A Palladium-Catalyzed Domino Coupling Process Leading to Annelated Pentafulvenes☆

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Annelated pentafulvenes **2**, **10**, **13**, and **14** are efficiently accessible by a palladium-catalyzed domino coupling process of aryl substituted vinylic bromides **1**, **9**, **11**, and **12**. 5-Membered palladacycles **3** are discussed as key intermediates.

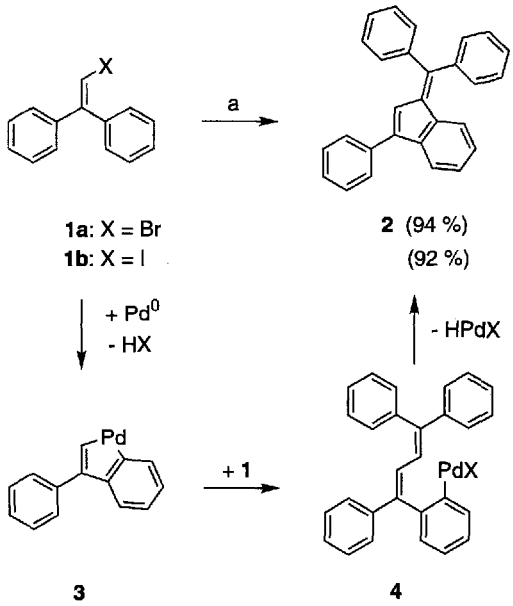
Palladium-catalyzed domino coupling processes open up efficient pathways from simple starting materials to complex target molecules[1]. Vinylic bromides are particularly versatile coupling components for this purpose: C–C bond formation takes place with alkenes or with alkynes affording dienes[2] and enynes[3], respectively. In some special cases intermolecular domino coupling processes are initiated that lead to interesting carbo- and heterocyclic frameworks[4]. Recently, we studied a cross-coupling reaction of *ortho*-methoxyiodoarenes with vinylic bromides as a new approach to substituted benzo[*b*]furans[5]. The examination of the by-products formed during this domino process revealed that an excess of vinylic bromides is consumed by homocoupling reactions. In the case of certain aryl-substituted vinylic bromides annelated pentafulvenes are formed. In this paper we report on the scope and limitations of this palladium catalyzed homocoupling process.

Results and Discussion

The phenyl-substituted olefinic bromide **1a** as well as the corresponding iodide **1b** are efficiently transformed into the annelated pentafulvene **2** by palladium catalysis. 1 mol-% of palladium acetate is sufficient: the active Pd^0 catalyst is formed in situ under the reaction conditions.

As the key step of this process we assume a cyclometalation to the 5-membered palladacycle **3**[6]. For this reactive intermediate the reductive elimination of Pd^0 is clearly inhibited, because the result would be a highly strained and antiaromatic benzocyclobutadiene. Instead, the palladacycle **3** adds another equivalent of starting material **1**, presumably to give the Pd intermediate **4**. Its regioisomer with the palladium atom at the vinylic position may be an alternative intermediate. Nevertheless, the final ring closure in the sense of an intramolecular Heck reaction[1] leads to the same product **2**.

Scheme 1. Additional ligands have been omitted for clarity; Reagents: a: 1 mol-% $Pd(OAc)_2$, K_2CO_3, *n*-Bu_4NBr, DMF, N_2, 3 d, 100°C



The cyclometalation as the key step of this sequence should be strongly influenced by structural features: by the introduction of a bridge between the phenyl substituents the conformational flexibility is decreased and, depending on the size of the central ring, additional ring strain is enforced, a factor that might particularly hinder cyclometalation.

The model compounds are efficiently accessible as illustrated for the vinyl bromide **9** (Scheme 2). In order to stabilize the exocyclic double bond of **9** a quaternary center in the 10-position had to be introduced. For this purpose a spiroannelation was chosen, easily achieved by alkylation of

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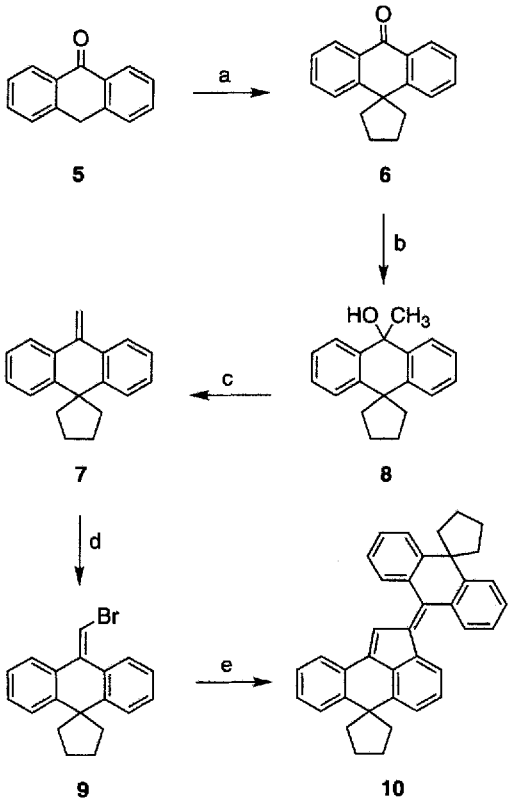
anthrone (**5**) with 1,4-dibromobutane. The three-step sequence transforming spirocycle **6** into the model compound **9** via intermediates **8** and **7** turned out to be most efficient. The palladium-catalyzed coupling reaction proceeds in the same manner as observed for substrate **1**, giving the polycyclic condensation product **10** in a remarkable 98% yield.

Scheme 2. Reagents: a: 1,4-dibromobutane, KOH/MeOH, reflux, 3 h, 48%. – b: MeMgCl, diethyl ether, 99%. – c: $MgSO_4$, toluene, reflux, 99%. – d: 1. Br_2, *n*-hexane/dichloromethane, −30°C; 2. potassium *t*-butoxide, −30°C, 77%. – e: 1 mol-% $Pd(OAc)_2$, K_2CO_3, *n*-Bu_4NBr, DMF, N_2, 3 d, 100°C, 98%



Analogously, substrates **11** and **12** lead to the annelated pentafulvenes **13** and **14** in about 90% yield. According to the X-ray structure[7] of compound **14** the dibenzocycloheptene moiety is perpendicular to the dibenzoazulene part, presumably due to steric reasons (Figure 1).

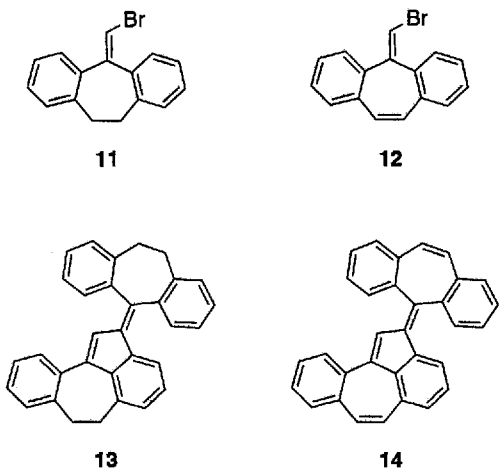
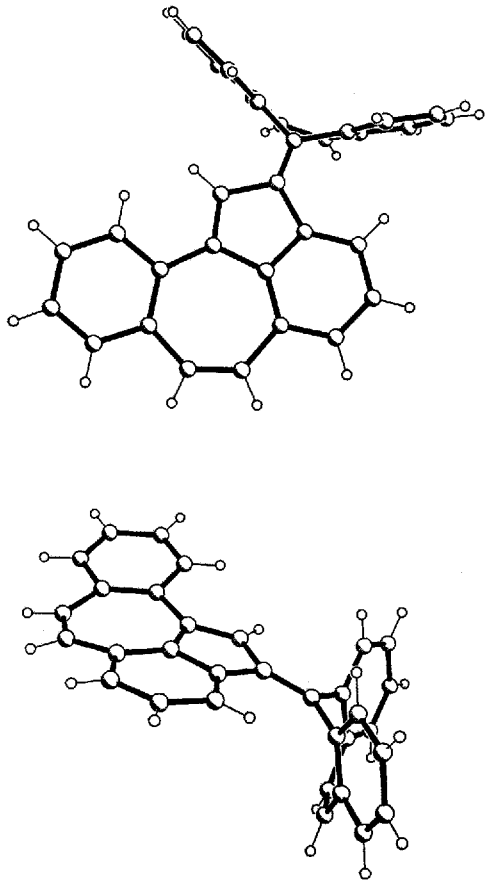
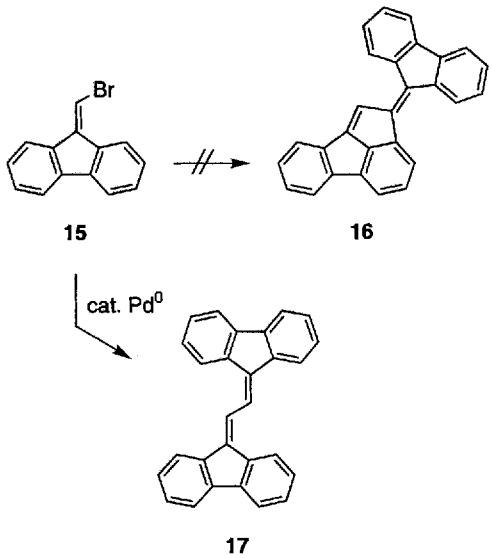


Figure 1. Perspective view of the X-ray structure of polycyclic hydrocarbon **14**. Radii are arbitrary



With the fluorenone-derived substrate **15** we have finally reached the limit of the new annelation reaction. In this case the strained pentafulvene **16** is not formed, probably because the cyclopalladation step is inhibited. Instead, a palladium-catalyzed Ullmann coupling reaction[8] takes place leading to product **17**.



In conclusion, the palladium-catalyzed homocoupling reaction of aryl-substituted vinylic bromides is an efficient en-

try to annelated pentafulvenes. We are currently investigating mechanistic details, especially concerning the formation and reactivity of the 5-membered palladacycles of type **3** postulated as intermediates.

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Experimental

General: Melting points are uncorrected. – IR: Nicolet 320. – UV/Vis: HP 8452 A. – NMR: Bruker AM 400. ^{1}H-NMR spectra are recorded at 400.1 MHz by using $CDCl_3$ as the solvent and TMS as the internal standard. ^{13}C-NMR spectra are measured at 100.6 MHz by using $CDCl_3$ as the solvent and the internal standard (δ = 77.05). – MS: Finnigan MAT 8430. Mass spectra are recorded at an ionizing voltage of 70 eV by electron impact. – For analytical TLC precoated plastic sheets "POLYGRAM SIL G/UV$_{254}$" from Macherey-Nagel are used. – The substrates **1a**[9], **1b**[9], **11**[10], and **15**[11] are synthesized according to literature procedures.

6: To a suspension of 10.0 g (51.5 mmol) of anthrone (**5**) and 12.1 g (55.8 mmol) of 1,4-dibromobutane in 60 ml of dry methanol a solution of 9.50 g (169 mmol) of potassium hydroxide in 50 m of dry methanol is added dropwise at reflux within 30 min. After the reaction mixture has been cooled to room temp. it is filtered through silica and the solvent is removed from the filtrate in vacuo. By flash chromatography of the residue (TLC: silica/toluene; R_f = 0.78, 0.70, 0.35, 0.14) the fraction with R_f = 0.35 is isolated and crystallized from ethanol to afford 6.07 g (48%) of **6** as colorless crystals with m.p. 105–106°C. – IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1}, 2968, 2952, 1656, 1601, 1476, 1457, 1328, 934, 756, 689. – UV (acetonitrile): λ_{max} (lg ε) = 192 nm (4.77), 202 (4.53, sh), 206 (4.48, sh), 214 (4.43, sh), 270 (4.26), 292 (3.74, sh). – ^{1}H NMR: δ = 2.17–2.21 (m, 4H), 2.34–2.38 (m, 4H), 7.39 ("dd", $J \approx$ 6.5, 1.6 Hz, 1H), 7.41 ("dd", $J \approx$ 6.5, 1.5 Hz, 1H), 7.57–7.64 (m, 4H), 8.31 (dd, J = 7.8, 1.4 Hz, 2H). – ^{13}C NMR: δ = 28.74 (t), 47.15 (t), 49.34 (s), 126.32 (d), 126.64 (d), 127.07 (d), 130.16 (d), 133.56 (s), 152.99 (s), 184.27 (s). – MS: *m/z* (%): 249 (22), 248 (100) [M$^+$], 247 (9), 233 (24), 220 (19), 219 (33), 215 (15), 206 (33), 191 (26), 189 (28), 178 (71), 176 (21), 165 (33), 163 (11), 152 (20), 151 (7). – $C_{18}H_{16}O$ (248.3): calcd. C 87.06, H 6.49; found C 86.97, H 6.48.

8: A solution of 6.44 ml (19.3 mmol) of 3 M methylmagnesium chloride in THF is added at 0°C under N_2 to a suspension of 2.40 g (9.66 mmol) of powdered **6** in 50 ml of dry diethyl ether. After the mixture has been stirred at room temp. for 1 h and at reflux for 16 h, it is hydrolyzed with 10 g of ice and with 30 ml of a saturated solution of ammonium dihydrogen phosphate in water and extracted three times with 50 ml of diethyl ether. The combined organic layers are filtered through silica and concentrated in vacuo. Crystallization of the residue from acetone gives 2.53 g (99%) of **8** as colorless crystals with m.p. 133–134°C. – IR (KBr): $\tilde{\nu}$ = 3064 cm^{-1}, 2980, 2955, 2947, 1476, 1444, 1083, 1045, 769, 756. – UV (acetonitrile): λ_{max} (lg ε) = 194 nm (4.83), 210 (4.41, sh), 214 (4.32, sh), 220 (4.21, sh), 228 (3.41, sh), 264 (2.88, sh). – ^{1}H NMR: δ = 1.60 (s, 3H), 1.88–1.97 (m, 4H), 2.16–2.23 (m, 3H, alkyl-H, OH), 2.60 (m, 2H), 7.31 (m, 4H), 7.41–7.45 (m, 2H), 7.83–7.87 (m, 2H). – ^{13}C NMR: δ = 27.39 (t), 28.46 (t), 36.40 (q), 49.21 (t), 49.26 (s), 70.61 (s), 125.38 (d), 125.79 (d), 126.36 (d), 127.65 (d), 141.73 (s), 143.78 (s). – MS: *m/z* (%): 264 (2) [M$^+$], 250 (22), 249 (100), 246 (21), 231 (8), 217 (10), 207 (26), 204 (9), 203 (11), 202 (15), 191 (9), 178 (13). – $C_{19}H_{20}O$ (264.4): calcd. C 86.32, H 7.63; found C 86.45, H 7.67.

7: A mixture of 2.52 g (9.55 mmol) of **8** and 15.0 (125 mmol) of dry magnesium sulfate in 50 ml of dry toluene is stirred for 60 h at room temp. After filtration through silica the solvent is removed in vacuo to give 2.34 g (99%) of crude product **7** which according to the ^{1}H-NMR spectrum is pure enough for further transformations. Colorless, air-sensitive crystals of **7** with m.p. 47–49°C are obtained by crystallization from acetone. – ^{1}H NMR: δ = 1.81–1.91 (m, 4H), 2.09–2.18 (m, 4H), 5.62 (s, 2H), 7.26 (m, 4H), 7.46 (m, 2H), 7.66 (m, 2H). – ^{13}C NMR: δ = 25.07 (t), 38.98 (t), 51.49 (s), 109.19 (t), 124.00 (d), 124.53 (d), 126.10 (d), 127.43 (d), 136.07 (s), 143.34 (s), 143.63 (s).

9: A solution of 1.65 g (10.3 mmol) of bromine in 5 ml *n*-hexane is added dropwise with stirring at –30°C to a solution of 2.31 g (9.36 mmol) of **7** in 50 ml of *n*-hexane/20 ml of dichloromethane. After addition of 1.31 g (11.7 mmol) of potassium *tert*-butoxide and 11 mg (42 µmol) of 18-crown-6 stirring is continued for 1 h. The reaction mixture is extracted with 40 ml of water and the organic layer is filtered through silica and concentrated in vacuo. By flash chromatography of the oily residue (TLC: silica/hexanes; R_f = 0.22, 0.02) the fraction with R_f = 0.22 is isolated and crystallized from 2-propanol to furnish 2.36 g (77%) of **9** as colorless needles with m.p. 85–86°C. – IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1}, 2962, 2940, 1463, 1448, 778, 759, 718, 621. – UV (acetonitrile): λ_{max} (lg ε) = 200 nm (4.57), 224 (4.29, sh), 234 (4.11, sh), 262 (4.12, sh), 268 (4.14). – ^{1}H NMR: δ = 1.80–1.90 (m, 4H), 2.10–2.20 (m, 4H), 6.79 (s, 1H), 7.21–7.32 (m, 4H), 7.44 (m, 2H), 7.47–7.49 (m, 1H), 8.03–8.07 (m, 1H). – ^{13}C NMR: δ = 24.32 (t), 37.07 (t), 52.34 (s), 102.64, 123.42, 123.55, 124.43, 125.15, 126.35, 127.40, 127.76, 127.91 (all d), 134.01, 137.70, 140.89, 142.84, 144.89 (all s). – MS: *m/z* (%): 327/325 (8/11), 326/324 (41/40) [M$^+$], 297/295 (10/11), 284/282 (11/11), 271/269 (16/16), 246 (26), 245 (100), 217 (17), 216 (20), 215 (35), 203 (17), 202 (37), 189 (13). – $C_{19}H_{17}Br$ (325.3): calcd. C 70.16, H 5.27; found C 70.20, H 5.30.

5-Bromomethylene-5H-dibenzo[a,d]cycloheptene (**12**): To a solution of 1.50 g (7.35 mmol) of 5-methylene-5*H*-dibenzo[*a,d*]cycloheptene[12] in 50 ml of $CHCl_3$ a solution of 1.17 g (7.35 mmol) of bromine in 10 ml $CHCl_3$ is added dropwise at 5°C. After the reaction mixture has been stirred at room temp. for 30 min, it is filtered through silica and the solvent (and HBr) is removed in vacuo. The residue is crystallized from ethanol or purified by flash chromatography (silica, toluene) to give 1.33–1.50 g (64–72%) of **12** as colorless crystals with m.p. 85°C. – IR (KBr): $\tilde{\nu}$ = 3015 cm^{-1}, 1487, 1434, 1212, 1093, 819, 806, 794, 775, 729, 701, 618. – UV (acetonitrile): λ_{max} (lg ε) = 228 nm (4.55), 238 (4.39, sh), 244 (4.33, sh), 248 (4.30, sh), 292 (4.01), 310 (3.86, sh). – ^{1}H NMR: δ = 6.37 (s, 1H), 6.85 (d, J = 11.9 Hz, 1H), 6.91 (d, J = 11.9 Hz, 1H), 7.28–7.36 (m, 6H), 7.40 ("td", $J \approx$ 7.2, 2.0 Hz, 1H), 7.47 ("d", $J \approx$ 7.3 Hz, 1H). – ^{13}C NMR: δ = 107.81 (d), 127.30 (d), 127.80 (d), 127.86 (d), 128.16 (d), 128.62 (d), 128.72 (d), 128.86 (d), 129.12 (d), 130.58 (d), 131.20 (d), 133.96 (s), 134.02 (s), 136.06 (s), 139.49 (s), 145.93 (s). – MS: *m/z* (%): 285/283 (12/13), 284/282 (70/69) [M$^+$], 204 (18), 203 (100), 202 (79), 200 (19), 101 (20). – $C_{16}H_{11}Br$ (283.2): calcd. C 67.87, H 3.92; found C 67.75, H 3.90.

Palladium-catalyzed Homocoupling Reactions of Vinylic Bromides; General Procedure: A mixture of 4 mmol of vinylic bromide, 1.11 g (8.0 mmol) of K_2CO_3, 645 mg (2.00 mmol) of *n*-Bu_4NBr, 11 mg (49 µmol) of $Pd(OAc)_2$, and 10 ml of DMF in a sealed tube (for convenience) is stirred under N_2 at 100°C for 3 d. After the reaction mixture has been diluted with 50 ml of water it is extracted three times with 50 ml diethyl ether. The ether extract is filtered through silica and concentrated. The crude product is purified by flash chromatography (hexanes/diethylether, silica gel) as specified below.

1-(Diphenylmethylene)-3-phenyl-1H-indene (**2**): 1.06 g, (4.07 mmol) of 1-bromo-2,2-diphenylethene (**1a**) is transformed by pal-

ladium catalysis according to the general procedure (see above). The crude product is recrystallized from diethyl ether to give 660 mg of **2**. The filtrate is concentrated and the residue purified by flash chromatography (silica, hexanes; $R_f = 0.23$) to give another 19 mg of **2**; total yield 679 mg (94%) of **2** as orange crystals with m.p. 205°C (from CH_2Cl_2/ethanol, ref.[13]: m.p. 204°C). – IR (KBr): $\tilde{\nu} = 3051\ cm^{-1}$, 1588, 1488, 1440, 1355, 780, 763, 757, 704, 699, 688, 608. – UV (acetonitrile): λ_{max} (lg ε) = 192 nm (4.90), 202 (4.76, sh), 228 (4.42), 250 (4.44), 298 (4.13), 348 (4.23). – ^1H NMR: δ = 6.68 (d, $J = 7.7$ Hz, 1H, 7-H), 6.76 (s, 1H, 2-H), 6.92 (td, $J = 7.6$, 1.1 Hz, 1H, 6-H), 7.19 (td, $J = 7.5$ Hz, $J = 1.1$ Hz, 1H, 5-H), 7.33–7.46 (m, 13H, phenyl H), 7.55 (d, $J = 7.5$ Hz, 1H, 4-H), 7.64 (m, 2H, phenyl H); assignments from H,H-COSY. – ^{13}C NMR: δ = 120.11 (d), 123.83 (d), 124.91 (d), 126.99 (d), 127.74 (d), 127.94 (d), 128.18 (d), 128.52 (d), 128.60 (d), 130.47 (d), 131.63 (d), 135.89 (s), 137.26 (s), 138.14 (s), 141.07 (s), 142.48 (s), 142.86 (s), 144.36 (s), 146.70 (s). – MS: *m/z* (%): 357 (31), 356 (100) [M^+], 279 (38), 276 (18), 178 (15), 57 (9). – $C_{28}H_{20}$ (356.5): calcd. C 94.35, H 5.65; found C 94.38, H 5.62.

10: 1.30 g (4.00 mmol) of **9** is transformed by palladium catalysis according to the general procedure (see above). By flash chromatography of the crude product (silica, hexanes; $R_f = 0.01$, 0.11) the fraction with $R_f = 0.11$ is isolated and crystallized from 2-propanol to yield 960 mg (98%) of **10** as red crystals with m.p. 205°C. – IR (KBr): $\tilde{\nu} = 2952\ cm^{-1}$, 1472, 1450, 1433, 759. – UV (acetonitrile): λ_{max} (lg ε) = 198 nm (4.90), 246 (4.35, sh), 264 (4.25, sh), 310 (4.29), 366 (4.29), 426 (4.11, sh). – ^1H NMR, at 25°C: δ = 1.1–2.8 (br. m, 16H), 7.09 (t, $J \approx 7.7$ Hz, 1H), 7.21–7.30 (m, 5H), 7.34 (m, 2H), 7.38 (s, 1H), 7.47 ("d", $J \approx 7.7$ Hz, 1H), 7.51 ("d", $J \approx 7.0$ Hz, 1H), 7.52 ("d", $J \approx 7.5$ Hz, 1H), 7.66 ("d", $J \approx 7.6$ Hz, 1H), 7.81 ("dd", $J \approx 7.3$, 1.1 Hz, 1H), 7.82 ("dd", $J \approx 7.8$, 1.3 Hz, 1H), 7.97 ("dd", $J \approx 7.4$, 1.3 Hz, 1H); aliphatic region at −40°C: δ = 1.50–1.60 (m, 2H), 1.84 (m, 2H), 2.04–2.22 (m, 6H), 2.07–2.41 (m, 4H), 2.52 (m, 2H). – ^{13}C NMR, at 25°C: δ = 24.19 (t), 28.83 (t), 50.25 (s), 52.96 (s), 117.20 (d), 121.34 (d), 123.25 (d), 123.50 (d), 124.08 (d), 124.34 (d), 124.88 (d), 125.40 (d), 125.84 (d), 126.68 (d), 126.77 (d), 127.60 (d), 127.98 (d), 128.10 (s), 128.54 (d), 129.06 (d), 129.57 (d), 134.50 (s), 135.60 (s), 137.57 (s), 137.85 (s), 137.91 (s), 140.13 (s), 141.05 (s), 141.44 (s), 145.38 (s), 146.45 (s), 148.76 (s); aliphatic region at −40°C: δ = 23.36 (t), 23.94 (t), 28.75 (t), 29.21 (t), 30.15 (t), 41.76 (t), 47.55 (t), 49.59 (s), 49.86 (t), 52.71 (s). – MS: *m/z* (%): 490 (10), 489 (42), 488 (100) [M^+], 459 (10), 433 (9), 403 (9), 389 (7), 208 (9), 202 (39), 201 (15), 200 (14), 194 (19), 193 (14), 86 (11), 84 (17). – $C_{38}H_{32}$ (488.7): calcd. C 93.40, H 6.60; found C 93.48, H 6.62.

2-(10,11-Dihydro-5H-dibenzo[a,d]cyclohepten-5-ylidene)-6,7-dihydro-2H-dibenz[cd,h]azulene (**13**): 1.14 g (4.00 mmol) of **11**[10] is transformed by palladium catalysis according to the general procedure (see above). The crude product is crystallized from diethyl ether to give 621 mg of **13**. The filtrate is concentrated and the residue purified by flash chromatography (silica, hexanes; $R_f =$ 0.23) to give another 120 mg of **13**; total yield 741 mg (91%) of **13** as a yellow solid with m.p. 196°C. – IR (KBr): $\tilde{\nu} = 2926\ cm^{-1}$, 1598, 1481, 1450, 1437, 1427, 1416, 1355, 775, 765, 759, 610. – UV (acetonitrile): λ_{max} (lg ε) = 194 nm (4.94), 208 (4.78, sh), 220 (4.55, sh), 230 (4.38), 250 (4.36), 300 (4.29), 324 (4.19), 342 (4.17), 392 (3.87). – ^1H NMR: δ = 2.81–2.97 (m, 2H), 3.06–3.18 (m, 4H, 6-H, 7-H), 3.36–3.49 (m, 2H), 6.73 (d, $J = 7.2$ Hz, 1H, 3-H), 6.81 ("t", $J \approx 7.6$ Hz, 1H, 4-H), 6.95 (d, $J = 7.7$ Hz, 1H, 5-H), 6.98 (s, 1H, 1-H), 7.14–7.33 (m, 9H), 7.42 (m, 2H), 7.65 (m, 1H, 11-H). – ^{13}C NMR: δ = 31.95 (t), 32.80 (t), 34.27 (t, C-6), 36.40 (t, C-7), 121.71 (d, C-3), 124.50 (d, C-4), 125.36 (d, C-1), 125.91 (d), 126.07 (d), 126.35 (d), 127.82 (d), 127.99 (d, C-5), 128.10 (d, C-11), 128.37 (d), 128.42 (d), 129.18 (d), 128.73 (d), 129.92 (d), 130.00 (d), 134.79 (s), 136.90 (s), 137.00 (s), 137.06 (s), 137.58 (s), 138.03 (s), 140.51 (s), 140.63 (s), 140.82 (s), 141.68 (s, C-7a), 143.91 (s, C-11b), 146.47 (s, C-5'); assignments from homonuclear H,H- and C,H-COSY. – MS: *m/z* (%): 409 (35), 408 (100) [M^+], 317 (14), 191 (53). – $C_{32}H_{24}$ (408.5): calcd. C 94.08, H 5.92; found C 94.08, H 5.96.

2-(5H-Dibenzo[a,d]cyclohepten-5-ylidene)-2H-dibenz[cd,h]azulene (**14**): 1.12 g (4.00 mmol) of **12** is transformed by palladium catalysis according to the general procedure (see above). – The crude product is crystallized from diethyl ether to give 533 mg of **14**. The filtrate is concentrated and the residue purified by flash chromatography (silica, hexanes/diethyl ether, 3:1; $R_f = 0.42$) to give another 135 mg of **14**; total yield 668 mg (84%) of **14** as orange-red needles with m.p. 213°C (from CH_2Cl_2/methanol). – IR (KBr): $\tilde{\nu} = 3049\ cm^{-1}$, 3019, 1592, 1481, 1359, 816, 801, 785, 781, 767, 756, 747, 736, 607. – UV (acetonitrile): λ_{max} (lg ε) = 192 nm (4.67), 218 (4.69), 258 (4.62, sh), 262 (4.64), 284 (4.34, sh), 300 (4.31), 316 (4.21, sh), 440 (3.80). – ^1H NMR: δ = 6.13 (s, 2H, 6-H, 7-H), 6.37 ("d", $J \approx 7.1$ Hz, 1H, 3-H), 6.69 ("t", $J \approx 7.7$ Hz, 1H, 4-H), 6.74 (s, 1H, 1-H), 6.95 (d, $J = 11.8$ Hz, 1H), 6.98 (d, $J = 11.8$ Hz, 1H), 7.01 (m, 1H, 8-H), 7.09 (m, 2H), 7.36–7.52 (m, 8H), 7.54–7.57 (m, 2H). – ^{13}C NMR: δ = 120.82 (d, C-1), 124.19 (d, C-3), 125.71 (d, C-4), 127.16 (d), 127.66 (d), 127.81 (d), 128.11 (d), 128.17 (d), 128.53 (d, C-11), 128.70 (C-9), 128.89, 128.94 (both d, C-3', C-4'), 129.92 (C-5), 130.95 (C-6), 130.97, 131.14 (both d, C-10', C-11'), 131.48 (s, C-5a), 132.07 (d), 132.84 (s), 133.78 (s), 133.84 (s), 134.30 (d, C-8), 134.49 (s), 135.29 (s, C-7a), 137.30 (s), 137.44 (s), 137.49 (s), 139.29 (s), 142.04 (s, C-5'), 143.39 (s, C-2), 143.99 (s, C-11b); assignments from homonuclear H,H- and C,H-COSY. – MS: *m/z* (%): 405 (35), 404 (100) [M^+], 403 (32), 402 (18), 389 (11), 193 (9). – $C_{32}H_{20}$ (404.5): calcd. C 95.02, H 4.98; found C 94.58, H 5.07.

Crystal Data for Compound **14**[7]: $C_{32}H_{20}$, space group $Pna2_1$, $a = 2132.5(3)$, $b = 1956.6(3)$, $c = 496.01(8)$ pm, $U = 2.0695\ nm^3$, $Z = 4$, λ(Mo-K_α) = 71.073 pm, $\mu = 0.07\ mm^{-1}$, $T = -100$°C. A red prism ca. 0.8 × 0.25 × 0.15 mm was mounted in an inert oil. 7737 intensities were measured with a Siemens R3 diffractometer to $2\Theta_{max}$ 50°, of which 3616 were unique (R_{int} 0.057). The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen). H atoms were included by using a riding model. The final $wR(F^2)$ was 0.075, with conventional $R(F)$ 0.041, for 290 parameters and 323 restraints; $S = 0.81$, max. Δρ 111 e nm^{-3}.

1,2-Bis(9-fluorenylidene)ethane (**17**): 1.05 g (4.10 mmol) of **15** are transformed by palladium catalysis according to the general procedure (see above). The crude product, scarcely soluble in CH_2Cl_2 and diethyl ether, is crystallized from toluene to give 442 mg (61%) of **17** as orange crystals with m.p. 374°C (ref.[14]: m.p. 374°C). – MS: *m/z* (%): 355 (29), 354 (100) [M^+], 353 (73), 352 (38), 350 (19), 339 (10), 177 (13), 175 (23).

☆ Dedicated to Professor Dr. *Peter Sartori* on the occasion of his 65th birthday.

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[7] Further details of the crystal structure investigation are available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405115 the names of the authors, and the journal citation.

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