Palladium-Catalyzed Naphthylation of Acenaphthylene

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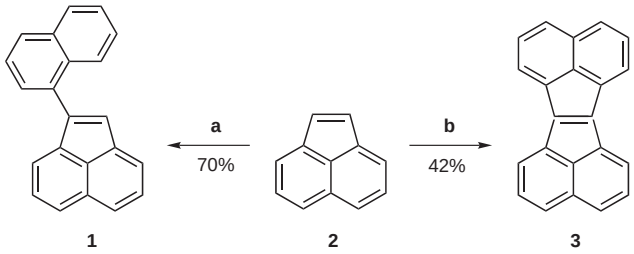
Dedicated to R. F. Heck on the occasion of his 75th birthday

Abstract: A bisnaphthyl-substituted acenaphthylene is synthesized via two independent two-step procedures, Pd-catalyzed and classically with Grignard reagents. The subsequent dehydrocyclization stops after the first carbon–carbon bond formation, leading to an octacyclic π-system as the main product.

Key words: palladium, Heck reaction, polycyclic aromatic, hydrocarbons, annulated cyclopentadienes

The discovery of the fullerenes has motivated numerous studies of the synthesis and the properties of polycyclic aromatic hydrocarbons with integrated five-membered carbocyles, thus representing partial structures of these nanospheres.[1–3] Our palladium-catalyzed single-step syntheses of the mononaphthyl-substituted acenaphthylene **1**[4] and of the strained hexacyclic hydrocarbon acenaphth[1,2-*a*]acenaphthylene (**3**) with two annulated pentagons (Scheme 1)[4] prompted us to investigate the naphthylation of acenaphthylene (**2**) in detail, targeting for the bisnaphthylacenaphthylene **5**, as an interesting candidate for oxidative ring-closing reactions.[5]



Scheme 1 a) 1-Iodonaphthalene, b) 1,8-diiodonaphthalene. *Reagents and conditions*: 5 mol% $Pd(OAc)_2$, K_2CO_3, DMF, 100 °C, 3 d.

Acenaphthylene (**2**) was arylated on a 1 mmol scale with an excess of 1-bromonaphthalene in the presence of palladium acetate as precatalyst under the optimized reaction conditions outlined in Figure 1, which had been successfully applied previously for the arylation of cyclopentadienes.[6] We were able to isolate four different products by flash chromatography: the monoarylation product **1** with 42% yield and the Ullmann coupling product **4**[4] from excess bromonaphthalene, as anticipated.

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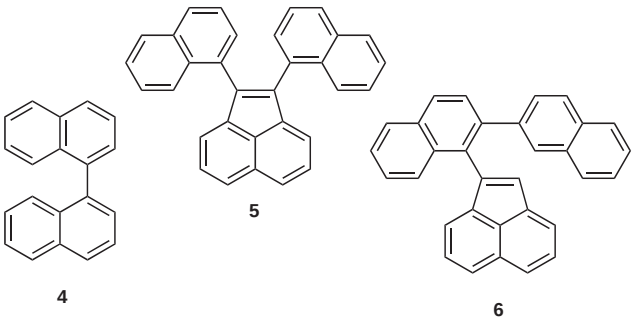
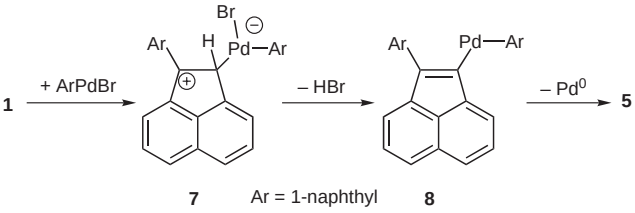


Figure 1 Additional products from the Pd-catalyzed naphthylation of acenaphthylene (**2**, 1 mmol) with 1-bromonaphthalene (4 mmol). *Reagents and conditions*: 5 mol% $Pd(OAc)_2$, 20 mol% P(*t*-Bu)$_3$, Cs_2CO_3, DMF, 140 °C, 2 d.



Scheme 2 A Heck-type reaction without carbopalladation step as mechanistic rationale.

The target molecule **5** was obtained with 19% yield, a remarkable result, since the intermolecular Heck reaction is known to be sensitive towards steric hindrance. In addition, the stereochemical requirements of the standard mechanism for the Heck reaction – involving *syn*-carbometallation and *syn*-β-hydrogen elimination – obviously are not in accord with the formation of **5**, and already for the formation of **1**. In both cases we assume that the electrophilic attack of the aryl-Pd species does not lead to a carbometalation step but to the formation of an intermediary benzyl cation **7** with subsequent elimination and intermediary aryl vinyl palladium complex **8** (Scheme 2) as suggested earlier in a review on palladacycles.[7]

In the ^{1}H NMR and ^{13}C NMR spectra of **5**, a double set of signals of a 1:1 mixture of rotamers was registered; this was in agreement with our PM3 calculation, which estimated the rotational barrier to about 20 kcal/mol. In addition, this calculation confirms our result, that the rotamers are not isolable by flash chromatography at room temperature, in contrast to the rotamers of the sterically somewhat more hindered bisnaphthylphenanthrene[8] (rotational barrier about 30 kcal/mol). However, by crystallizing **5**

out of a pentane solution, exclusively the chiral rotamer *trans*-**5** (Figure 2)was obtained as single crystals, obviously being favored in the centrosymmetric crystal lattice with the space group $P2_1/n$.[9]

Byproduct **6** was identified by X-ray crystal-structure analysis (Figure 3). The mechanistic rationale[10] for the domino process to **6** involves carbopalladation, cyclometalation and even retro-carbopalladation steps with the acenaphthylene moiety as template for C–C-coupling processes, closely related to Heck-type reactions at the norbornene moiety, which have been convincingly explained and preparatively utilized by Catellani et al.[11]

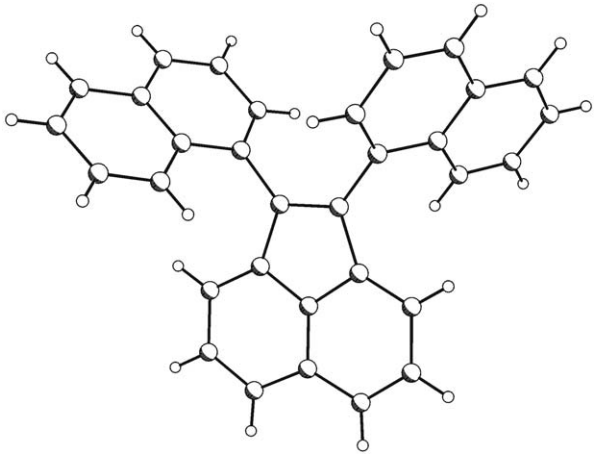


Figure 2 Structure of the chiral rotamer *trans*-**5** in the crystal.[9]

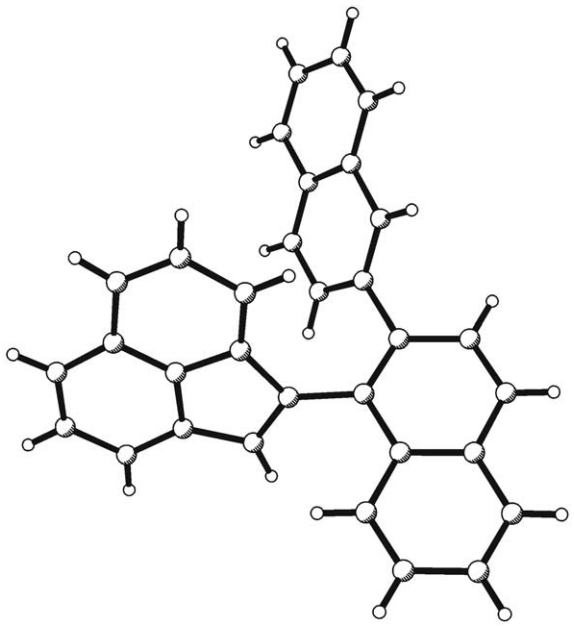
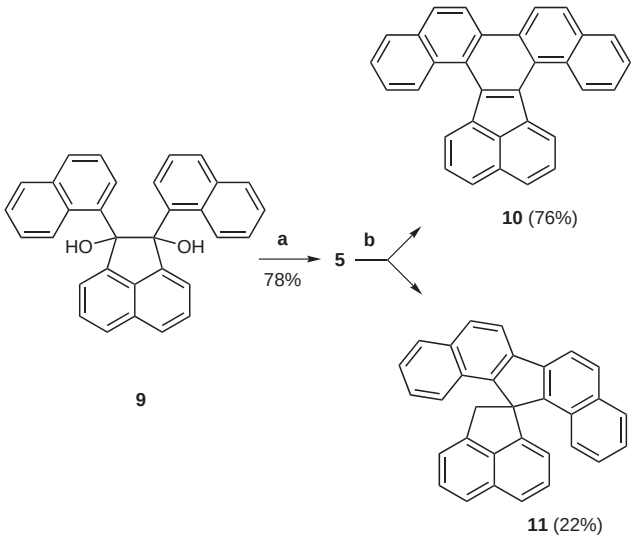


Figure 3 Structure of domino product **6** in the crystal.[9]

As an independent access to the bisnaphthyl acenaphthylene **5** we successfully reduced diol **9**[12] with sodium iodide/trichloromethyl silane[13] in acetonitrile (Scheme 3). Subsequent dehydrocyclization[14] with $AlCl_3/CuCl_2$ gave the octacyclic π-system **10** in 59% yield (over two steps).



Scheme 3 Independent access to **5** and subsequent cyclodehydration. *Reagents and conditions*: a) $MeSiCl_3$, NaI, MeCN, 3 h, r.t.; b) $CuCl_2$, $AlCl_3$, CS_2, 5 min, r.t.

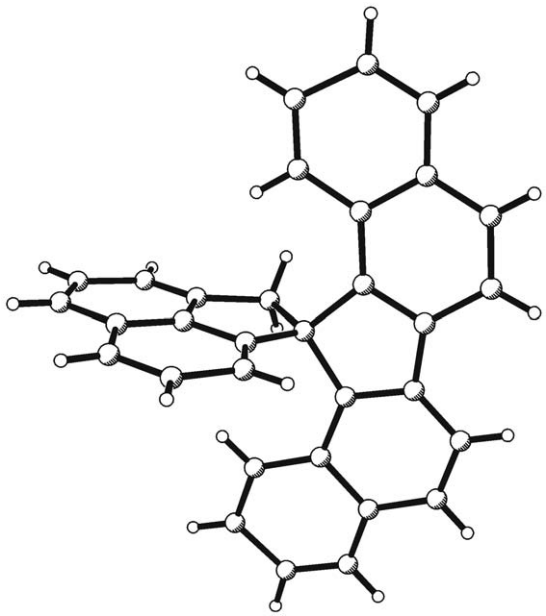


Figure 4 Structure of rearrangement product **11** in the crystal.[9]

Therefore this procedure is somewhat superior to the one-step transformation of **9** to **10** in superacidic medium, reported to give a 39% yield.[15] In addition, we isolated spirocycle **11** (Figure 4) as byproduct and confirmed its structure by X-ray crystal analysis. While details of the mechanism of its formation have yet to be revealed, rearrangement product **11** is about 19 kcal/mol thermodynamically favored to **5** according to semiempirical calculations (PM3).

The Pd-catalyzed synthesis of the bisnaphthyl-substituted acenaphthylene **5** is another example for the capacity of this type of reactions for the arylation in sterically hindered positions, closely related to the one-step synthesis

of pentakisnaphthyl cyclopentadiene.[6] The dehydrocyclization of **5** under moderate conditions stops after one C–C bond formation; further cyclization steps would cause a curvature, certainly requiring higher activation energies.

NMR spectroscopic data were recorded either at a Bruker DPX 200 (200 MHz) or at a Bruker DPX 400 (400 MHz). Mass spectroscometric data were recorded on a VG Instruments Autospec mass spectrometer.

Pd-Catalyzed Arylation of Acenaphthylene (2) with 1-Bromonaphthalene (3)

A mixture of acenaphthylene (**2**, 152 mg, 1.00 mmol), 1-bromonaphthalene (828 mg, 4.00 mmol), Cs_2CO_3 (1.30 g, 4.00 mmol), $Pd(OAc)_2$ (12 mg, 50 μmol), and tris-*tert*-butylphosphane (41 mg, 200 μmol) in anhyd DMF (10 mL) were stirred for 2 d at 140 °C under argon in a screw-capped flask. The reaction mixture was diluted with of EtOAc (90 mL) and acidified with PTSA monohydrate (2.28 g, 12.0 mmol). After filtration through a pad of silica (4 g) the organic phase was extracted three times with H_2O (50 mL), dried with Na_2SO_4 and the solvent was removed by rotatory evaporation. TLC of the crude product: silica, PE–MTBE (2:1), R_f = 0.35 (**4**), 0.28 (**1**), 0.18 (**5**), 0.16 (**6**), 0.00. The products were separated by flash chromatography and dried in vacuo (0.2 mbar, 50 °C); 1st fraction: 1,1′-binaphthyl **4** as colorless crystals (290 mg, 57% based on the amount of aryl bromide) with mp 159 °C; 2nd fraction: the monoarylated product **1** (117 mg, 42%) as yellow crystals with mp 92 °C; 3rd fraction: the bisarylated product **5** (77 mg, 19%) as orange crystals with mp 268–270 °C.^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, double set of signals): δ = 7.09–7.13 (m, 1 H), 7.22–7.24 (m, 2 H), 7.30–7.39 (m, 4 H), 7.44–7.57 (m, 5 H), 7.70–7.76 (m, 3 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.5 Hz, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 8.07 (d, *J* = 8.5 Hz, 1 H), 8.10 (d, *J* = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, double set of signals): δ = 124.55 (d), 124.63 (d), 125.23 (d), 125.48 (d), 125.65 (d), 125.70 (d), 125.80 (d), 126.87 (d), 127.18 (d), 127.42 (d), 127.46 (d), 127.92 (d), 127.97 (d), 128.06 (d), 128.13 (d), 128.26 (d), 128.55 (d), 132.19 (s), 133.09 (s), 133.18 (s), 133.49 (s), 133.78 (s), 133.84 (s), 139.39 (s), 140.27 (s), 141.38 (s), 141.44 (s). UV/Vis (MeCN): λ (log ε) = 220 (4.23), 308 (3.46) nm. MS–FAB: *m/z* (%) = 406 (7), 405 (36), 404 (100), 276 (4). Anal. Calcd for $C_{32}H_{20}$ (404.50): C, 95.02; H, 4.98. Found: C, 94.66; H, 5.04; 4th fraction: the 2,2′-bisnaphthyl derivative **6** (20 mg, 5%) as dark yellow crystals with mp 279 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.78 (s, 1 H), 7.27 (d, *J* = 7.0 Hz, 1 H), 7.32–7.40 (m, 5 H), 7.44–7.52 (m, 4 H), 7.63–7.69 (m, 2 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.75 (d, *J* = 8.5 Hz, 2 H), 7.87 (s, 1 H), 7.94 (d, *J* = 8.5 Hz, 1 H), 7.96 (d, *J* = 8.5 Hz, 1 H), 8.00 (d, *J* = 8.5 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 124.01 (d), 124.23 (d), 125.74 (d), 125.93 (d), 126.04 (d), 126.29 (d), 127.04 (d), 127.17 (d), 127.33 (d), 127.45 (d), 127.63 (d), 127.66 (d), 127.83 (d), 128.03 (d), 128.06 (d), 128.10 (d), 128.23 (d), 128.30 (s), 128.39 (d), 128.61 (s), 128.83 (d), 130.66 (d), 131.92 (s), 132.16 (s), 133.02 (s), 133.35 (s), 133.49 (s), 139.27 (s), 139.60 (s), 140.23 (s), 141.24 (s), 141.55(s). UV/Vis (MeCN): λ (log ε) = 220 (4.19), 224 (4.18), 296 (3.34), 328 (3.36) nm. MS–FAB: *m/z* (%) = 406 (8), 405 (35), 404 (100), 276 (4). Anal. Calcd for $C_{32}H_{20}$ (404.50): C, 95.02; H, 4.98. Found: C, 94.78; H, 4.53.

Independent Synthesis of 1,2-Dinaphthalen-1-yl-acenaphthylene (5)

To a solution of NaI (1.50 g, 1.00 mmol) in anhyd MeCN (20 mL) $MeSiCl_3$ (1.49 g, 1.00 mmol) and 1,2-dinaphthalen-1-yl-acenaphthylen-1,2-diol (**12**,[12] 877 mg, 2.00 mmol) were successively added under stirring. After 3 h at r.t. the reaction mixture was poured onto crushed ice (50 g), followed by threefold extraction with MTBE (40 mL) each. The organic layer was treated with an aq $Na_2S_2O_3$ solution, washed with brine, dried with $MgSO_4$ and concentrated in vacuo. Flash chromatography of the residue (silica, PE–MTBE, 2:1) gave 631 mg (78%) of **5** orange crystals with mp 268–270 °C.

Acenaphthyleno[1,2-*i*]picene (10) and 13*H*-Spiro-[acenaphthen-1,13′-dibenzo[*a*,*i*]fluorene] (11)

$CuCl_2$ (269 mg, 2.00 mmol), $AlCl_3$ (267 mg, 2.00 mmol), and the disubstituted acenaphthylene (**5**, 404 mg 1.00 mmol) in CS_2 (200 mL) were stirred under argon at r.t. for 5 min. Then, EtOH (200 mL) was added, the resulting suspension was filtered and the residue was extracted with EtOAc (100 mL). The combined solution was concentrated and the crude product mixture separated by flash chromatography; TLC (silica, PE–MTBE 2:1); R_f = 0.12 (**11**), 0.10 (**10**), 0.00). First fraction: spirocycle **11** (89 mg 22%) as slightly yellow crystals with mp 218 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19 (s, 2 H, H-2), 6.51 (d, *J* = 7.0 Hz, 1 H, H-8), 6.82 (d, *J* = 8.5 Hz, 2 H, H-1′), 6.99 (ddd, *J* = 1.5, 8.5 Hz, 2 H, H-2′), 7.20 (dd, *J* = 7.0 Hz, 1 H, H-7), 7.27 (ddd, *J* = 1.5, 8.5 Hz, 2 H, H-3′), 7.64 (d, *J* = 6.5 Hz, 1 H, H-3), 7.70 (d, *J* = 8.0 Hz, 1 H, H-6), 7.76 (dd, *J* = 7.0 Hz, 1 H, H-4), 7.87 (d, *J* = 8.5 Hz, 2 H, H-4′), 7.90 (d, *J* = 6.5 Hz, 1 H, H-5), 7.95 (d, *J* = 8.5 Hz, 2 H, H-5′), 8.07 (d, *J* = 8.5 Hz, 2 H, H-6′). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.88 (t, C-2), 63.34 (s, C-1), 118.45 (d, C-6′), 119.60 (d, C-8), 121.03 (d, C-3), 122.95 (d, C-1′), 123.72 (d, C-6), 123.77 (d, C-5), 124.99 (d, C-3′), 126.80 (d, C-2′), 128.50 (d, C-7), 128.61 (d, C-4), 129.14 (s, C-13b′), 129.53 (d, C-5′), 129.58 (d, C-4′), 132.25 (s, C-5a), 133.99 (s, C-4a′), 138.21 (s, C-6a′), 139.85 (s, C-8b), 143.51 (s, C-2a), 148.70 (s, C-13a′), 149.54 (s, C-8a). UV/Vis (MeCN): λ (log ε) = 220 (4.10), 226 (4.11), 268 (4.24), 282 (3.90), 292 (3.74), 332 (3.42) nm. MS–FAB: *m/z* (%): 406 (6), 405 (36), 404 (100) [M^+], 329 (5), 307 (16), 289 (9), 176 (18), 154 (74), 136 (54). Anal. Calcd for $C_{32}H_{20}$ (404.50): C, 95.02; H, 4.98. Found: C, 94.76; H, 4.97. Second fraction: the angularly fused aromatic hydrocarbon **10** (305 mg, 76%) as orange crystals with mp 309 °C (lit.[15]: mp 306–310 °C).

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(9) X-ray data for **5** were collected on a Bruker AXS-SMART 1000 (Mo Kα radiation). The structure was solved by direct methods and refined by full matrix least squares using SHELXTL-97 All non-hydrogen atoms were refined using anisotropic thermal parameters.
Crystal Data for 5
T = 213(2) K, $C_{32}H_{20}$, *M* = 404.48, monoclinic space group $P2_1/n$, *a* = 12.190(5) Å, *b* = 10.104(4) Å, *c* = 17.237(7) Å, *β* = 102.484(9)°, *V* = 2072.9(15) Å^3, *Z* = 4, D_C = 1.296 g/cm^3, μ = 0.073 mm^{-1}, 2.35° < Θ < 25.15°, reflections collected/unique 10788/3646 [R_{int} = 0.0489], data/restraints/parameters 3646/0/289, GOF 1.021, final $R[I > 2\sigma(I)]$ *R*1 = 0.0416, *wR*2 (all data) = 0.1082, residual density 0.134 and –0.190 e A^{-3}.

Crystal Data for 6

The crystals were of poor quality, twinned and weakly diffracting. $C_{32}H_{20}$, M = 404.48, monoclinic space group $P2_1/c$, a = 11.352(3) Å, b = 24.248(4) Å, c = 7.835(2) Å, β = 96.80(2)°, V = 2141.4(8) Å^3, Z = 4, T = 293(2) K, μ = 0.071 mm^{-1}, 32624/3877/2025 reflections collected/unique/observed, R_{int} = 0.1775, $R1$ = 0.1268, $wR2$ (all data) = 0.2319, 290 parameters. All non-hydrogen atoms calculated anisotropic; positions of the H atoms calculated for idealized positions. The structure was solved and refined using SHELXTL-97 (G. M. Sheldrick, Universität Göttingen 1997).

Crystal Data for 11

Again, the crystals were of poor quality and weakly diffracting. $C_{32}H_{20}$, M = 404.48, tetragonal space group $I\bar{4}$, a = 20.673(2) Å, c = 10.448(1) Å, V = 4465.4(9) Å^3, Z = 8, T = 293(2) K, μ = 0.068 mm^{-1}, 2380/1798/934 reflections collected/unique/observed, R_{int} = 0.0670, $R1$ = 0.1283, $wR2$ (all data) = 0.3307, 289 parameters. All non-hydrogen atoms calculated anisotropic; positions of the H atoms calculated for idealized positions. The structure was solved and refined using SHELXTL-97 (G. M. Sheldrick, Universität Göttingen 1997).

X-ray data have been deposited at the Cambridge Crystallographic Data Centre (deposition numbers CCDC-611565 for **5,** CCDC-614432 for **6** and CCDC-614433 for **11**. Copies of the data can be obtained free of charge at www.ccdc.cam.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ [fax: +44 (1223)336033; e-mail: deposit@ccdc.cam.ac.uk].

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