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The Palladium Way to *N*-Heteroacenes

Uwe H. F. Bunz*[a] and Jens U. Engelhart[a]

Abstract: Novel synthetic methodologies access known organic materials effectively and/or allow the preparation of species otherwise inaccessible. Pd-catalyzed coupling of aromatic dihalides to *ortho*-diaminoarenes furnishes embedded stable *N,N'*-dihydropyrazines in expediently and in often excellent yields. The embedded *N,N'*-dihydropyrazines are oxidized by MnO_2 into substituted azatetracenes, azapentacenes, azahexacenes and azaheptacenes, soluble, processible and stable. This powerful Pd-methodology allows the preparation of diaza-, tetraaza- and hexaazaacenes. Azaacenes are now accessible using this powerful tool. We find that Buchwald-type biarylphosphines in combination with a suitable Pd-precursor gives excellent results. Activated dihalides such as 2,3-dihaloquinoxalines couple easily under simplified conditions, while 2,3-dibromoacenes need more stringent conditions and advanced catalyst precursors. Pd-catalysis assembles azaacenes with otherwise difficult to obtain substitution patterns; high yields and flexibility make this method most attractive.

Introduction

The development of new synthetic methodologies is critical in organic materials science, as they allow efficient access to known key-compounds, and enable preparation of new classes of materials, with both issues being important. We have tackled this task for the synthesis of larger azaacenes, developing Pd-catalyzed coupling reactions of aromatic *ortho*-dihalides to aromatic *ortho*-diamines.

N-Heteroacenes: [1] Acenes massively impact organic electronics, particularly as charge transport layers in organic thin film transistors. Pentacene and its stabilized and substituted derivatives are heavily deployed in this field. And since Anthony's TIPSpen (**2**) is commercially available, both vacuum processed but also solution processed OFETs of this material are easily prepared.[2] Pentacene (**3**) and its derivatives are hole transporters, as the oxidation of the pentacene nucleus is much easier than its reduction, necessary for the generation of negative charge carriers in the organic semiconductor material. Problems with water, oxygen and trap states render pentacenes difficult for electron transport.[3]

Charge transport is, in a simplified way, proportional to the rate of degenerate charge transfer between two identical neighboring molecules (Figure 1). The charge transfer rate is dependent upon the transfer integral *t*, which denotes the electronic overlap[4] of two neighboring molecules and the reorganization energy λ, defined as the energy gain of a radical anion or a radical cation upon structural relaxation from the equilibrium structure in the uncharged state to the equilibrium structure in its charged state. As seen from eq. 1, *t* should be maximized, while λ should be minimized. Generally, both factors can be favorable in the larger acenes; particularly the rigid structure but also the size of the acenes minimizes λ.

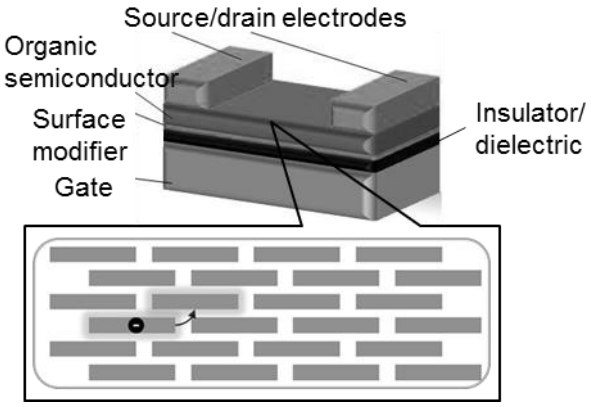

Figure 1. Schematic view of an organic thin film transistor with simplified charge (electron) transport in the film.

$$\mu \sim k_{ET} \sim \frac{1}{\sqrt{T}}\, t^2\, e^{\left(-\frac{\lambda}{4kT}\right)} \qquad \text{(eq 1)}$$

Here μ = charge carrier mobility, k_{ET} = charge transfer rate constant, T = temperature, k = Boltzmann constant, *t* = transfer integral and *λ* = reorganization energy.

As the "normal" pentacenes are poor electron transport materials one has to modify their structure. Lowering the energetic cost of electron injection and uptake, i.e. increasing electron affinities, yet still retaining the superb properties of pentacenes would be desirable. A number of groups has exploited the attachment of halogen atoms to pentacene.[5] The alternative is the introduction of electronegative atoms directly into the perimeter of the acenes. Doing this, results in the *N*-heteroacenes such as **1**; **1** packs most similarly in the solid state as TIPSpen **2** does.

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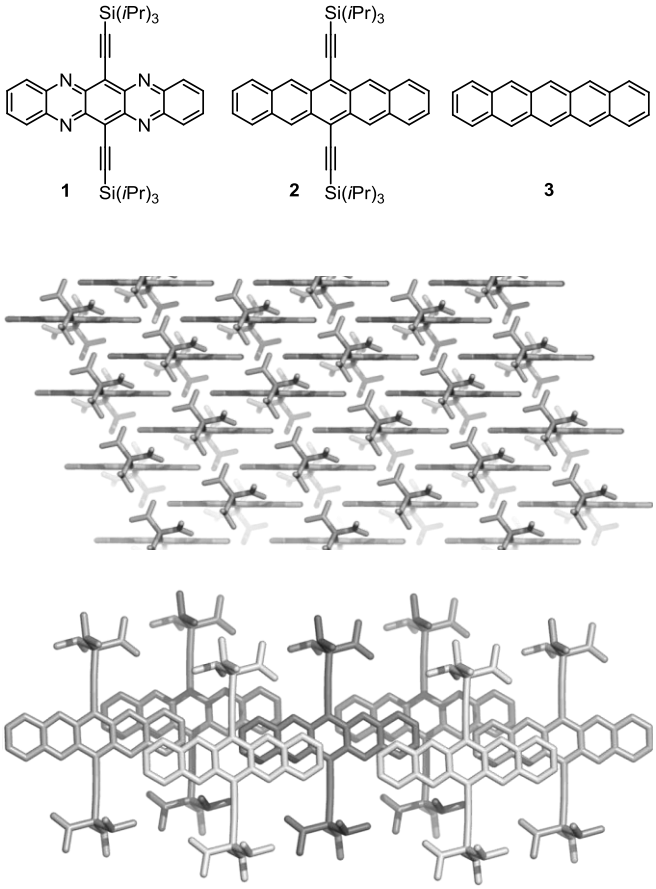


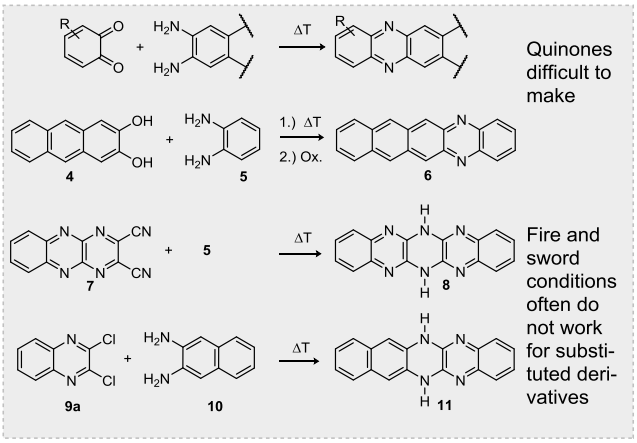
Figure 2. Packing of compound **1** in the solid state. This tetraazapentacene shows electron mobilities of up to $\mu_{E(1)}$ = 3.3 $cm^2 V^{-1}s^{-1}$ with I_{on}/I_{off} = $6x10^6$.

Winkler and Houk[6] calculated several *N*-heteropentacenes to display small reorganization energies and frontier orbital positions that should make them useful as electron transporting materials. Several years later, compound **1** was prepared;[7] Miao reported spectacular electron transporting properties of **1** with mobilities of up to 3.3 $cm^2V^{-1}s^{-1}$.[8] **1** (Figure 1) is now a state of the art electron transporting material.

Hartwig-Buchwald amination for cyclizing C-N-bond formation: The Pd-catalyzed formation of C-N-bonds is an established and important reaction that forms sp^2-C-N-bonds through a variety of different catalysts and Pd-precursors.[9,10] The coupling was developed in many different variants. Five-membered rings of the indole etc. type are described and the Pd-catalyzed synthesis of acridines is reported, [8] but the synthesis of other six-membered *N*-heterocycles using Pd-catalysis is a much less explored area. The Pd-catalyzed synthesis of *N,N´*-dihydropyrazines was unexplored, before we started to investigate this area.

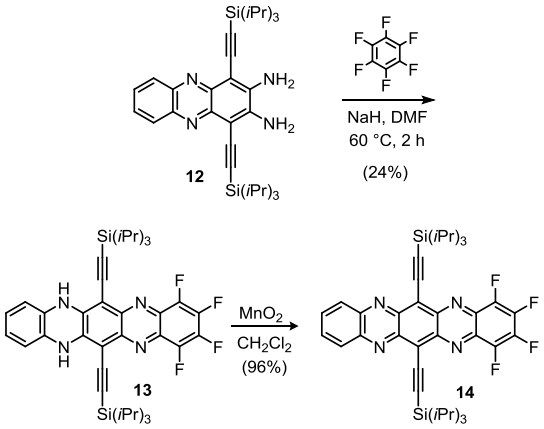
Classic Syntheses of Azaacenes

Azaacenes have been known for a long time and to understand the issues in the synthesis of large *N*-heteroacenes we examine the conventional way of preparation. As an aside, for most of the direct condensation methods that will be discussed, aza*tetra*cenes form directly in their oxidized form, while aza*pent*acenes (with some exceptions) and aza*hex*acenes are produced in their *N,N´*-dihydro forms. Breaking of the azapentacene into two aromatic naphthalene-type subsystems plus one large 4n-pi-system commences; according to calculations[11] two Clar sextets are energetically much more favorable than the presence of one large aromatic system. For the azatetracenes the equilibrium is on the side of the large aromatic species, the oxidized form is more stable than the *N,N´*-dihydro-compound, which in air spontaneously oxidizes back into the azaacene. *N,N´*-dihydro azapentacenes are more stable. They are oxidized slowly under the influence strong bases and heat. This cannot be found for higher *N,N´*-dihydro azaacenes.

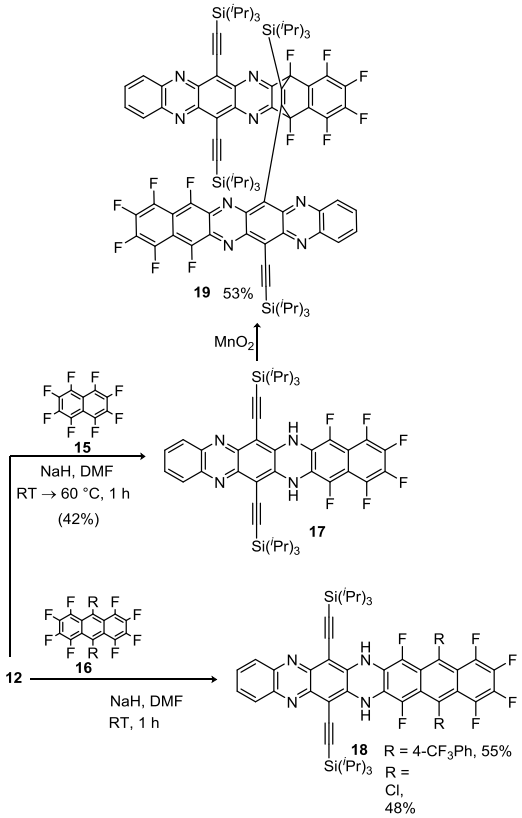


Scheme 1. Classic synthetic approaches towards azaacenes.

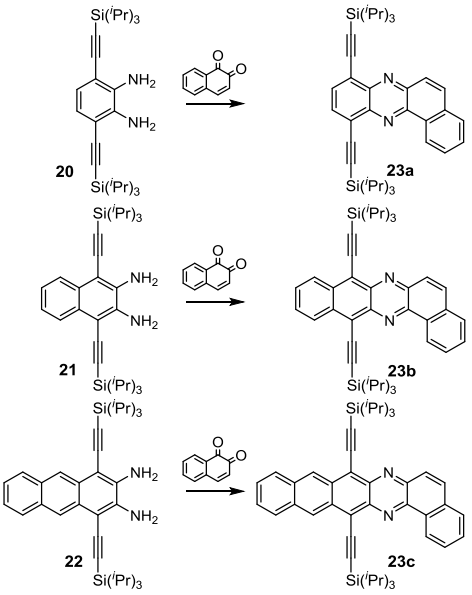
In the oldest syntheses (Scheme 1) one melts together dihydroxyarenes such as **4**, dichloroquinoxaline **9a**, or dicyanoquinoxaline **7** with *ortho*-phenylenediamine **5** or –naphthalenediamine **10**. These fire and sword methods furnish unsubstituted azaacenes, often in good to excellent yields. If pentacenes or hexacenes are produced, they form as their *N,N´*-dihydro-compounds, such as **11** or **8**. A similar reaction that works in solution phase is the reaction of *ortho*-quinones with diamines. While more reactive than the dihydroxy-compounds, *ortho*-quinones often (not always) are more sensitive and therefore hard to synthesize but also more reactive and can lead to azaacenes and various extended azaarenes.[12] Mastalerz et al. assembled up to **11** six-membered rings using this condensation strategy. [13] The direct formation of azatetracenes deploying *ortho*-quinones works well, while for aza-pentacenes yields are variable.[14] Very recently Zhang and co-workers synthesized hexaazapentacenes by the condensation of teraaminophenazine with various diketones.[15]



Scheme 2. Synthesis of a partially fluorinated tetraazapentacene **14** using an addition-elimination route.

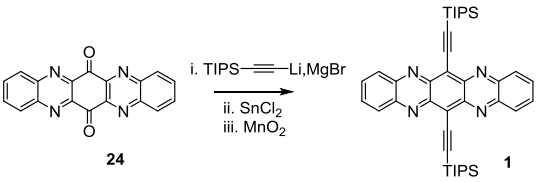


Scheme 3. Synthesis of fluorinated azaacenes using nucleophilic aromatic substitution.



Scheme 4. Synthesis of kinked azaarenes **23a-c** by condensation of the diamines **20**-**22** with 1,2-naphthalenedione.

A variant of this condensation (Scheme 2) is the nucleophilic reaction of the diamine **12** in the presence of sodium amide with hexafluorobenzene to give the tautomerized *N,N´*-dihydro compound **13** in 24% yield.[16] **13** is oxidized in good yields into the tetraazaacene **14**. Extension of this concept (Scheme 3) generates the *N,N´*-dihydro compounds **17** and **18** in reasonable yields. For **18** oxidation is not possible anymore, due to their deep HOMO, while for **17** only the dimer **19** is observed upon oxidation with MnO_2, probably through the intermediacy of the fleeting tetrafluorotetraazahexacene. Harnessing quinones, we reacted the aromatic diamines **20-22** with naphthalene-1,2-dione. 1,2-Naphthoquinone is stable and condenses in high yields to give bent, phenanthrene-like azaarenes **23a-c** (Scheme 4) in good to excellent yields.[17] A critical way to introduce substituents into azaacenes is the alkynylation of para-quinone structures such as **24** (Scheme 5). This works well for **1**, if one uses a magnesium acetylide and then deoxygenates with tin chloride. Oxidation of the intermediate furnishes **1**.[6] This approach should be suitable for all heterocyclic quinones, which are obtained by aggressive oxidation of *N,N'*-dihydroazaacenes.



Scheme 5. Synthesis of compound **1** using Anthony's alkynylation strategy.

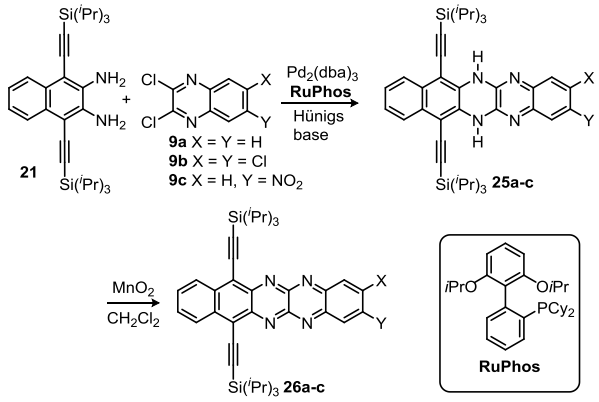
Yet the arsenal of established methods can fail in the synthesis of substituted azaacenes. The harsh conditions do not allow the coupling of the alkynylated diamines **20-22** to

dichloroquinoxaline **9a** or towards dihydroxy arenes. **20-22** are great starting materials; it was an important challenge to find synthetic methods transforming them into azaacenes. Pd-catalyzed coupling reactions were an attractive proposition.

Coupling of Activated Halides to 20-22. The Simple Pd-Protocol

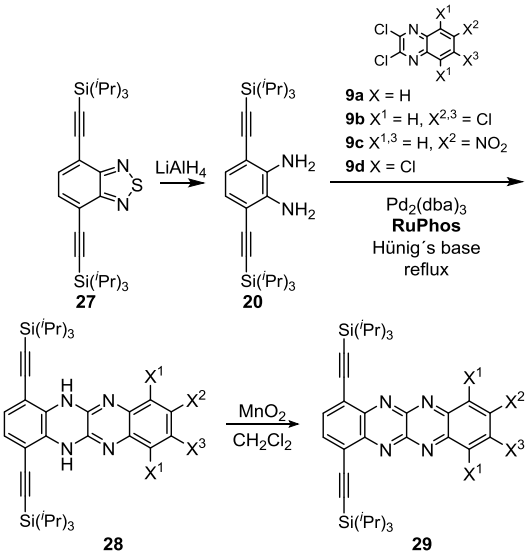
In our first experiments we reacted the diaminonaphthalene **21** with dichloroquinoxaline **9a** in the presence of $(Ph_3P)_2PdCl_2$ in boiling Hünig's base (*N,N*-di-*iso*-propylethylamine). Traces of the desired product **25a** formed. Upon changing the catalyst system into $Pd_2(dba)_3$ as a Pd source and RuPhos as ligand, we obtained the coupling product **25a** in good yields (>75 %, Scheme 6). We also tested other Buchwald-type ligands, most of which worked also satisfactorily. In an extension of this concept, we also reacted substituted dichloroquinoxalines **9b,c** to **21**, to give substituted, stable tetraazapentacenes **26b,c** in good yields after coupling and oxidation as stable compounds.

We observe that the coupling of **21** works with the tetrachloride **9b**, in which only two of the four chloride substituents partake, i.e. only the activated ones react. 5-Nitro-2,3-dichloroquinoxaline **9c** also couples easily with the diamine **21**. The coupling reactions proceed smoothly in Hünig´s base (14-18 h) at its boiling temperature. In all cases 5 mol% of catalyst were used. The isolated *N,N´*-dihydro tetraazapentacenes are all easily oxidized by MnO_2.



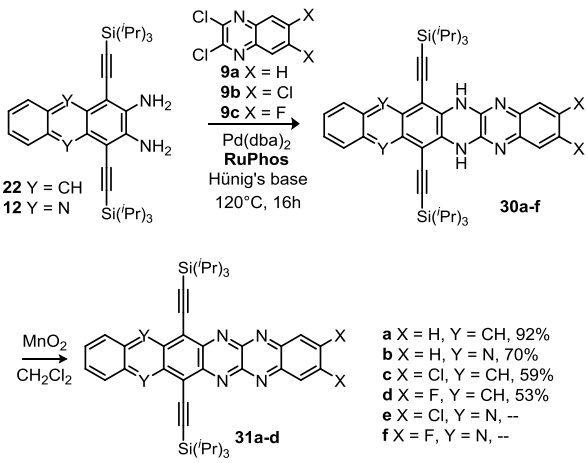
Scheme 6. Synthesis of tetraazapentacenes **26a-c** using Pd-catalysis.

This approach (Scheme 7) accesses tetraazatetracenes. While the Pd-catalyzed coupling of **5** to dichloropyrazines works only in traces, the diaminobenzene **20**, obtained through reduction of diethynylbenzothiadiazole (**27**) couples to dichloroquinoxalines **9a-d** to give the *N,N*'-dihydrotetraazatetracenes **28a-d**; one of the few cases where *N,N*'-dihydroazatetracenes are isolated. MnO_2 then oxidizes **28a-d** into the tetraazatetracenes **29a-d**.



Scheme 7. Pd-catalyzed synthesis of tetraazatetracenes **29a-d**.

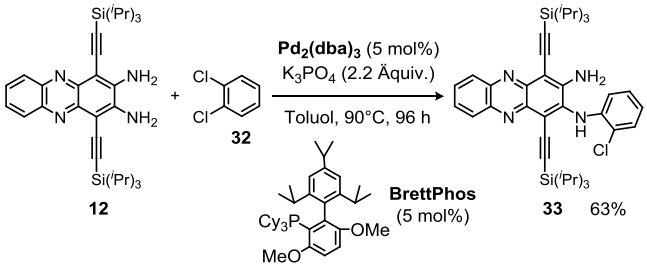
This reaction cascade extends to the synthesis of the first azahexacenes (Scheme 8). [18] Both tetraaza- as well as hexaaza-hexacenes were obtained by the Pd-catalyzed coupling of the substituted diaminoanthracene (**22**) or -phenazine (**12**), employing the activated dichloroquinoxalines **9a-c** (Scheme 8). While all of the possible six *N,N'*-dihydroazahexacenes **30a-f** are obtained in high yield, only the derivatives **30a-d**, leading to **31a-d** could be oxidized by MnO_2. The other two dihydro-derivatives (**30e,f**) display HOMOs that were energetically too deep; they could not be oxidized into azahexacenes **31**.



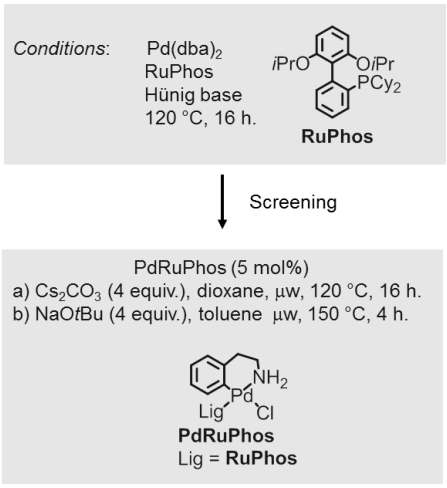
Scheme 8. Pd-catalyzed synthesis of tetraazahexacenes **31a-d**.

The Problem of Coupling De-Activated Dihalides[19]

The Pd-catalyzed coupling of **20-22** to activated *ortho*-dihalides is facile and furnishes the coupling products in good to excellent yields. The coupling to un-activated aromatic halides such as 2,3-dibromonaphthalene (**34**) or 2,3-dibromoanthracene (**43**) was not yet possible. Therefore, we carefully optimized the reaction to find conditions under which we could couple the non-activated *ortho*-dihalides.



Scheme 9. Coupling of dichlorobenzene with diamine **12**.



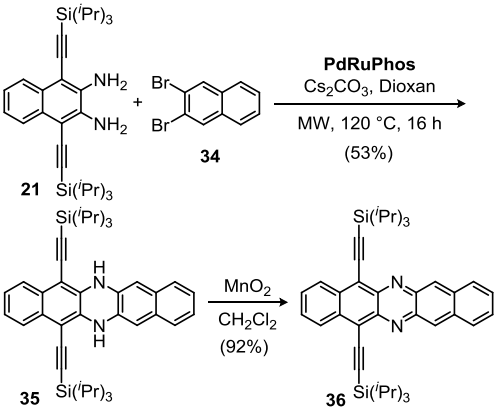
Scheme 10. Developing reaction conditions for the coupling of non-activated aromatic dihalides to aromatic diamines.

While the choice of the phosphane ligand was relatively clear, as the Buchwald ligands are by far the best systems we had tested, and most Buchwald-type ligands worked. The Pd source Pd_2dba_3 was not ideal (Scheme 9). In a first experiment, coupling of **12** to **32** under modified standard conditions furnished (Scheme 9) the monoarylated species **33** in 63% yield, without any ring-closed products. A cyclometalated Pd-complex with a RuPhos ligand was the most suitable system (Scheme 10). Good results were achieved with 5 mol% of pre-catalyst. Less than 5 mol% of PdRuPhos loading led to decreased yield. 10 mol% of the pre-catalyst increased the yield only slightly. As base/solvent combination we could either employ Cs_2CO_3 in dioxane or toluene in the presence of NaOtBu, both under microwave irradiation at temperatures between 120-150°C.

There are limits to this approach. We were never able to couple **12** with dichloro- (**32**) or dibromobenzene **37** to the cyclic product. In the best case mono-arylated product were isolated. If strong bases were used, catalyst decomposition was observed, while weak bases did not give any reaction. Bidentate and sterically encumbered phosphine ligands worked best but only gave low conversion with dibromides. Ortho-dichlorobenzene worked best with a hightest 63% of the monoarylated open product. We assumed the superiority of chlorides is due a steric effect indicating the reaction leads through sterically crowded intermediate. Consecutive optimizations to ring-close **33** were not very successful either, as sterically encumbered ligands provide stability but suppress ring closure.

Azapentacenes

The diamine **21** reacted with dibromonaphthalene **34** into the formation of **35** in 53% yield if the optimized reaction conditions (Scheme 11) were used. The choice of base and temperature is critical for the formation of dihydro azapentacenes. When strong bases and temperatures over 120°C were applied, catalyst



Scheme 11. Synthesis of diazapentacenes using non-activated dihalides.

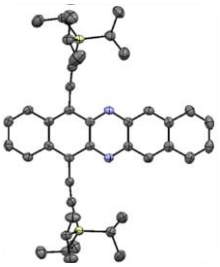
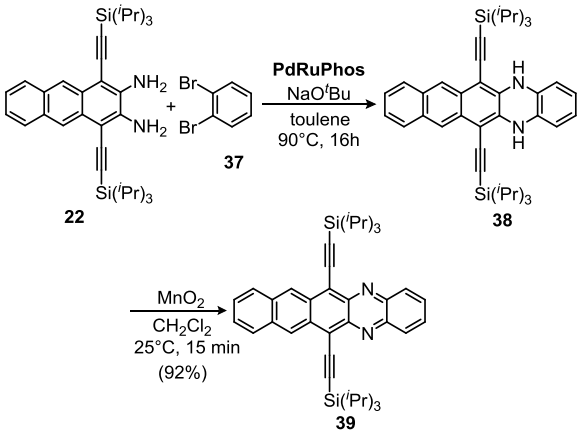
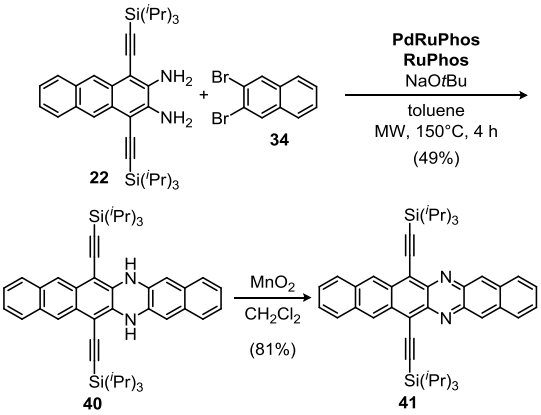


Figure 3. Single crystal X-ray structure of the diazapentacene **36**.



Scheme 12. Pd-catalyzed synthesis of isomeric diazapentacene **39** using *ortho*-dibromobenzene.



Scheme 13. Pd-catalyzed synthesis of the substituted diazahexacene **41**.

degradation was observed due to catalyst poisoning. We are convinced that oxidation of the formed dihydro azaacene **35** caused the poisoning. Strong bases increase this tendency by deprotonation of **35**, forming an even stronger reductant at these high temperatures. Oxidation of **35** with MnO_2 gave the azaacene **36** in 92% yield. An X-ray crystal structure of **36** was obtained (Figure 3). In the same way (Scheme 12) dibromobenzene **37** couples to the diamino-anthracene **22** to furnish **39** in 53% yield. However, there was always some monoarylated product present, even if benzoquinone was employed to re-oxidize the Pd-catalyst. These modified conditions are powerful to make azapentacenes that are otherwise available only with difficulty. This Pd-catalyzed coupling has also been employed by Müllen *et al.* to prepare some attractive bisanthracenothiadiazoles.[20]

Azahexacenes and Azaheptacenes

Could one make diazahexacenes and possibly diazaheptacenes using Pd-catalyzed coupling sequences (vide supra). While the tetraaza and hexaaza-hexacenes had been prepared by us, diazahexacenes and diazaheptacenes were unknown at the beginning of our synthetic endeavor. With the experience from the synthesis of the diazapentacenes we coupled **22** to **34** and obtained the *N,N'*-dihydrodiazahexacene **40** in 49% yield (Scheme 13). More forcing conditions were applied in this case, as *N,N'*-dihydrodiazahexacenes are more resistant towards oxidation in contrast to *N,N'*-dihydrodiazapentacenes (see above) during Hartwig-Buchwald cyclization step. Oxidation of **40** with MnO_2 gave the diazahexacene **41** in 81% yield (Scheme 13). The diazahexacene **41** is stable in solution, but attempts to obtain a single crystal X-ray structure of **41** failed, and we isolated the butterfly dimer **42**, the structure of which was solved and is analog to that of the dimerization products formed from Anthony's hexacenes (Figure 4).[21]

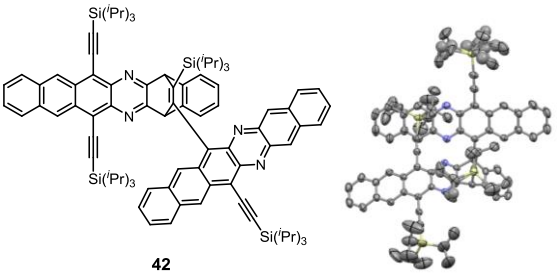
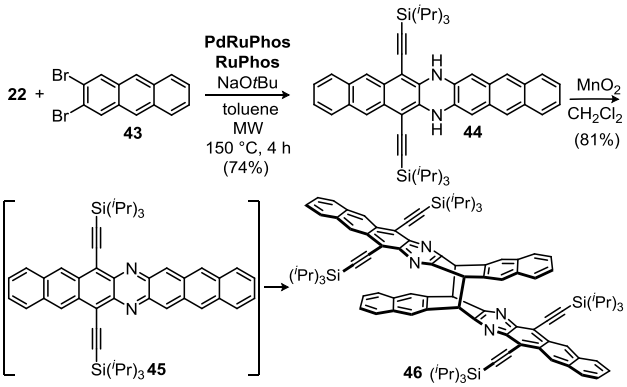


Figure 4. Diels-Alder dimerization product **42** of azahexacene **41**.



Scheme 14. Pd-catalyzed synthesis of an azaheptacene

Employing the same strategy (Scheme 14) we coupled 2,3-dibromoanthracene **43** to the diamine **22**. The *N,N'*-dihydrodiazaheptacene **44** forms in 74% (Scheme 14), however, oxidation of **44** by MnO_2 only produced the butterfly dimer **46**. The preceding diazaheptacene **45** was elusive, even using Uv-vis spectroscopy of the reaction solution. The diazaheptacene **45** apparently is too reactive and immediately dimerized. We could though ascertain the structure of the butterfly dimer **46** by a single crystal X-ray structure (Figure 5). It features the same

topology, the analogous hydrocarbon-based heptacenes incur, when they dimerize, as reported by Anthony et al.[21]

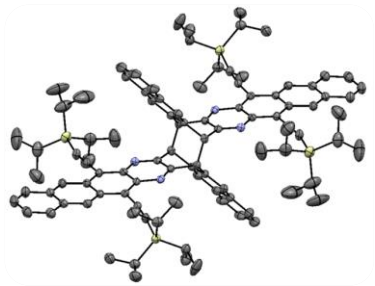
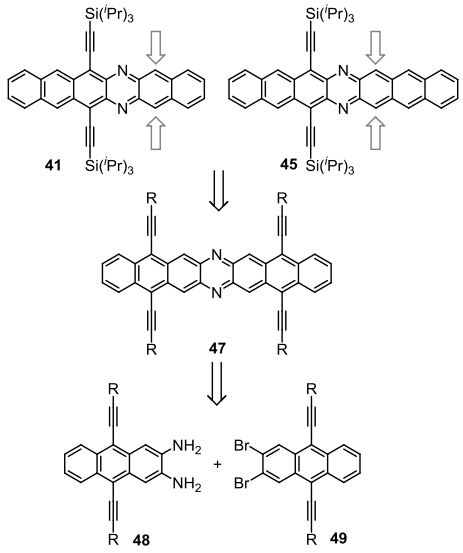


Figure 5. Single crystal X-ray structure of the butterfly dimer **46**.

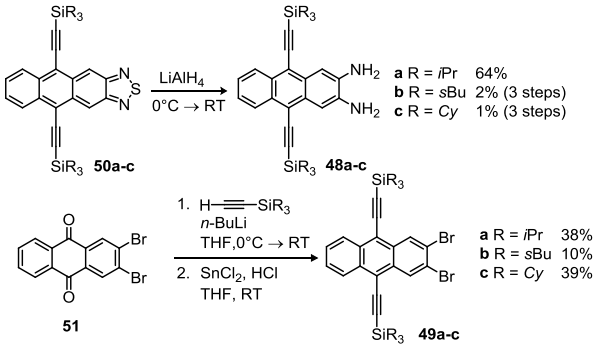
What would be the solution to the problem of dimerization of the azaheptacenes? [22] The introduction of a second set of TIPS-ethynyl groups might stabilize an azaheptacene sufficiently to allow its isolation. The two positions that participate in the cycloadditions (Scheme 15) are the positions closest to the central pyrazine ring. Blocking these sites in 41 or 45 should result in stabilization of such a large diazaacene. Retro-synthetic analysis suggests 48 and 49 as coupling partners, but neither of these two building blocks were known.

Reduction of the anthracenothiadiazole **50a-c** (Scheme 16), obtained from their respective quinones, furnished the diamines **48a-c**. The best yields are obtained for R = *iso*-Pr, with 64%. For the sterically more encumbered derivatives, the yields are lower. In the case of the dibromides **49** the yield is variable but less afflicted by steric bulk. Surprising is the decreased stability of the anthraceneothiadiazoles **50** and their reduced diamines **48a-c**, when compared to the much higher stability of isomeric **22**.

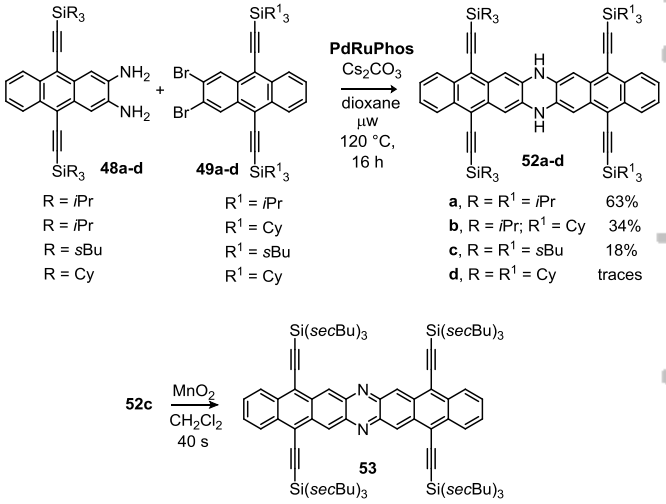


Scheme 15. Retrosynthetic scheme for the identification of the target diaza-heptacene **47** and the necessary building blocks **48** and **49**.

Coupling of **48** to **49** under optimized Pd-catalysis conditions rendered the *N,N'*-dihydrodiazaheptacenes **52a-d** in yields ranging from traces to 63% (Scheme 17). The higher the steric burden on the starting materials, the lesser the yield of the coupling. For R and R^1 = *sec*-Bu practically acceptable coupling yields are still obtained. The formed *N,N'*-dihydrodiaza-heptacenes **52** are easily oxidized by MnO_2 to give the diazaheptacenes in less than a minute (!) reaction time. Only the diazaheptacene **53** is reasonably stable and persists in solution for some time. For smaller substituents, the diazaheptacenes dimerize quickly into structures **54** and **55**.



Scheme 16. Synthesis of the diaminoanthracenes **51a-c** and the substituted dibromoanthracenes **52a-c**.



Scheme 17. Synthesis of the diazaheptacene **53**.

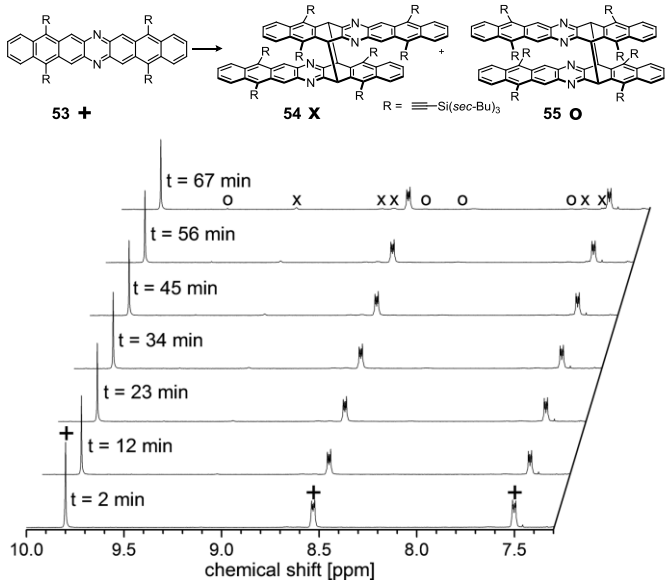


Figure 6. Time dependent ^{1}H NMR spectra of the diazaheptacene **53**. (Reproduced with permission from the American Chemical Society).

Time dependent NMR-measurements (Figure 6) reveal that **53** is stable in moderately concentrated solution for several hours. It barely starts to form the butterfly dimers **54** and **55**. We obtained a ^{13}C NMR spectrum of **53**, and in comparison to its *N,N'*-dihydro-precursor **52c** all of the signals shift to lower field, when oxidizing into **53**.

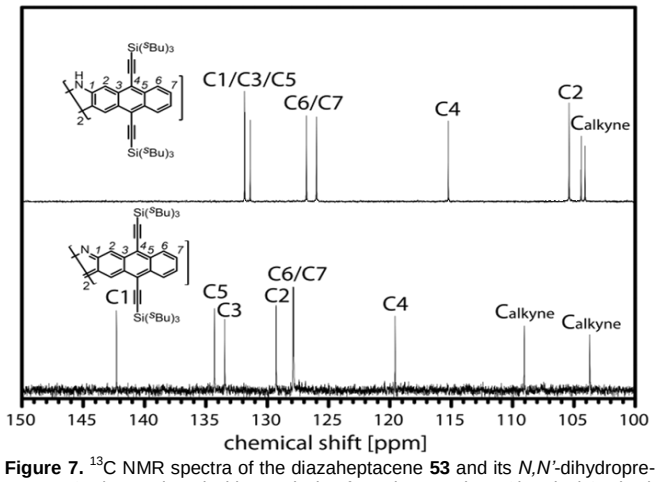


Figure 7. ^{13}C NMR spectra of the diazaheptacene **53** and its *N,N'*-dihydropre-cursor **52c** (Reproduced with permission from the American Chemical Society).

While the diazaheptacene **53** is the largest linearly annulated azaacene, its persistability only moderate. It is not clear if larger *N*-heteroacenes will be sufficiently stable to be isolated. This problem could be overcome if synthetic routes towards sterically overloaded azaacenes evolve from the currently employed strategies. Up to then, the diazaheptacene **53** is the largest available representative.

The situation is entirely different if one introduces biphenyl etc. units that enforce electronic separation of the aromatic units through the presence of more than one Clar-sextet. Under such conditions, one can make considerably larger *N*-heteroarenes,[23] however, these materials then do not show the extremely red-shifted absorption bands so prominent in the "real" azaacenes. If one allows *N,N'*-dihydropyrazine rings embedded into the system, the size limitation of seven rings is also not an issue. Interestingly enough, there is no knowledge, if band structures containing *N,N'*-dihydropyrazine units at certain intervals, would present stable and persistable materials.[24]

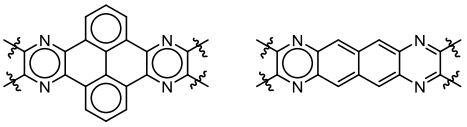
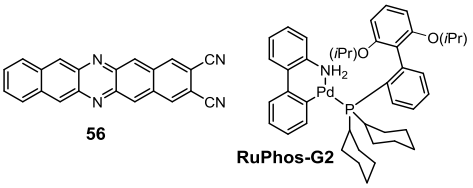


Figure 8. Separation of aromatic units according to Clar in hetero*arenes* (left) and hetero*acenes* (right). The hetero*acenes* do only have one Clar sextet, while heteroarenes have more than one Clar sextet.

Conclusions

N-Heteroacenes have come a long way from the backwaters of organic chemistry to well-performing materials for organic electronics. The substitution of an electron accepting nitrogen group into the acene framework leads to changes both with respect to their synthesis but also with respect to their properties. We and others have mostly concentrated on the introduction of pyrazine units into azaacenes. Pyrazines are -from a retrosynthetic point of view - modularized into azaacenes, as they can be quickly built up by the combination of an aromatic *ortho*-diamine with an aromatic *ortho*-dielectrophile. When employing aromatic *ortho*-dihalides as electrophiles, Pd-catalyzed coupling with *ortho*-diamines is a powerful new method to build up such *N,N'*-dihydroazaacenes. The accessibility of different aromatic *ortho*-dihalides, coupled with the modules **12** and **20-22**, makes series of different azaacenes easily available in a construction-set type approach.



Recently Koert et al.[25] have employed 2,3-diaminonaphthalene as coupling partner for different dibromonaphthalenes, giving rise to interesting diazapentacenes, including the dicyano-diazapentacene **56** and other, fluorinate azaacenes. These elegant coupling reactions were successful, as the authors employed RuPhos-G2 as the active catalyst precursor.

Questions for the synthesis of larger heteroacenes remain, and it is for example not clear if long-term stable azaheptacenes and stable azaoctacenes can be prepared. It might be useful to look at targets with at least four nitrogen atoms, as they apparently

are less prone towards Diels-Alder dimerization. An important issue is the relative sensitivity of the Pd-catalyzed couplings towards steric pressure, an issue that will have to be addressed by the use of more advanced phosphine ligands, as recently demonstrated by Koert et al.[25]

Over all, the Pd-catalyzed formation of the dihydropyrazines is a major progress in the preparation of novel diaza- and tetraazapentacenes–heptacenes. This powerful methodology has accessed molecular topologies that simply can otherwise not be achieved.

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Keywords: Acene • *N*-Heteroacene • Pd-catalysis • electron transport materials • *N,N'*-Dihydropyrazine

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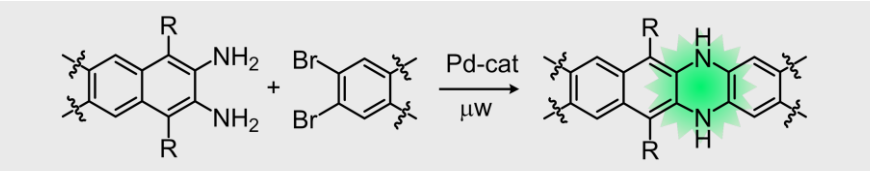
Entry for the Table of Contents

CONCEPT



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Page No. – Page No.

The Palladium way to the larger N-heteroacenes