ChemPubSoc Europe

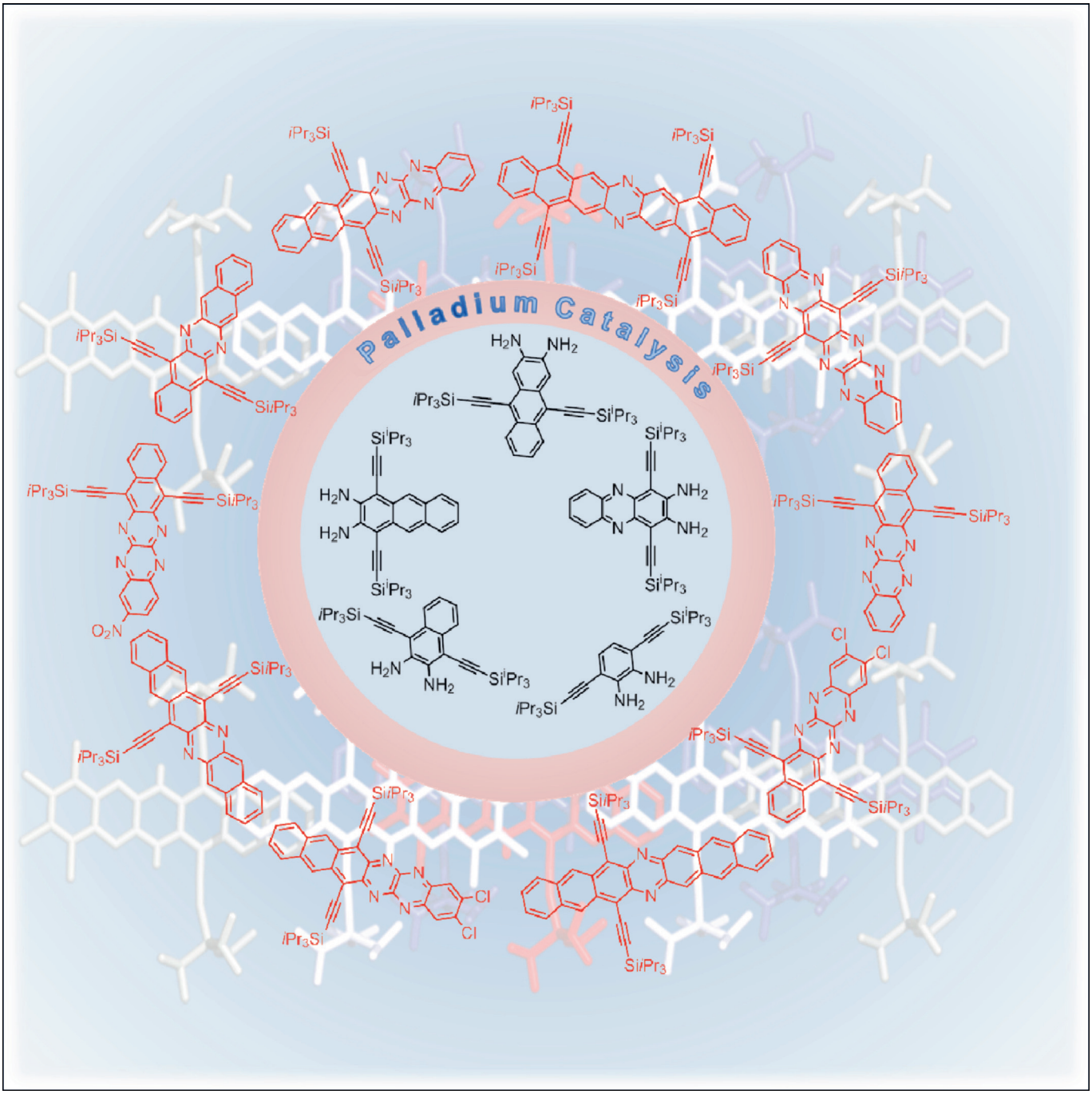
DOI: 10.1002/chem.201505018

CHEMISTRY A European Journal Concept

Palladium Catalysis

The Palladium Way to N-Heteroacenes

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



© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Abstract: Novel synthetic methodologies allow increasingly efficient access to known organic materials, as well as the preparation of otherwise inaccessible species. Pd-catalyzed coupling of aromatic dihalides to *ortho*-diaminoarenes furnishes embedded stable *N*,*N*′-dihydropyrazines expediently and in often excellent yields. The embedded *N*,*N*′-dihydropyrazines can then be oxidized by MnO_2 to give substituted azatetracenes, azapentacenes, azahexacenes, and azaheptacenes, which are soluble, processable, and stable. This powerful Pd-catalyzed methodology allows the preparation of azaacenes, including diaza-, tetraaza- and hexaazaacenes. In combination with a suitable Pd precursor, Buchwald-type biarylphosphines have been shown to give excellent results. Activated dihalides such as 2,3-dihaloquinoxalines are coupled easily under simplified conditions, whereas 2,3-dibromoacenes require more stringent conditions and advanced catalyst precursors. Pd catalysts effect the assembly of 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, besides allowing increasingly efficient access to known key compounds, they enable the preparation of new classes of materials, with both issues being important. In recent years, we have tackled this task for the synthesis of larger azaacenes by developing Pd-catalyzed coupling reactions of aromatic *ortho*-dihalides to aromatic *ortho*-diamines.

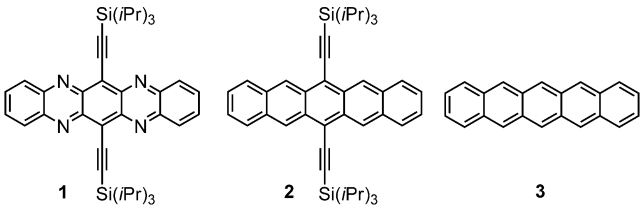
N-Heteroacenes[1]

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. Moreover, since Anthony's TIPSpen (**2**) is commercially available, both vacuum-processed and solution-processed organic field effect transistors (OFETs) of this material are easily prepared.[2] Pentacene (**3**) and its derivatives are hole transporters, as oxidation of the pentacene nucleus is much easier than its reduction, which is necessary for the generation of negative charge carriers in the organic semiconducting materials. Problems with water, oxygen, and trap states render difficult the use of pentacenes for electron transport.[3]

[a] *Prof. U. H. F. Bunz, Dr. J. U. Engelhart*
Organisch-Chemisches Institut
Ruprecht-Karls Universität Heidelberg
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
E-mail: uwe.bunz@oci.uni-heidelberg.de

[b] *Dr. J. U. Engelhart*
New Address: Department of Chemistry, MIT
77 Massachusetts Av., Cambridge, MA 02139 (USA)

Charge transport is, in a simplified way, proportional to the rate of degenerate charge transfer between two identical neighboring molecules (Figure 1).



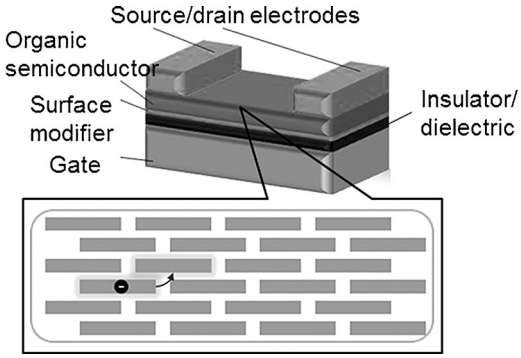


Figure 1. Schematic view of an organic thin-film transistor with simplified charge (electron) transport in the film.

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. To optimize charge carrier mobility μ, *t* should be maximized, whereas λ should be minimized [Eq. (1)]. Generally, both factors can be favorable in larger acenes; particularly the rigid structure, but also the size of the acenes minimizes λ.

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

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, that is, increasing electron affinities, yet still retaining the superb properties of pentacenes would be desirable. Several groups have exploited the attachment of halogen atoms to pentacene.[5] The alternative is the introduction of electronegative atoms directly into the perimeter of the acenes, as is the case in N-heteroacene **1**. In the solid state, **1** packs in a similar manner to TIPS–pentacene **2** (Figure 2).

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

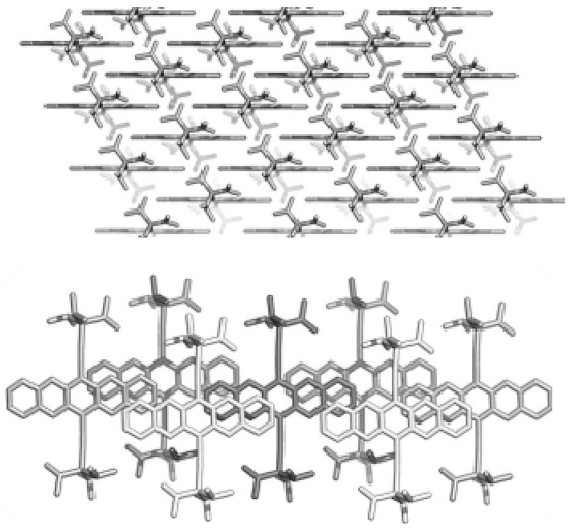


Figure 2. Packing of compound **1** in the solid state. This tetraazapentacene shows electron mobilities of up to $\mu_{E(1)} = 3.3\ cm^2V^{-1}s^{-1}$ with $I_{on}/I_{off} = 6\times10^6$.

In 2007, Winkler and Houk[6] calculated that several N-heteropentacenes display small reorganization energies and frontier orbital positions that should make them useful as electron transport materials. Several years later, Miao et al. reported the preparation of compound **1**,[7] which exhibited spectacular electron transporting properties with mobilities of up to $3.3\ cm^2V^{-1}s^{-1}$.[8] Compound **1** is now a state-of-the-art electron-transport material.

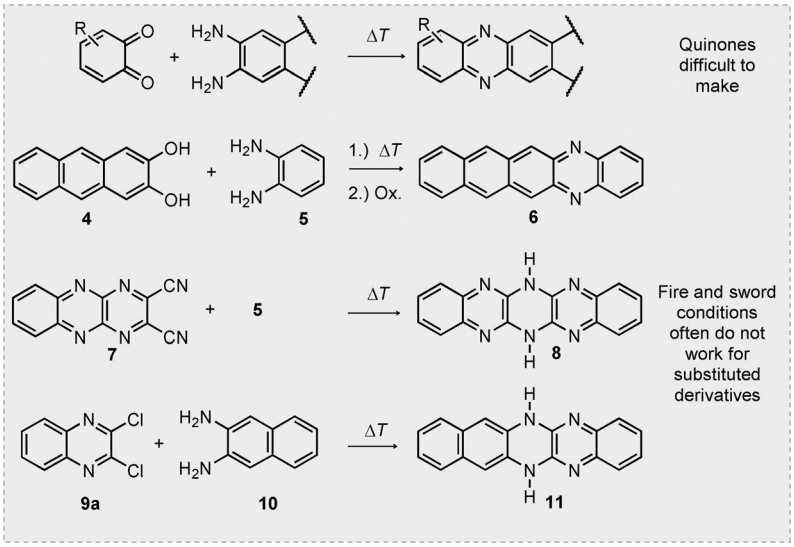
Buchwald–Hartwig amination for cyclizing C–N bond formation

The Buchwald–Hartwig amination is an established and important reaction that forms sp^2 C–N bonds with a variety of different catalysts and Pd precursors.[9,10] Many variants of this coupling have been developed. The synthesis of five-membered rings, such as those of the indole type, have been described and the Pd-catalyzed synthesis of acridines has also been reported,[8] but the use of Pd catalysis of other six-membered N-heterocycles 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 means of their preparation. As an aside, for most of the direct condensation methods that will be discussed, aza*tetra*cenes form directly in their oxidized form, whereas 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 $4n$ π-system commences; according to calculations,[11] two Clar sextets are energetically much more favorable than the presence of one large aromatic system. For 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 of strong base and heat, which is not the case for higher *N*,*N*′-dihydro azaacenes.

In the earliest azacene syntheses (Scheme 1), dihydroxyarenes such as **4**, dichloroquinoxaline **9a**, or dicyanoquinoxaline **7** were melted together with *ortho*-phenylenediamine **5** or *ortho*-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 *N*,*N*′-dihydro compounds, such as **11** or **8**. A similar reaction that works in the solution phase is that of *ortho*-quinones with

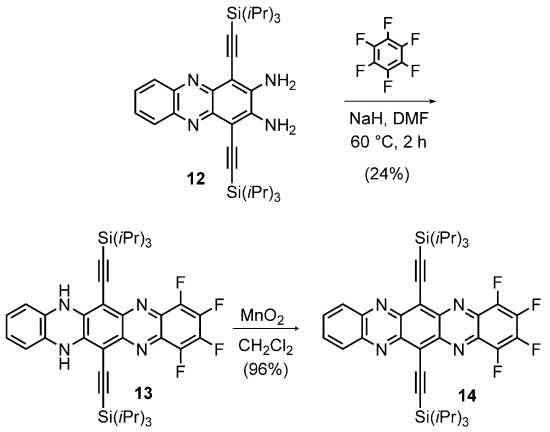


Scheme 1. Classic synthetic approaches towards azaacenes.

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

diamines. Although they are more reactive than the dihydroxy compounds, *ortho*-quinones are often (not always) more sensitive and therefore harder to synthesize, but also more reactive and can lead to azaacenes and various extended azaarenes.[12] Mastalerz and co-wokers assembled aromatic systems consisting of up to 11 fused six-membered rings by using this condensation strategy.[13] The direct formation of azatetracenes by deploying *ortho*-quinones worked well, but for azapentacenes yields were variable.[14] Very recently, Zhang and co-workers synthesized hexaazapentacenes by condensation of tetraaminophenazine with various diketones.[15]

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 to give tetraazaacene **14**.

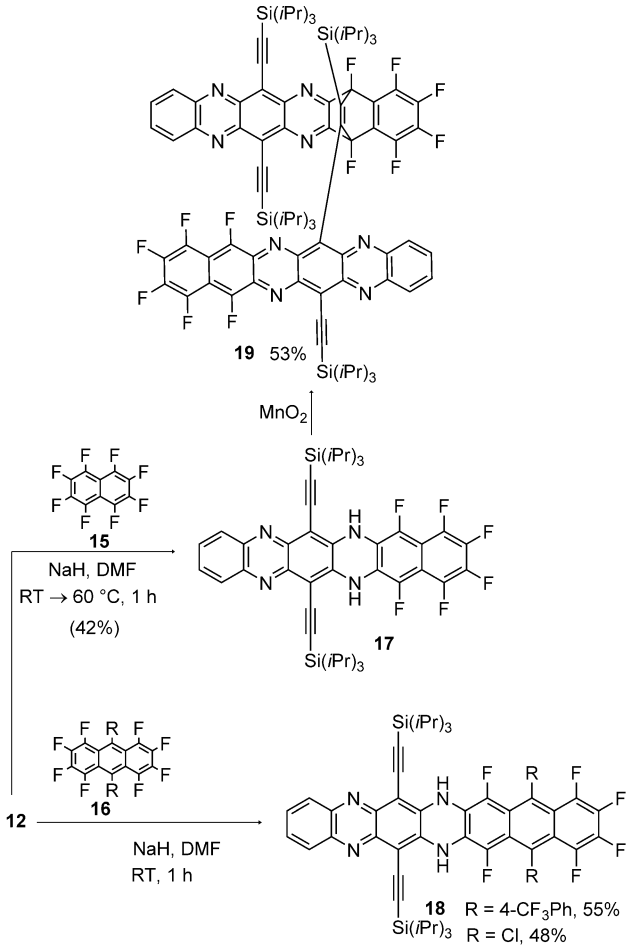


Scheme 2. Synthesis of a partially fluorinated tetraazapentacene **14** by an addition–elimination route.

Extension of this concept generates the *N,N'*-dihydro compounds **17** and **18** in reasonable yields (Scheme 3).[16] For **18**, oxidation is no longer possible, due to its low-lying HOMO, whereas for **17** only the dimer **19** is formed upon oxidation with MnO_2, probably via the fleeting intermediate tetrafluorotetraazahexacene.

Harnessing quinones, we treated 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** in good to excellent yields (Scheme 4).[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.

However, this arsenal of established methods can fail in the synthesis of substituted azaacenes. The harsh conditions do not allow the coupling of alkynylated diamines **20**–**22** to dichloroquinoxaline **9a** or the formation of dihydroxyarenes. Compounds **20**–**22** are excellent starting materials and it was



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

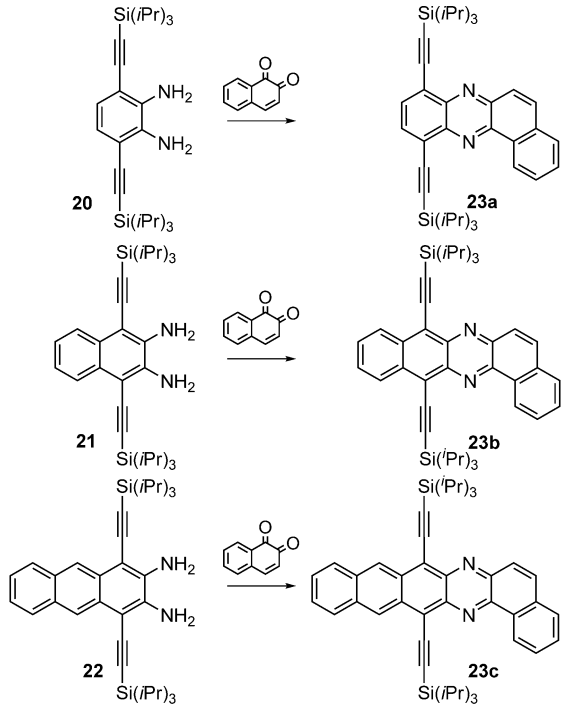
an important challenge to find synthetic methods to transform them into azaacenes. Pd-catalyzed coupling reactions were an attractive proposition.

Coupling of Activated Halides to Alkynylated Diamines by Pd Catalysis

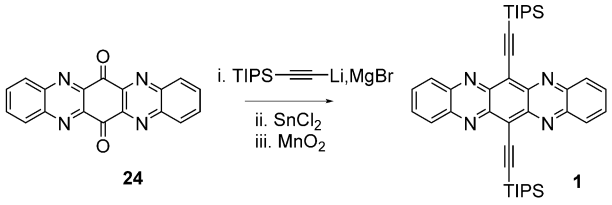
In our first experiments, we treated the diaminonaphthalene **21** with dichloroquinoxaline **9a** in the presence of $[(Ph_3P)_2PdCl_2]$ in boiling Hünig's base (*N,N*-diisopropylethylamine), forming traces of the desired product **25a**. Upon changing the catalyst system into $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) 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 also worked satisfactorily. In an extension of this concept, we also treated substituted dichloroquinoxalines **9b** and **c** with **21**, to give substituted, stable tetraazapentacenes **26b** and **c** as stable compounds in good yields after coupling and oxidation.

In the coupling of **21** with the tetrachloride **9b**, only two of the four chloride substituents participate, that is, only the activated chlorides react. 5-Nitro-2,3-dichloroquinoxaline **9c**

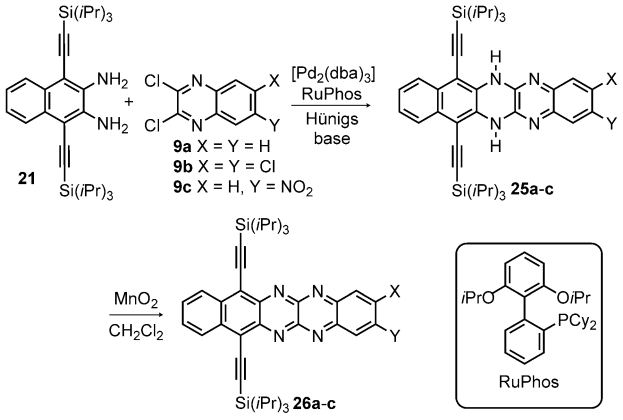
© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



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



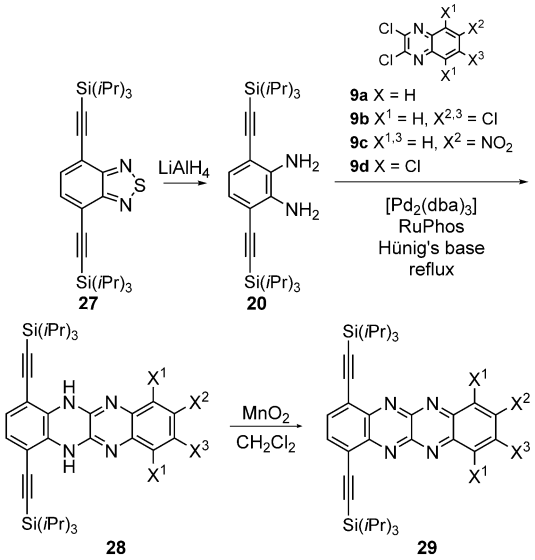
Scheme 5. Synthesis of compound **1** by using Anthony's alkynylation strategy.



Scheme 6. Synthesis of tetraazapentacenes **26a–c** by Pd catalysis.

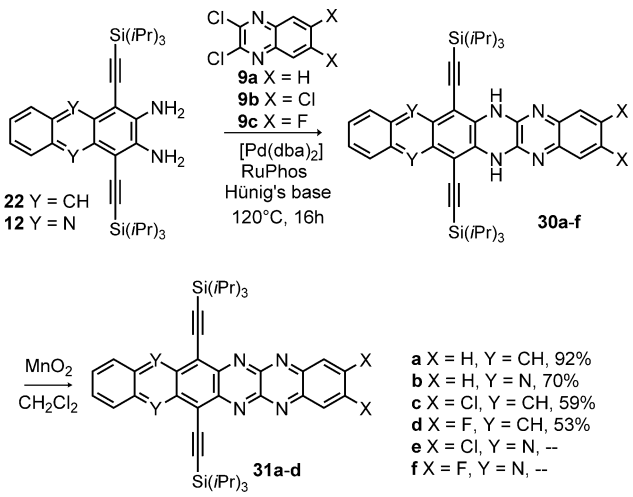
also couples easily with diamine **21**. The coupling reactions proceed smoothly in Hünig's base (14–18 h) at its boiling temperature. In each case, 5 mol% of catalyst was used. The isolated *N,N'*-dihydro tetraazapentacenes were all easily oxidized by MnO_2.

This approach provides access to tetraazatetracenes (Scheme 7). Although the Pd-catalyzed coupling of **5** to dichloropyrazines worked only in traces, the diaminobenzene **20**, obtained through reduction of diethynylbenzothiadiazole (**27**) coupled to dichloroquinoxalines **9a–d** to give the *N,N'*-dihydrotetraazatetracenes **28a–d**; one of the few cases where *N,N'*-dihydroazatetracenes were isolated. MnO_2 then oxidized **28a–d** to give the tetraazatetracenes **29a–d**.



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

This reaction cascade was extended to the synthesis of the first azahexacenes (Scheme 8).[18] Both tetraaza- and hexa-azahexacenes were obtained by Pd-catalyzed coupling of the substituted diaminoanthracene (**22**) or -phenazine (**12**) with activated dichloroquinoxalines **9a–c** (Scheme 8). Although all



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

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

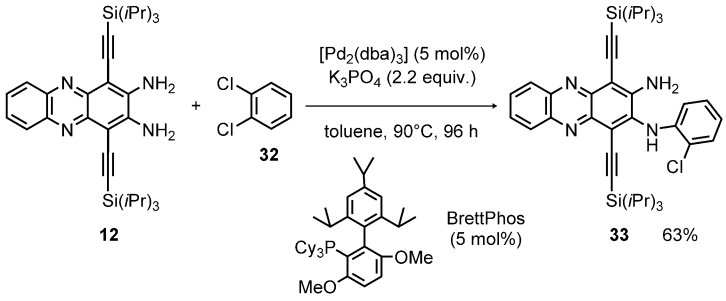
of the possible six *N,N′*-dihydroazahexacenes **30a–f** were obtained in high yields, only the derivatives **30a–d**, leading to **31a–d**, could be oxidized by MnO_2. The other two dihydro derivatives (**30e** and **f**) had HOMOs that were energetically too low-lying, and could not be oxidized into azahexacenes **31**.

The Problem of Coupling Deactivated Dihalides[19]

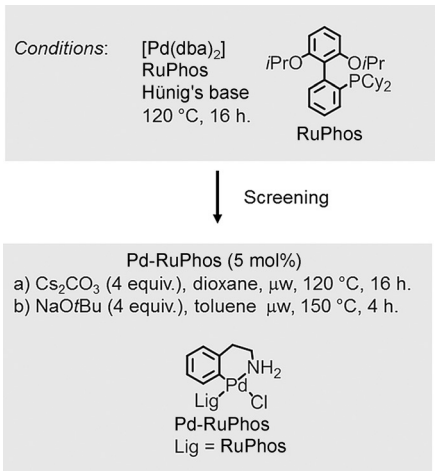
The Pd-catalyzed coupling of **20–22** to activated *ortho*-dihalides is facile and furnishes the coupling products in good to excellent yields. However, the coupling to unactivated aromatic halides, such as 2,3-dibromonaphthalene (**34**) or 2,3-dibromoanthracene (**43**), was not yet possible. Therefore,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

While the choice of the phosphane ligand was relatively clear, as the Buchwald-type ligands were by far the best systems we had tested and most such ligands worked, the Pd source $[Pd_2(dba)_3]$ was not ideal (Scheme 9). In a first experiment, coupling of **12** to **32** under modified standard conditions furnished the monoarylated species **33** in 63% yield (Scheme 9), 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 Pd–RuPhos precatalyst, whereas lower loadings of Pd–RuPhos led to decreased yields and 10 mol% of the precatalyst increased the yield only slightly. As base/solvent combination, we could either employ Cs_2CO_3 in dioxane or NaO*t*Bu in toluene, both under microwave irradiation at temperatures of 120–150 °C.

There are limits to this approach. We were never able to couple **12** with dichloro- (**32**) or dibromobenzene (**37**) to form the cyclic product. In the best cases, monoarylated products were isolated. If strong bases were used, catalyst decomposition was observed, whereas weak bases did not give any reaction. Bidentate and sterically encumbered phosphine ligands worked best, but only gave low conversions with dibromides. *Ortho*-dichlorobenzene worked best with a highest monoarylated open product yield of 63%. We assumed the superiority of chlorides to be due to steric effects, indicating that the reaction proceeded via a sterically crowded intermediate.



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

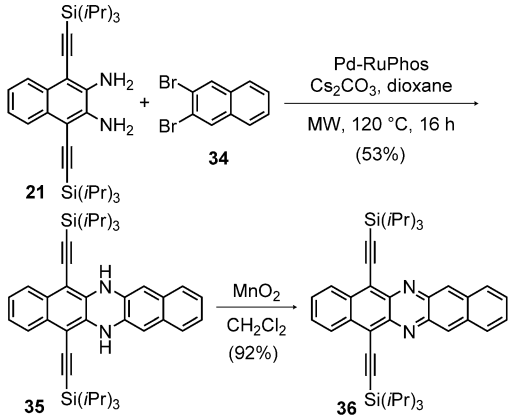


Scheme 10. Developing reaction conditions for the coupling of non-activated aromatic dihalides to aromatic diamines.

Consecutive optimizations to ring-close **33** were not very successful either, as sterically encumbered ligands provided stability but suppressed ring closure.

Azapentacenes

The diamine **21** reacted with dibromonaphthalene **34** to form **35** in 53% yield under the optimized reaction conditions (Scheme 11). 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 poisoning was observed. We believe that the catalyst poisoning was due to the oxidation of the formed dihydro azaacene **35**. 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). According to a similar reaction scheme, dibromobenzene **37** was coupled to the diaminoanthracene **22** to furnish **39** in 53%



Scheme 11. Synthesis of diazapentacenes from unactivated dihalides.

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

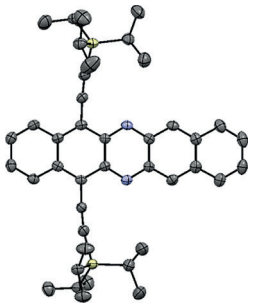
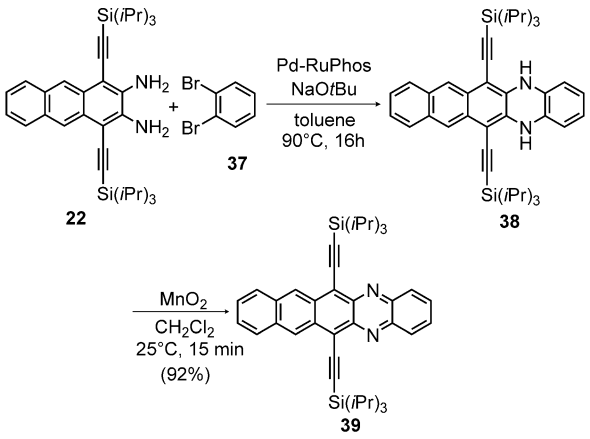


Figure 3. Single-crystal X-ray structure of the diazapentacene **36**. Thermal ellipsoids are set at 50% probability and hydrogen atoms are omitted for clarity.

yield (Scheme 12). However, some monoarylated product was always formed, even when benzoquinone was employed to re-oxidize the Pd catalyst. These modified conditions provide a powerful strategy to access azapentacenes that are otherwise available only with difficulty. This Pd-catalyzed coupling was also employed by Müllen and coworkers to prepare some attractive bisanthracenothiadiazoles.[20]

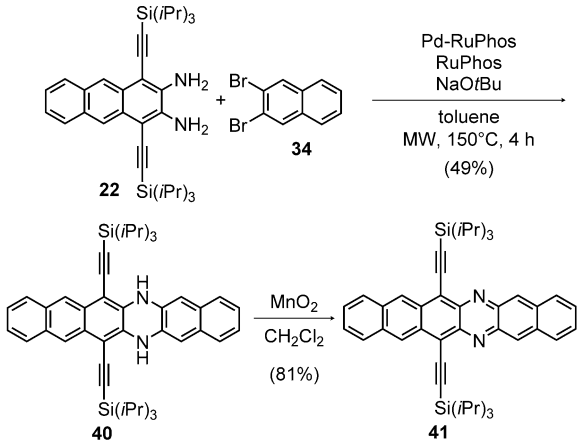
Azahexacenes and Azaheptacenes

Could one make diazahexacenes and possibly diazaheptacenes



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

using Pd-catalyzed coupling sequences (see above)? Although we had previously prepared tetraaza- and hexaazahexacenes, diazahexacenes and diazaheptacenes were unknown at the beginning of our synthetic endeavor. With the experience of 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 the Buchwald–Hartwig 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 analogous to that of the dimerization products formed from Anthony's hexacenes (Figure 4).[21]



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

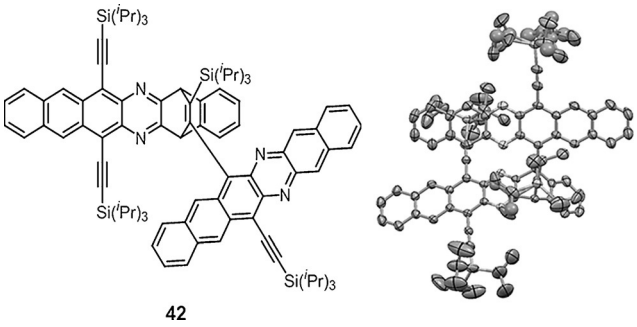
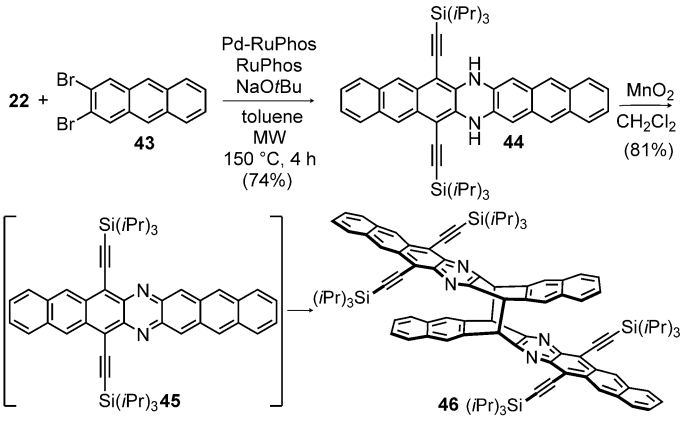


Figure 4. Diels-Alder dimerization product **42** of azahexacene **41** (left) and single-crystal X-ray structure of **42** (right). Thermal ellipsoids are set at 50% probability and hydrogen atoms are omitted for clarity.

By employing the same strategy (Scheme 14), we coupled 2,3-dibromoanthracene **43** to the diamine **22**. The *N*,*N*′-dihydrodiazaheptacene **44** was formed in 74% yield (Scheme 14). However, oxidation of **44** by MnO_2 only produced the butterfly dimer **46**. The preceding diazaheptacene **45** was elusive, going undetected even by UV/Vis spectroscopy of the reaction solu-



Scheme 14. Pd-catalyzed synthesis of an azaheptacene.

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

tion. Diazaheptacene **45** was apparently too reactive and immediately dimerized. We could, however, ascertain the structure of the butterfly dimer **46** by a single-crystal X-ray structure (Figure 5), which adopts the same topology that the analogous hydrocarbon-based heptacenes incur when they dimerize, as reported by Anthony and co-workers.[21]

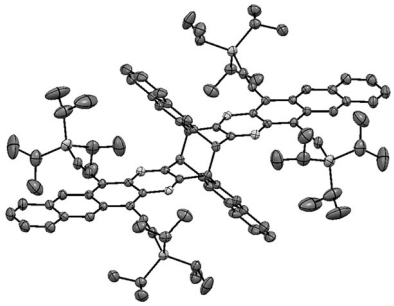
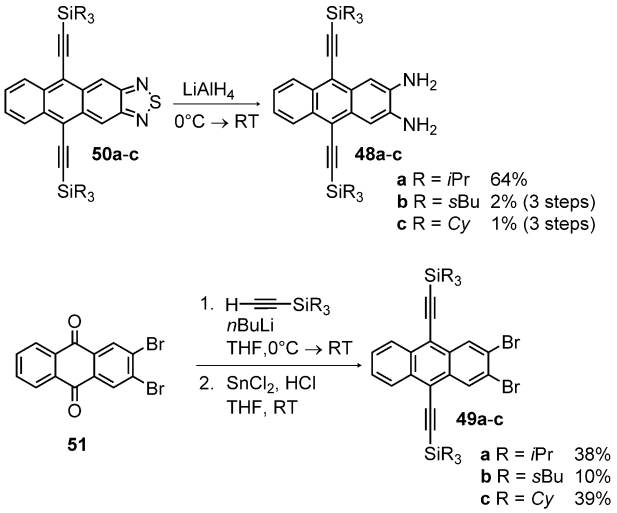


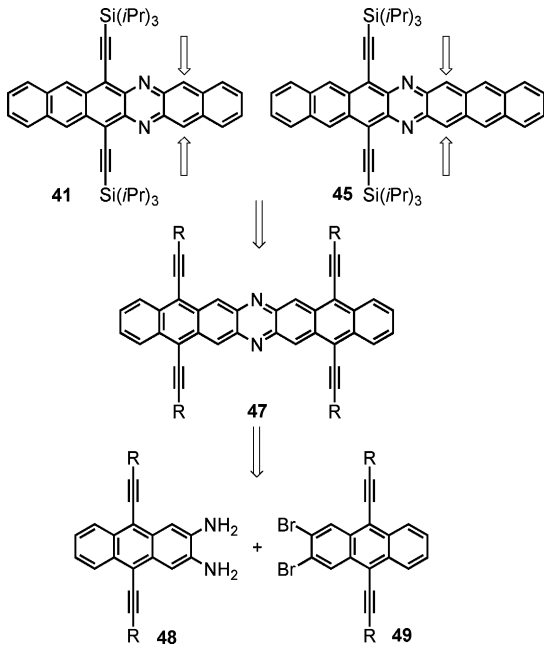
Figure 5. Single-crystal X-ray structure of the butterfly dimer **46**. Thermal ellipsoids are set at 50% probability and hydrogen atoms are omitted for clarity.



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

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

Reduction of the anthracenothiadiazoles **50a–c** (Scheme 16), obtained from their respective quinones, furnished the diamines **48a–c**. The best yield (64%) was obtained for R = *i*Pr. For the sterically more encumbered derivatives, the yields were lower. In the case of the dibromides **49a–c**, the yields were variable but less afflicted by steric bulk. Surprisingly, the stability of the anthraceneothiadiazoles **50** and their reduced diamines **48a–c** was much decreased in comparison to the isomeric structure (**22**).



Scheme 15. Retrosynthetic scheme for the identification of target diazaheptacene **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 were still obtained. The formed *N*,*N*′-dihydrodiazaheptacenes **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 to form structures **54** and **55**.

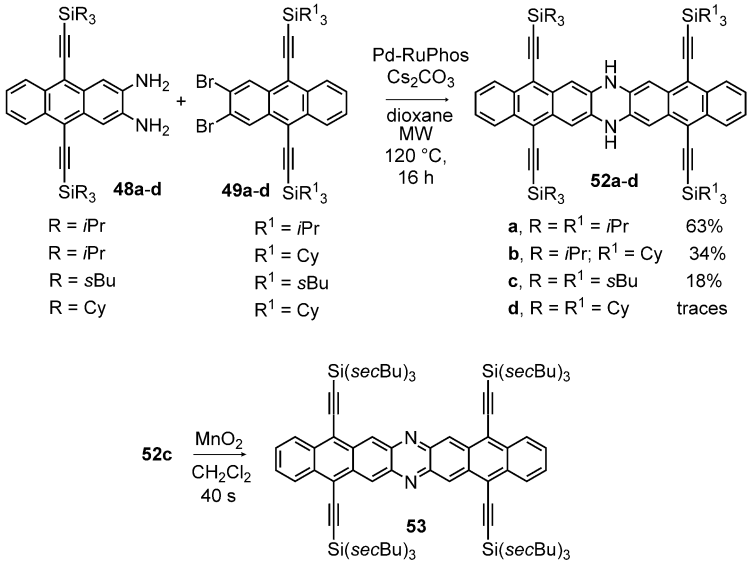
Time-dependent NMR spectroscopy measurements (Figure 6) revealed that **53** is stable in moderately concentrated solution, barely having started to form the butterfly dimers **54** and **55** after several hours.

We obtained a ^{13}C NMR spectrum of **53**, and, in comparison to its *N*,*N*′-dihydro-precursor **52c**, all of the signals had shifted to lower field, when oxidizing to **53** (Figure 7).

The diazaheptacene **53** is the largest linearly annulated azaacene reported to date, but its stability is only moderate. It is not clear whether 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. Until then, diazaheptacene **53** will remain the largest isolable representative.

The situation is entirely different if one introduces, for example, pyrene units, which enforce electronic separation of

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



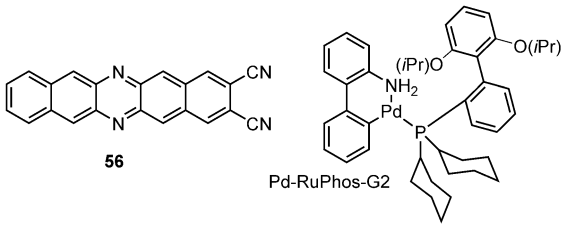
Scheme 17. Synthesis of diazaheptacene **53**.

the aromatic units through the presence of more than one Clar sextet (Figure 8). Under such conditions, one can make considerably larger N-heteroarenes.[23] However, these materials then do not show the extremely redshifted absorption bands that are 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, it is not known whether band structures containing *N*,*N*′-dihydropyrazine units at certain intervals would present stable and persistent materials <.[24]

Conclusion

N-Heteroacenes have come a long way from the backwaters of organic chemistry to high-performance materials for organic electronics. The substitution of an electron-accepting nitrogen group into the acene framework leads to changes with respect to both their synthesis and their properties. Our group 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 and co-workers reported the use of 2,3-diaminonaphthalene as coupling partner for different dibromonaphthalenes,[25] giving rise to interesting diazapentacenes, including the dicyanodiazapentacene **56** and other,



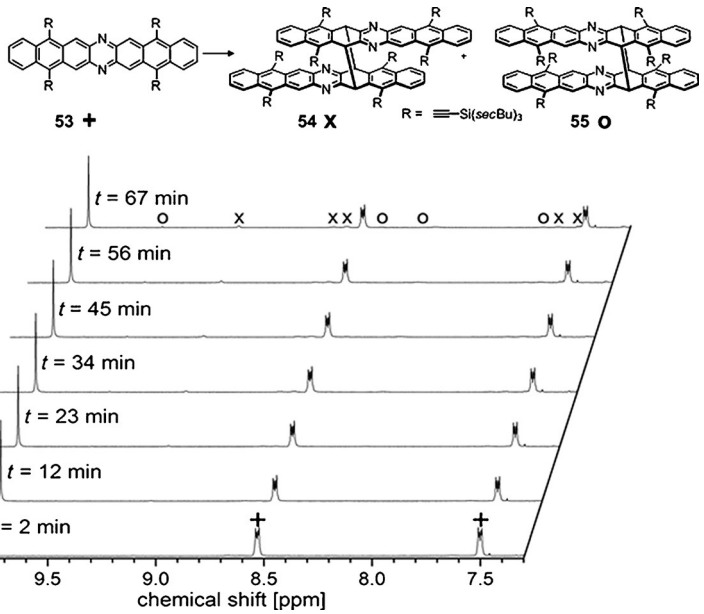


Figure 6. Time-dependent ^{1}H NMR spectra of the diazaheptacene **53** (reproduced with permission from the American Chemical Society).

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

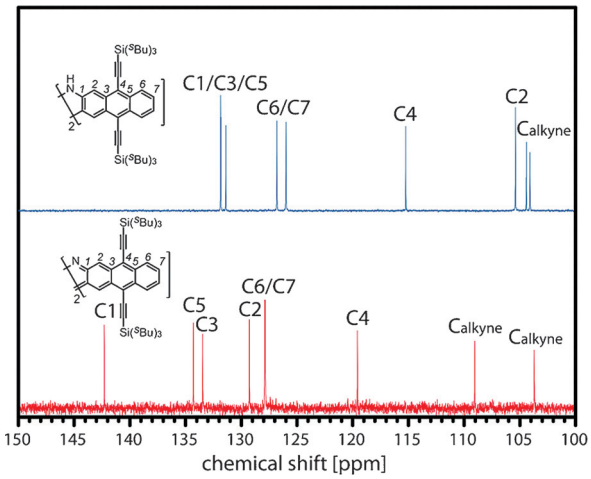


Figure 7. ^{13}C NMR spectra of the diazaheptacene **53** and its *N,N'*-dihydro precursor **52 c** (reproduced with permission from the American Chemical Society).

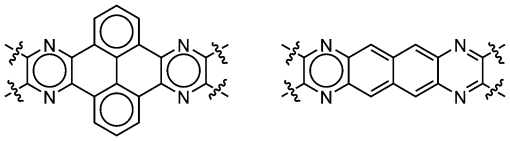


Figure 8. Separation of aromatic units according to Clar in hetero*arenes* (left) and hetero*acenes* (right). The hetero*acenes* only have one Clar sextet, whereas heteroarenes have more than one.

fluorinated azaacenes. These elegant coupling reactions were successful, as the authors employed Pd–RuPhos-G2 as the active catalyst precursor.

Questions regarding 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 are apparently less prone to Diels–Alder dimerization. An important issue is the relative sensitivity of the Pd-catalyzed couplings to steric crowding, an issue that will have to be addressed by the use of more advanced phosphine ligands, as demonstrated by Koert and co-workers.[25]

In summary Pd-catalyzed formation of dihydropyrazines represents a major advance in the preparation of novel diaza- and tetraazapenta-, -hexa-, and -heptacenes. This powerful methodology enables access to molecular topologies that can otherwise not be simply achieved.

Acknowledgements

U.H.F.B. thanks the DFG (Bu771/7-2) for funding and J.U.E. thanks the Stiftung Telekom for a scholarship.

Keywords: acenes · electron transport materials · homogeneous catalysis · N-heterocycles · palladium

[1] Reviews on this topic a) U. H. F. Bunz, *Acc. Chem. Res.* **2015**, *48*, 1676–1686; b) U. H. F. Bunz, J. U. Engelhart, B. D. Lindner, M. Schaffroth, *Angew. Chem.* **2013**, *52*, 3810–3821; c) U. H. F. Bunz, *Pure Appl. Chem.* **2010**, *82*, 953–968; d) U. H. F. Bunz, *Chem. Eur. J.* **2009**, *15*, 6780–6789; e) Q. Miao, *Synlett* **2012**, 326–336; f) G. J. Richards, J. P. Hill, T. Mori, K. Ariga, *Org. Biomol. Chem.* **2011**, *9*, 5005–5017; g) J. Li, Q. Zhang, *ACS Appl. Mater. Interfaces* **2015**, *7*, 28049–28062.

[2] a) J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028–5048; b) J. E. Anthony, *Angew. Chem.* **2008**, *47*, 452–483; c) J. E. Anthony, J. S. Brooks, D. L. Eaton, S. R. Parkin, *J. Am. Chem. Soc.* **2001**, *123*, 9482–9483.

[3] C. Bock, D. V. Pham, U. Kunze, D. Käfer, G. Witte, C. Wöll, *J. Appl. Phys.* **2006**, *100*, 114517.

[4] J. L. Bredas, J. P. Calbert, D. A. da Silva, J. Cornil, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5804–5809.

[5] a) Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato, S. Tokito, *J. Am. Chem. Soc.* **2004**, *126*, 8138–8140; b) M. L. Tang, J. H. Oh, A. D. Reichardt, Z. N. Bao, *J. Am. Chem. Soc.* **2009**, *131*, 3733–3740.

[6] M. Winkler, K. N. Houk, *J. Am. Chem. Soc.* **2007**, *129*, 1805–1815.

[7] S. Miao, A. L. Appleton, N. Berger, S. Barlow, S. R. Marder, K. I. Hardcastle, U. H. F. Bunz, *Chem. Eur. J.* **2009**, *15*, 4990–4993.

[8] Z. X. Liang, Q. Tang, J. B. Xu, Q. A. Miao, *Adv. Mater.* **2011**, *23*, 1535–1539.

[9] a) D. S. Surry, S. L. Buchwald, *Angew. Chem.* **2008**, *47*, 6338–6361; b) D. S. Surry, S. L. Buchwald, *Chem. Sci.* **2011**, *2*, 27–50; c) Z. X. Huang, Y. Yang, Q. Xiao, Y. Zhang, J. B. Wang, *Eur. J. Org. Chem.* **2012**, *2012*, 6586–6593.

[10] J. F. Hartwig, *Acc. Chem. Res.* **2008**, *41*, 1534–1544.

[11] J. I. Wu, C. S. Wannere, Y. Mo, P. v. R. Schleyer, U. H. F. Bunz, *J. Org. Chem.* **2009**, *74*, 4343–4349.

[12] B. Kohl, F. Rominger, M. Mastalerz, *Org. Lett.* **2014**, *16*, 704–707.

[13] B. Kohl, F. Rominger, M. Mastalerz, *Angew. Chem.* **2015**, *54*, 6051–6056.

[14] S. Miao, S. M. Brombosz, P. v. R. Schleyer, J. I. Wu, S. Barlow, S. R. Marder, K. I. Hardcastle, U. H. F. Bunz, *J. Am. Chem. Soc.* **2008**, *130*, 7339–7344.

[15] a) G. Li, W. Wu, J. Gao, C. Wang, J. Li, H. Zhang, Y. Zhao, Y. Zhao, Q. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 20298–20301; b) G. Li, J. Miao, J. Cao, J. Zhu, B. Liu, Q. Zhang, *Chem. Commun.* **2014**, *50*, 7656–7658.

[16] J. U. Engelhart, B. D. Lindner, O. Tverskoy, F. Rominger, U. H. F. Bunz, *J. Org. Chem.* **2013**, *78*, 10832–10839.

[17] S. Hahn, P. Biegger, M. Bender, F. Rominger, U. H. F. Bunz, *Chem. Eur. J.* **2016**, *22*, 869–873.

[18] a) J. U. Engelhart, B. D. Lindner, M. Schaffroth, D. Schrempp, O. Tverskoy, U. H. F. Bunz, *Chem. Eur. J.* **2015**, *21*, 8121–8129; b) B. D. Lindner, J. U. Engelhart, O. Tverskoy, A. L. Appleton, F. Rominger, A. Peters, H.-J. Himmel, U. H. F. Bunz, *Angew. Chem.* **2011**, *50*, 8588–8591.

[19] J. U. Engelhart, B. D. Lindner, O. Tverskoy, F. Rominger, U. H. F. Bunz, *Chem. Eur. J.* **2013**, *19*, 15089–15092.

[20] D. Xia, X. Guo, L. Chen, M. Baumgarten, A. Keerthi, K. Müllen, *Angew. Chem.* **2016**, *55*, 941–944.

[21] B. Purushothaman, S. R. Parkin, J. E. Anthony, *Org. Lett.* **2010**, *12*, 2060–2063.

[22] a) J. U. Engelhart, O. Tverskoy, U. H. F. Bunz, *J. Am. Chem. Soc.* **2014**, *136*, 15166–15169; b) A. Mateo-Alonso, *Chem. Soc. Rev.* **2014**, *43*, 6311–6324.

[23] a) Y. Fogel, M. Kastler, Z. H. Wang, D. Andrienko, G. J. Bodwell, K. Müllen, *J. Am. Chem. Soc.* **2007**, *129*, 11743–11749; b) B. X. Gao, M. Wang, Y. X. Cheng, L. X. Wang, X. B. Jing, F. S. Wang, *J. Am. Chem. Soc.* **2008**, *130*, 8297–8306; c) A. Mateo-Alonso, N. Kulisic, G. Valenti, M. Marcaccio, F. Paolucci, M. Prato, *Chem. Asian J.* **2010**, *5*, 482–485; d) C. Y. Wang, J. Zhang, G. K. Long, N. Aratani, H. Yamada, Y. Zhao, Q. C. Zhang, *Angew. Chem.* **2015**, *54*, 6292–6296.

[24] L. P. Yu, M. Chen, L. R. Dalton, *Chem. Mater.* **1990**, *2*, 649–659.

[25] J. Schwaben, N. Münster, M. Klues, T. Breuer, P. Hofmann, K. Harms, G. Witte, U. Koert, *Chem. Eur. J.* **2015**, *21*, 13758–11377.

Received: December 13, 2015
Published online on February 17, 2016

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim