commercially available 1-bromo-2-iodobenzene, molecule **4** could be assembled quickly in two steps (23% yield) via palladium chemistry.¹³ A drawback to this route though are that higher cyclooligomers are produced as well, making isolation of pure **4** somewhat tedious.¹⁴



The group that instigated the DBA renaissance was that of Francois Diederich (ETH). During the early 1990s, their research focused on the preparation of cyclic polyacetylene macrocycles and of planar polymeric networks based on tetraethynylethene (*e.g.*, **6**).¹⁵ Another group influential in this field was that of Jeff Moore (Illinois). The last six years has seen a large number and variety of phenylacetylene macrocycles and dendrimers produced by Moore's team (*e.g.*, **7**).¹⁶ Although neither research group was working directly on DBAs, many of their discoveries potentially could be applied to such systems (*vide infra*).



Biographical Sketch



It was during this DBA resurgence that I decided to jump into the fray. I believed my postdoctoral stay in Peter Vollhardt's labs had prepared me for the task that lay ahead. I specifically went to Peter's group as I knew I could pick up a wealth of experience with acetylene chemistry, something I could have used back in Essen. Armed with this new-found knowledge, I joined the faculty at Oregon in July 1993 and set out to build the molecules I had been thinking about for the previous three years.



3. Monoacetylenic DBAs

Our first synthetic attempts at Oregon were directed towards the graphyne substructures **2**, **8**, and **9**. Even though I was eager to begin work on the molecules, I had difficulty convincing graduate students that these systems were worthwhile targets. Nevertheless, eager undergraduates were abundant and soon the ball began to roll. The initial experiments for **2** and **8** utilized an intermolecular approach, similar to what had been used previously to prepare other DBAs.¹³ We quickly learned that this was not the route to pursue. Instead of furnishing the desired macrocycles, we obtained copious amounts of polymeric materials. Use of high dilution conditions had no effect. This was not how I wanted things to start.

Reassessment of the situation suggested use of an intramolecular approach. We redesigned the synthetic routes and Josh Kehoe, a very talented undergraduate that I "inherited" when I moved into my labs at Oregon, set off to make these molecules a reality. Since we were going back to step 1, it was best to test and fine-tune our methods on a known system; thus we first prepared the simplest graphyne subunit, annulene 4 (Scheme 1). Alkyne protection/deprotection,¹⁷ Pd-catalyzed alkynylation,⁹ and conversion of masked iodides¹⁸ comprised most of the chemistry involved in the construction of 4, as well as 2 and 8. Using the proven methods mentioned above, we were able to quickly assemble diyne 10, then triyne 11. Iodination, desilylation, and intramolecular alkynylation with Pd(dba)₂ under high dilution conditions¹⁹ furnished 4 as the sole product.²⁰ Although our route had several more steps than the two-step bromoiodobenzene pathway, the overall yield was higher –

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35% for Scheme 1 versus the reported 23% yield.¹³ More importantly, no cyclooligomeric molecules were detected, thus making product isolation and purification extremely easy.



Buoyed by this success, we turned our attention to the larger graphyne models. The routes used to construct 2 and 8 were quite similar to the one for 4 in that we took advantage of many of the same reaction sequences; unfortunately, these compounds proved to be synthetically more difficult to prepare. At this stage, we decided to introduce *tert*-butyl groups strategically placed on the aromatic rings to aid with any solubility problems we might encounter. As mimics of carbon networks, the larger models would be expected to exhibit poor solubility characteristics.



I assigned the synthesis of 2 to a new undergraduate, Jamie Kiley, and the elaborate route he accomplished is depicted in Scheme $2.^{21}$ Starting with *p*-*t*-butylaniline, Jamie was able to construct first **13**, then **14**.

Iodination, desilylation, and double intramolecular coupling gratifyingly furnished 2 as a bright yellow solid. To date, attempts to obtain X-ray diffracting crystals have failed; nevertheless, the spectral properties were fully in accordance with the proposed structure. The most disappointing feature of this work was the abysmal overall yield – 0.6% for 13 steps. Three key steps (g, i, and j) each proceeded in under 30% yield. Despite numerous efforts (varying reagent amounts, altering the order of addition, changing catalysts and solvents), we have been unable to dramatically improve yields or adequately scale-up the reactions for 2.



Scheme 3. Reagents: a) K₂CO₃, MeOH; b) 1,5-dibromo-2,4diiodobenzene, PdCl₂(PPh₃)₂, CuI, Et₃N; c) TMSA, PdCl₂(PPh₃)₂, CuI, Et₃N; d) MeI, 120 °C; e) Pd(dba)₂, PPh₃, CuI, Et₃N

The next system, molecule 8, proved to be equally challenging. Since Josh had already prepared compound 10 earlier (Scheme 1), we figured we would go ahead and try for the parent system. Using the same general sequence of reactions, the carbon backbone $(16a \rightarrow 17a)$ was easily assembled (Scheme 3). Closure of 17a gave after vacuum sublimation a yellow solid which proved to be sparingly soluble in organic solvents. This problem prevented the acquisition of NMR data; nevertheless, mass spectrometry, IR, and UV-Vis data confirmed the formation of 8a.²⁰ Even though it was eventually expected for large models, we were surprised by the severity of the solubility problem at this stage. We attributed the low yield of the cyclization step (<15%) mainly to this problem. Repetition of the synthetic sequence with p-tbutylaniline (Scheme 3) resulted in a worse outcome. Although the same general set of reactions was used, the conversion of $(16b \rightarrow 17b)$ proved to be exceedingly difficult as, quite inexplicably, yields varied wildly. To date we have been unable to isolate cyclized material 8b via this route.

Over the course of 18 months, we tried several variations of the above theme hoping to prepare **8b**. In the process, three valiant undergraduates expended their research lives, but all our efforts came to naught.²² Given our synthetic problems, work on the more complex model **9** never even got off the ground. Christmas 1995 was quickly approaching. For my first 2.5 years at Oregon, I had very little to show for the large amount of work – a "new" synthesis of known **4**, an abysmal route to **2**, horribly insoluble **8a**, and many dead-end intermediates for **8b**. This would

certainly not get me tenure. Something had to change, and change soon, or I would be forced to "pull the plug" on my pet project.

4. Diacetylenic DBAs

Two important events happened shortly after New Year's Eve 1996: (1) two graduate students began to work on the acetylene molecules -Stephen Brand changed research areas and Josh Pak joined my group. Although the undergraduates had made good progress, now I had the manpower that could be devoted full-time to this project. (2) The decision was made to move from monoacetylenes to diacetylenes. Preliminary DSC experiments on the thermal chemistry of 2 and 4 showed these molecules to be exceedingly stable, polymerizing only above 350 °C and over a wide 50+ °C range.23 These results did not bode well for preparing ordered, carbon-rich materials. Strained diacetylenes (e.g., 18), on the other hand, had been recently shown by Swager et al. to polymerize below 200 °C and over a relatively narrow range.²⁴ Although they had been unable to conclusively identify the thermal products, their results looked promising. Shortly before the end of 1995, Vollhardt and Youngs published their results on strained diacetylene 19.25 This came as some surprise as I was unaware that Peter's group was involved with DBA chemistry at that time.²⁶ Their beautiful results for 19 seemed to suggest that the molecule underwent topochemical polymerization to give a tube-like structure with a polydiacetylene backbone. After consulting with both groups to ensure we did not tread on their turf, we set off on making diacetylenic macrocycles.



Macromolecular network 20 and model compounds 21-24 were the next set of molecules we focused on. Graphdiyne 20 differs from graphyne 1 by inclusion of an extra alkyne unit between the aromatic rings. Our interest in these larger systems is fourfold: (1) graphdiyne should exhibit most, if not all the interesting materials properties predicted for graphyne.⁴ (2) The diacetylenic composition of 20-24 is particularly attractive as the topochemical polymerization of diacetylenes (vide supra) creates single crystals of organic polymers with conjugated backbones.²⁷ The resultant polydiacetylenes are known to exhibit NLO properties and are photogenerated carriers with mobilities much higher than other organic polymers.^{27a} (3) The extra alkyne units in **20** result in a pore size of about 2.5 Å, a cavity which can easily incorporate atoms as large as cesium. This should lead to interesting redox applications, as the large holes in the planar sheets can accommodate through-sheet transport of metal ions and can provide a unique method of dopant storage by intrasheet intercalation. (4) The designed synthetic pathways to these molecules should be significantly shorter. This hopefully will translate into easier preparation of greater quantities of material. Surprisingly, the simplest model, compound 21, had eluded synthesis, though some alkylated derivatives were prepared by Swager's group by the same cyclooligomerization reaction of 1,2-diethynylbenzenes used to produce 18.24 As with the two-step route to 4, complex product mixtures were produced which made separation of the dimers, trimers, and tetramers very difficult and resulted in low isolated yields of a given macrocycle. Additionally, the variation in product structures was severely limited by the ease of construction, or lack thereof, of the starting o-diethynylbenzene.



In order to ensure formation of a single product, an intramolecular dimerization of α , ω -polyynes was envisaged to prepare models 21-24. Synthesis of each polyyne would necessitate use of a suitably functionalized phenylbutadiyne. In the case of 21, the synthon we needed was 25 (Scheme 4).28 Selective desilylation with K2CO3 should afford the free phenylbutadiyne, which would then be subjected to standard Pd-coupling conditions. When this was indeed tried, concentration of the reaction mixture gave a dark brown gum instead of a free-flowing oil. Disaster had struck! Had we done our homework, we would have known that the parent molecule, 1-phenyl-1,3-butadiyne, is a highly reactive compound which polymerizes rapidly when neat or in concentrated solution; even a dilute solution at -20 °C polymerizes within a few hours.²⁹ This extreme reactivity has limited the synthetic utility of phenylbutadiynes to date. Indeed, all of our attempts to use unprotected phenylbutadiynes in Pd-catalyzed alkynylation reactions provided intractable polymeric gums. We had just started down this track and we were already derailed. Still, my 4+ years training as a cyclopropene chemist had taught me that there are many ways to circumvent instability problems.

The answer to this impasse was *in situ* generation of the phenylbutadiynes under standard Pd-coupling conditions.³⁰ The question was what base should we use to remove the trimethylsilyl group? The first attempt using K_2CO_3 gave us back starting materials.



Scheme 4. Reagents: a) (TMS)butadiyne, PdCl₂(PPh₃)₂, CuI, Et₃N;
b) TIPSA, PdCl₂(PPh₃)₂, CuI, Et₃N; c) 1,2-diiodobenzene, KOH, PdCl₂(PPh₃)₂, Pd(PPh₃)₄, CuI, Et₃N, THF, H₂O; d) Bu₄NF, EtOH; e) Cu(OAc)₂, pyridine

Addition of NaOMe did furnish the desired product, but in less than 5% yield; again, we isolated mainly starting materials. The third time was indeed a charm – addition of a few milliliters of a concentrated KOH solution provided the bis-coupled product in 71% yield. Desilylation and use of high dilution conditions in the oxidative dimerization reaction gave **21** as the sole product in moderate yield. As with **8**, compound **21** is poorly soluble in common organic solvents; nevertheless, all spectral data (NMR, IR, UV, MS) support this structure. The minimal solubility of the product is no doubt responsible for the low isolated yield.



Scheme 5. Reagents: a) TIPSA, PdCl₂(PPh₃)₂, CuI, Et₃N; b) MeI, 120 °C; c) (TMS)butadiyne, PdCl₂(PPh₃)₂, CuI, Et₃N; d) 1,2,4,5-tetraiodobenzene, KOH, Pd(PPh₃)₄, CuI, Et₃N, THF, H₂O; e) Bu₄NF, EtOH; f) Cu(OAc)₂, pyridine

Assembly of bismacrocycle **22** is depicted in Scheme 5.²⁸ From the outset, we recognized the need for including solubilizing substituents. The required triynes **26** were easily prepared by standard Pd-catalyzed reactions. Fourfold *in situ* desilylation/alkynylation gave the fluorescent dodecaynes **27** in *ca*. 35% yield. Although modest, this yield implies an average conversion of about 90% for each of the eight transformations necessary. Desilylation of **27** and intramolecular oxidative dimerization gave **22**. Once again, poor solubility was a factor. Even with four *t*-butyl groups, **22a** proved to be virtually insoluble in common solvents, hence the low yield. Fortunately, the *n*-decyl moieties worked quite well, with **22b** now isolated in 83%(!) yield after purification.

The *in situ* deprotection/alkynylation protocol has proven to be exceedingly useful in our laboratory. In addition to macrocycles **21** and **22**,^{28,31} we have prepared a wide variety of other DBA topologies. As a project for summer 1996, three capable undergraduate students (Mike Bell, Jamieson English, and Charles Johnson) synthesized DBAs **28**-**32**.³⁰ Extension of the simple, one-pot procedure to the iodoarenes in Table 1 allowed us to prepare a series of bis(triisopropylsilyl) protected





^a Step c in Scheme 4. ^b Combined yields of steps d & e in Scheme 4

 α, ω -polyynes in very good yields. Subsequent deprotection and cyclization provided DBAs that were inaccessible by traditional routes (28, 30, 31) or previously available only in low yield (29,³² 32³³). Fortunately, product solubility was not an issue as these macrocycles either possessed lower symmetry (*e.g.*, 28 vs. 21) or were non-planar (29-32).

5. Triacetylenic DBAs

1997 saw two new graduate students come on board. The first task for Dave Kimball and Brad Wan was to extend our process to substituted phenylhexatriynes,³⁴ as illustrated in Scheme 6.³⁵ The necessary polyyne 33 was prepared with some difficulty from 34, an intermediate in the syntheses of 28-30 that is readily available in multigram Modified Cadiot-Chodkiewicz coupling³⁶ quantities. using monodesilylated 34 and known TMS-C=CC=C-Br³⁷ gave 33 in moderate yield, which in turn was converted into 35 by our standard procedures. As with DBA 28, 35 proved to be readily soluble. Additionally, since our syntheses produce only single macrocycles, extensive separation and purification procedures which result in material loss were avoided. We have successfully prepared 36-38 using similar methodology. Together, these macrocycles represent the very first hexatrivneand/or hexaenediyne-connected examples of dehydroannulenes, benzannelated or otherwise.

6. Tetraacetylenic DBAs

The more time I spend in the chemistry arena, the more I am convinced serendipity plays a role. Sometimes it can be a major part of the discovery. The following is a perfect case in point. Although Scheme 4 makes the assembly of **25** look trivial, anyone who has worked with butadiynyltrimethylsilane can tell you that synthesis of this molecule is



Scheme 6. Reagents: a) TMSA, PdCl₂(PPh₃)₂, CuI, Et₃N; b) TIPSA, PdCl₂(PPh₃)₂, CuI, Et₃N, piperidine, 120 °C; c) K₂CO₃, MeOH; d) i] BuLi, ii] CuBr, iii] TMS-C≡CC≡C-Br, pyridine; e) 1,2-diiodobenzene, KOH, Pd(PPh₃)₄, CuI, Et₃N, THF, H₂O; f) Bu₄NF, EtOH; g) Cu(OAc)₂, CuCl pyridine



large quantities is most certainly non-trivial. Thus triyne **25** is guarded jealously in the lab and is not to be wasted. Nevertheless, failure to degas a solution properly in a Pd-catalyzed alkynylation results in a side reaction where an appreciable amount of the terminal acetylene dimerizes. Although formation of such a side product is part of the initiation process of the catalytic cycle (Pd^{II→}Pd⁰), usually the amount of alkyne dimer is quite small (< 5 mg). Unfortunately, during one of his reactions making the α, ω -polyyne precursor to **31**, Mike Bell forgot to degas the mixture before adding **25**. The first band off the chromatography column was 50 mg of a light brown gum. ¹³C NMR data showed only 6 resonances in the alkyne region, and the aromatic region of ¹H NMR spectrum was far too simple to be the desired α, ω -polyyne. Conclusion – it had to be dimer **39a**.

I had mixed emotions about 39a. I was disappointed with Mike as he had worked in my group long enough to know better than not to degas a reaction solution. On the other hand, I knew that 39a could be useful in its own right. I started wondering out loud in the lab. Surely there must be a way to intentionally produce 39a?!? Someone piped up that it would be neat if we could do the dimerization in situ as well. That was it! The answer was so easy - addition of K2CO3 to Eglinton dimerization conditions (Scheme 7). Mike set up the reaction late that afternoon and redeemed himself by noon the next day - a 61% yield of pure 39a. We have tried this modification on a variety of monoynes and diynes, obtaining product yields as high as 98%.³⁸ With an ample supply of 39a in hand, desilylation with Bu₄NF and cyclization with $CuCl/Cu(OAc)_2^{39}$ under pseudo-high dilution conditions provided the orange cyclodimer 40a as the sole product; neither higher cyclooligomers nor the highly strained macrocycle arising from intramolecular ring closure were detected. Despite being non-planar, compound 40a proved to be somewhat soluble in common solvents. Repetition of the synthetic sequence using 26a furnished macrocycle 40b. As expected, inclusion of the *t*-butyl substituents noticeably improved product solubility and thus the isolated yield. To the best of our knowledge, the 32-membered macrocycle, possessing an unprecedented number of four acetylenes between the aromatic rings, makes **40** the largest tetrabenzo-DBA yet characterized.



Scheme 7. Reagents: a) Cu(OAc)₂•H₂O, K₂CO₃, pyridine, MeOH; b) Bu₄NF, EtOH; c) Cu(OAc)₂, CuCl, pyridine

7. Derivatized DBAs

One of the limitations of the traditional copper-mediated cyclooligomerization reaction is generation of differentially substituted DBAs. The substitution pattern in the starting *o*-diethynylbenzene must be maintained on each and every benzene moiety in the oligomeric mixture of DBAs that is produced. Thus, it is impossible to prepare less symmetric systems like **41** via the older route.



Until recently, we had focused solely on preparation of the parent hydrocarbons. With our synthetic approach, however, it should be possible to construct a wide variety of derivatized structures. Due to the stepwise pattern of molecule assembly, double introduction of one or two functional groups, thus forming macrocycles based on 41, should be a straightforward process. One pattern in which we are particularly interested is "push-pull" derivatives like 41f and 41g. It should be possible to enhance the physical properties of the molecule for potential use of the annulenic monomers or polymers as conjugated materials for electronics and photonics.⁴⁰ Specifically, we hope that our systems could find use as highly active, second and third-order non-linear optical materials.⁴¹ To this end, we have successfully prepared several donor and/or acceptor macrocycles, as illustrated in Table 2.42 The assembly of 41a-g is easily accomplished as the starting arenes 42 and 43 are readily prepared via literature methods. UV-Vis spectral results for 41f and 41g show enhanced delocalization in these macrocycles - the absorption bands are significantly broadened and are red-shifted by up to 75 nm.42

8. Organometallic DBAs

While "push-pull" derivatization is one method for modifying the electrooptical properties of our annulenes, another promising route is incorporation of a metal fragment.⁴³ Specifically, the electronic interaction in transition metal σ -acetylide complexes⁴⁴ leads to

Table 2. Yields for construction of derivatized DBAs

DBA	R ₁	R ₂	Pd-coupling (%)	Cyclization (%)
41a	Dec	Н	80	56
41b	OMe	Н	71	59
41c	OOct	Н	94	92
41d	Н	NO_2	53	
41e	Dec	NO_2	20	90
41f	OMe	NO ₂	26	67
41g	OOct	NO ₂	34	46

electronic delocalization across the metal center.⁴⁵ This characteristic has indeed been suggested to influence the electrooptical properties of metal acetylenic system, as recent studies of organometallic rigid-rod polymers with bridging polyyne units found enhanced nonlinear optical behavior.⁴⁶ With the above objective in mind, Josh Pak set about exploring the inclusion of *trans*-bis(triethylphosphine)platinum fragments in our annulenic systems.

Shown in Scheme 8 is our successful preparation of platinum-containing macrocycle **44**.⁴⁷ Whereas the parent hydrocarbon **21** proved to be poorly soluble, inclusion of the *trans*-bis(triethyl-phosphine)platinum fragment in the carbon backbone dramatically improved product solubility. The X-ray crystal structure of **44** (Figure 1) clearly shows retention of the *trans* geometry and the additional strain placed on the molecule by metal incorporation – the bond angles on the side containing the platinum fragment are distorted up to 10° from linearity.



Scheme 8. Reagents: a) Bu4NF, EtOH; b) Me₃SnNMe₂, THF; c) *trans*-PtCl₂(PEt₃)₂, CuI, toluene



Figure 1. X-ray crystal structure of 44

A rough estimate for the extent of electron delocalization in platinacycle **44** can be obtained by comparison of its absorption spectrum with that of **21**. The λ_{max} of the highest end adsorption in **44** is shifted bathochromically by about 25 nm when compared with the analogous

absorption in **21**. These data are contrary to those found with a highly conjugated, acyclic system, where insertion of the bis(triethylphosphine)platinum fragment resulted in a hypsochromic shift.^{44b} Our work strongly suggests that electronic delocalization in the platinum complex is indeed functional throughout the entire macrocycle.

An alternate use of organometallic fragments that we have been pursuing is use of such species to stabilize highly strained DBAs with the subsequent liberation of the free hydrocarbons. Despite significant efforts on the part of several research groups, systems containing contiguous, *bent* triynes and higher polyynes have proven elusive;¹⁵ only strained monoyne and diyne derivatives (such as **18**) are known.^{24,25} Although we have prepared triyne- and tetrayne-linked systems (*vide supra*), calculations show these to be relatively strainfree.⁴⁸ The most "highly strained" is compound **36**. Even then, the largest bending in the acetylenes is calculated to be only 5.1°.

In hindsight, our first attempt was overly ambitious – macrocycle **45** was our target.⁴⁹ With *sp* bond angles around 162° , **45** would be highly strained and therefore was expected to be quite reactive. The octacobalt complex **46**, on the other hand, should be readily isolable. Indeed, we prepared **46** as stable, deep maroon crystals (Scheme 9). All spectroscopic data supported formation of the strain-free dimeric structure. Unfortunately, all attempts to liberate **45** from the cobalt units led only to insoluble materials. Diederich *et al.* have observed similar problems trying to prepare the cyclocarbons.¹⁵ Whether the failure to prepare these two classes of macrocycles is due to the extreme reactivity of the distorted polyyne moiety or to the lack of a viable synthetic route is not certain. Thus, isolation and characterization of smaller bent hexatriyne– and octatetrayne–containing systems should help answer these questions.



Scheme 9. Reagents: a) 1,4-diiodobenzene, Pd(PPh₃)₂Cl₂, CuI, Et₃N; b) Co₂(CO)₈, Et₂O; c) dppm, toluene; d) Bu₄NF, THF, EtOH; e) Cu(OAc)₂•H₂O, pyridine

9. Conclusion and Outlook

The chemistry presented herein provides an entry into the synthesis of a diverse array of dehydrobenzoannulene topologies. Although the Pd-catalyzed alkynylation/Cu-mediated dimerization strategy is not new, our ability to construct a plethora of previously inaccessible α , ω -polyynes breathes new life into this old route.

Where do we go from here? There are several important avenues which we are currently pursuing: (1) bent polyynes. Is it possible to prepare highly strained polyynes like **45** or **47**? We are hoping the answer is

"yes". (2) Aromaticity. Systems like 21 are Hückel [4n+2] π -electron aromatics. To date, though, it has been difficult to quantify just how weak the diatropic ring current is. Annelating the DBA to a dimethyldihydropyrene core (e.g., 48) should provide the answer.⁵⁰ (3) Organometallics. The use of DBAs as ligands in transition metal chemistry is very limited.^{14,47,49} We feel that there is a wealth of unexplored chemistry utilizing these systems. Macrocycle 49 is but one such complex we are actively seeking to prepare. (4) Materials properties. As mentioned several times in this account, DBAs have the potential for forming novel materials with useful properties. We have only scratched the surface of this facet. Our synthetic methods allow us to prepare a wide variety of DBAs in sufficient quantity to permit further study. This should allow us to systematically study the reaction chemistry and possible materials properties of our macrocycles. With perseverance and a little luck, we just might "find a diamond in the rough". On the other hand, given the subject of this account, it might be more appropriate to "find the fullerene in the soot"!



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