Synthesis of Polycyclic Hydrocarbons by Palladium-Catalyzed Cross-Coupling Reactions of Vinylic Bromides with Diphenylacetylene

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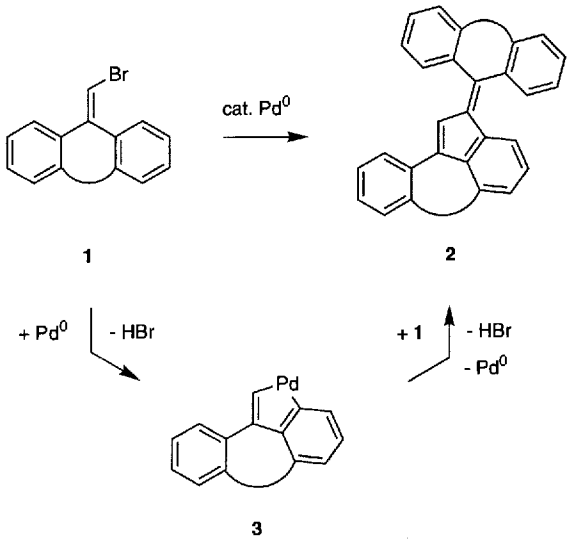
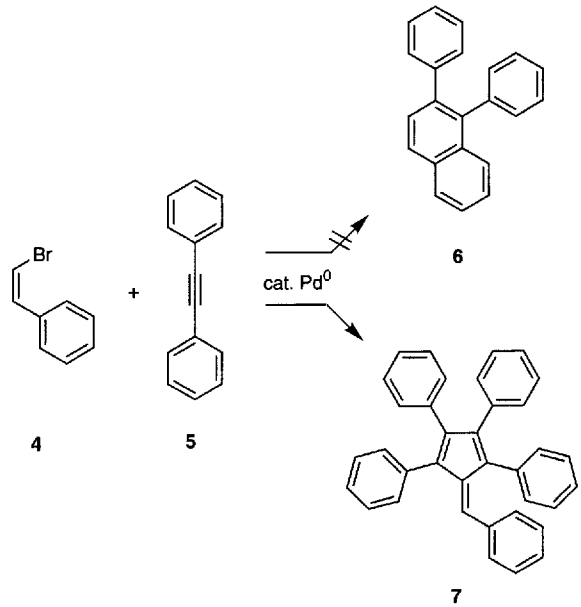
Vinylic bromides of type **1** undergo cross-coupling reactions with diphenylacetylene (**5**) leading to various polycyclic hydrocarbons. The ratio of the 1:1 to the 1:2 products can readily be controlled by varying the reaction conditions.

Vinylic halides are known as versatile coupling components for palladium-catalyzed processes[1]. The readily accessible aryl-substituted vinylic bromides of type **1**, with a variable central ring, are of special interest as building blocks for polycyclic hydrocarbons. Recently, we studied a palladium-catalyzed homo-coupling process of such substrates, leading to annelated pentafulvenes **2** in good to excellent yields[2] (Scheme 1, for 6- and 7-membered central rings). Five-membered palladacycles **3** are assumed to be key intermediates[3] in this domino process. Since 5-membered palladacycles have been shown to readily add substituted acetylenes[4], we envisaged that under reaction conditions favoring palladacycle formation, a cross-coupling reaction of the vinylic bromides **1** with one equivalent of substituted acetylene would occur, resulting in 1:1 annelation products. However, an attempt by Silverberg et al.[5] to achieve such an annelation reaction, using *cis*-bromostilbene (**4**) and diphenylacetylene (**5**) as model substrates, was unsuccessful (Scheme 2). Instead of the anticipated 1:1 product **6**, the substituted fulvene **7** was obtained as a 1:2 product[6]. In this paper we report on cross-coupling reactions of vinylic bromides of type **1** with diphenylacetylene (**5**), which result in both 1:1 and 1:2 products, depending on the size of the central ring and on the reaction conditions.

Scheme 1. Palladium-catalyzed homo-coupling reaction of vinylic bromides of type **1**; additonal ligands have been omitted for clarity



Scheme 2. Palladium-catalyzed cross-coupling reaction of bromostilbene **4** with diphenylacetylene (**5**)[5]



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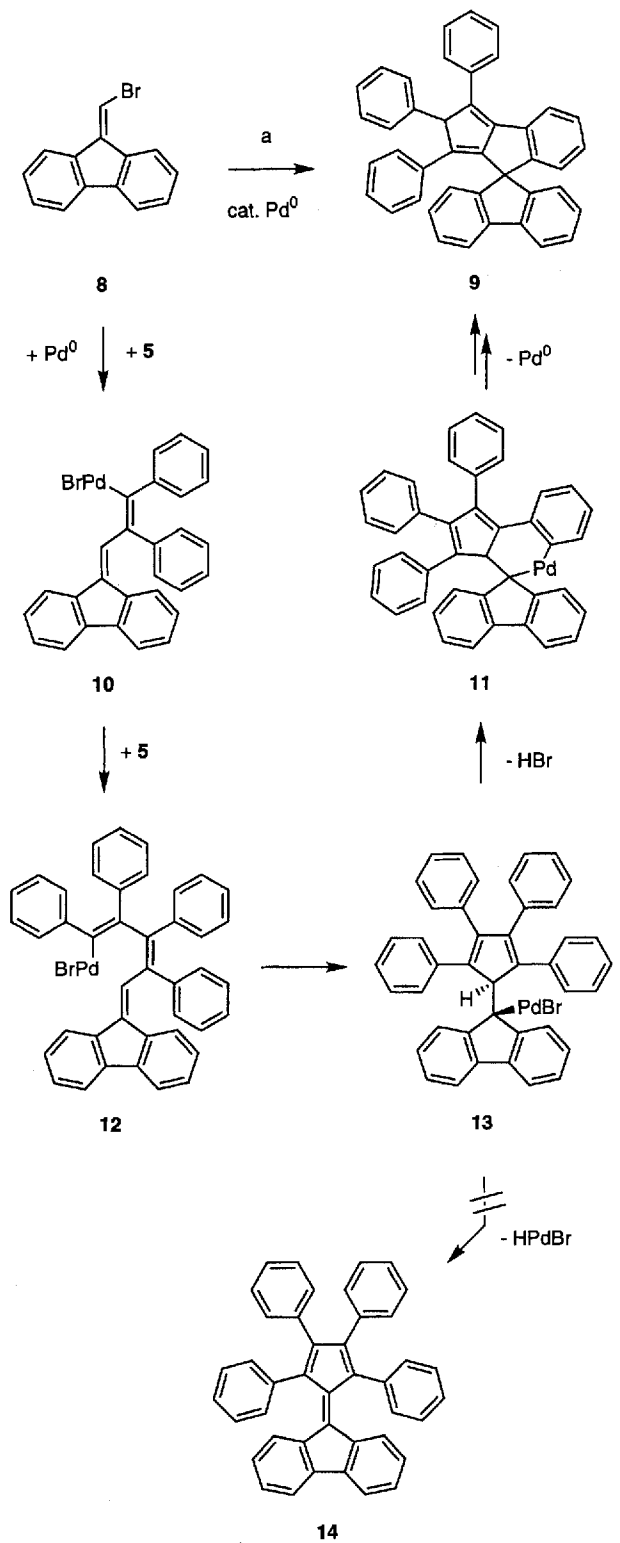
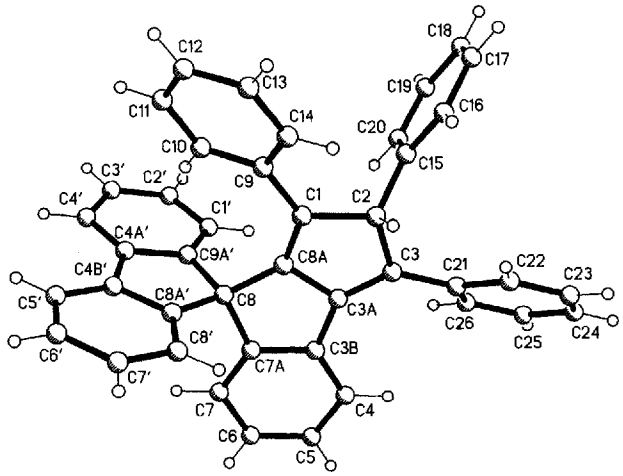
Scheme 3. Reagents: a: 4 equiv. of **5**, 6 mol-% $Pd(OAc)_2$, K_2CO_3, nBu_4NBr, DMF, N_2, 3 d, 100°C; 45% yield



Results and Discussion

We started our investigation with the fluorenone-derived vinylic bromide **8**[2] (Scheme 3). The palladium-catalyzed cross-coupling reaction with diphenylacetylene (**5**) led to the isolation of the spiro-annelated product **9** as a single

Figure 1. X-ray structure analysis of the spirocyclic hydrocarbon **9**; radii are arbitrary

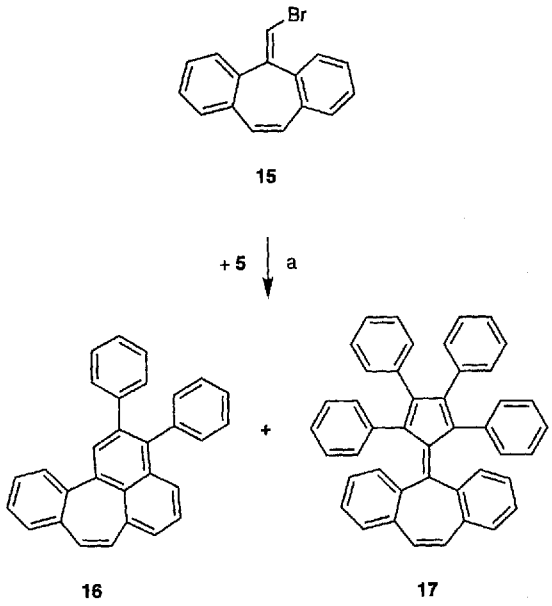


regioisomer, as confirmed by an X-ray structure analysis (Figure 1)[7]. Concerning the mechanistic interpretation, substrate **8** with the 5-membered central ring is to some extent a special case, in that the initial formation of a palladacycle, as in Scheme 1, is inhibited due to geometric constraints[2]. The stereoselective *syn* addition of two equivalents of the acetylene **5** presumably leads to a trienyl-substituted Pd^{II} complex **12**. The intramolecular carbopalladation giving rise to intermediate **13** should then proceed in a *syn* manner. Consequently, rotation about the central C–C bond would be necessary, in order for the *syn*-β-hydrogen elimination to the pentafulvalene **14** to occur. This process does not occur for steric reasons. Instead, the cyclopalladation to a phenyl substituent to give **11** successfully competes. From this 6-membered palladacycle the reaction pathway leads to the observed product **9** by reductive elimination of the active Pd^0 catalyst and subsequent double-bond isomerization. According to semiempirical calculations (AM1) **9** is indeed the thermodynamically most stable of the five possible isomers (by 2.1 to 7.7 kcal/mol).

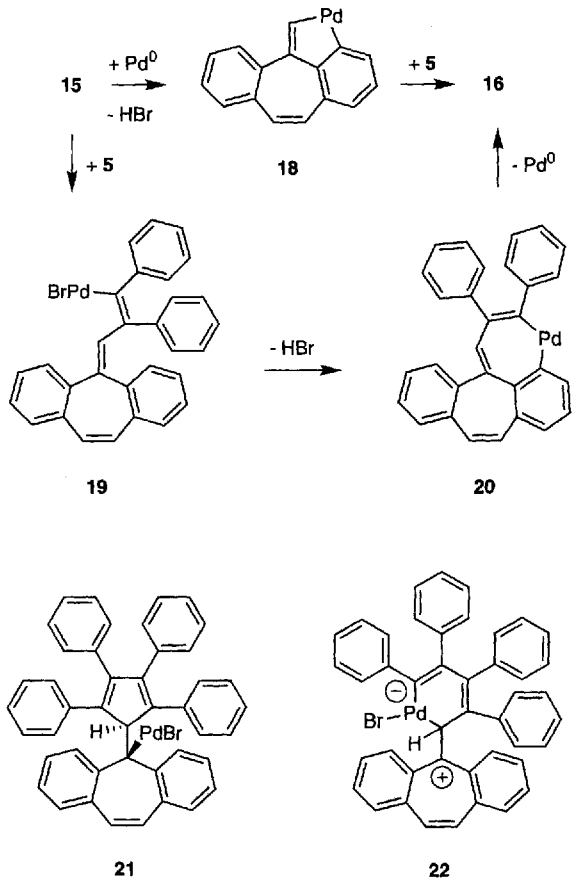
The vinylic bromide **15**[2] with a 7-membered central ring behaved differently (Scheme 4); two main products were formed by the condensation with diphenylacetylene (**5**): the benzopleiadiene[8] **16** and the dibenzo-annelated sesquifulvalene[9] **17**. The product ratio was strongly influenced by the reaction conditions. A higher concentration of the vinylic bromide **15** with an excess of the alkyne **5** led mainly to the formation of the 1:2 product **17** (64%). At higher dilution, with the use of a 1:1 ratio of the coupling components, the 1:1 product **16** predominated; **16** was isolated in 57% yield, whereas **17** was only a very minor product (3%).

Formation of **16** requires C–H activation at the *peri* position. This probably takes place by a cyclopalladation with the 5-membered palladacycle **18** as the key intermediate (Scheme 5). The cyclopalladation should be favored at higher dilution and without using an excess of **5**, precisely the reaction conditions that were found to favor the 1:1 product **16**. Nevertheless, an alternative reaction pathway via the 7-membered palladacycle **20** cannot be ruled out.

Scheme 4. Reagents: a: 6 mol-% $Pd(OAc)_2$, K_2CO_3, nBu_4NBr, DMF, N_2, 3 d, 100°C; for c_{15} = 0.056 M and 4 equiv. of **5**: 14% of **16** and 64% of **17**; for c_{15} = 0.015 M and 1 equiv. of **5**: 57% of **16** and <3% of **17**

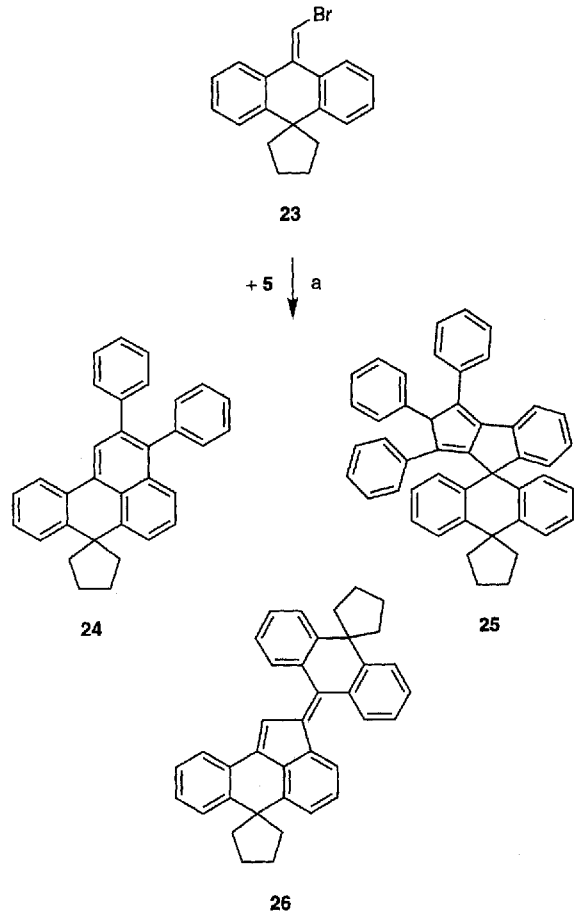


Scheme 5. Palladium complexes as reactive intermediates in the formation of the polycyclic hydrocarbons **16** and **17**



For the formation of the 1:2 product **17** the ring closure is once again the crucial reaction step. Here also, two

Scheme 6. Reagents: a: 6 mol-% $Pd(OAc)_2$, K_2CO_3, nBu_4NBr, DMF, N_2, 3 d, 100°C; for c_{23} = 0.05 M and 4 equiv. of **5**: 34% of **24**, 6% of **25** and 0.8% of **26**; for c_{23} = 0.0125 M and 1 equiv. of **5**: 36% of **24** and 53% of **26**



alternative pathways have to be considered. As in the case of intermediate **13** (Scheme 3) in the reaction sequence starting from **8**, the sterically crowded carbopalladated intermediate **21** would have to rotate about the central C–C single bond for the *syn*-β-hydrogen elimination to occur. Although **21** may be somewhat more flexible than **13** (the fluorene unit of **13** is sterically less demanding but more rigid compared to the suberene unit of **21**), the high steric barrier for this process should result in some by-products analogous to spirocycle **9**. As this was not found experimentally, we are inclined to rule out intermediate **21**. Instead, a cyclopalladation route to **17** seems more likely. We assume the palladate complex **22**, with an aromatic, cationic dibenzocycloheptatrienyl substituent, to be the key intermediate.

Finally, we tested the vinylic bromide **23**[2] with a 6-membered central ring as a coupling component with diphenylacetylene (**5**) (Scheme 6). By employing an excess of **5** a complex product mixture was obtained, from which three components were isolated and identified. Besides a small amount of the homo-coupling product **26**, we found the 1:1 product **24**, which resembles the suberenone-derived product **16**, and the substituted cyclopentadiene **25**, which corresponds to the fluorenone-derived product **9**. For the identification of **25** its NMR spectra were compared to those of

compound **9**; the diagnostic signals of the benzylic C–H group have very similar chemical shifts (^{1}H: δ = 5.59 compared to 5.56; ^{13}C: δ = 67.1 compared to 67.3). Again, we have confirmed by semiempirical calculations that the proposed structure **25** is by far the thermodynamically most stable of the five possible double-bond isomers. At higher dilution and using a 1:1 ratio of the coupling components, the annelation product **24** and the homo-coupling product **26** were strongly favored. Clearly, the reactions of **23** exhibit similarities to those of both **8** and **15**.

In summary, we have shown that vinylic bromides of type **1** undergo cross-coupling reactions with diphenylacetylene (**5**) leading to various polycyclic hydrocarbons, whereby the product distribution can easily be controlled by variation of the reaction conditions.

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Experimental Section

Melting points are uncorrected. – IR: Nicolet 320. – UV/Vis: HP 8452 A. – NMR: Bruker AM 400. – ^{1}H-NMR spectra were recorded at 400.1 MHz by using $CDCl_3$ as the solvent and TMS as the internal standard. – ^{13}C-NMR spectra were measured at 100.6 MHz by using $CDCl_3$ as the solvent and as the internal standard (δ = 77.05). – MS: Finnigan MAT 8430. Mass spectra were recorded at an ionizing voltage of 70 eV by electron impact. – For analytical TLC, precoated plastic sheets "POLYGRAM SIL G/UV254" from Macherey-Nagel & Co. were used.

Palladium-Catalyzed Cross-Coupling Reactions of Vinylic Bromides of Type **1** *with Diphenylacetylene* (**5**). – *General Procedure:* A mixture of 0.56–1.00 mmol of vinylic bromide, 4 equiv. of **5** (or 1 equiv. for the experiment at higher dilution), 1.11 g (8.0 mmol) of K_2CO_3, 645 mg (2.00 mmol) of nBu$_4$NBr, 7.0 mg (31 μmol) of $Pd(OAc)_2$ and 10 ml of dry DMF (or 40 ml for the experiment at higher dilution) in a sealed tube (for convenience) was stirred under N_2 at 100 °C for 3 d. The reaction mixture was then diluted with 50 ml of water and then extracted three times with 50 ml of diethyl ether. The combined ether extracts were filtered through silica gel and concentrated. The crude product mixture was separated by flash chromatography [petroleum ether, b.p. 50–70 °C, or petroleum ether/diethyl ether (100:1), silica gel] and the isolated hydrocarbons were dried in vacuo.

Coupling Reaction of Vinylic Bromide **8**: 257 mg (1.00 mmol) of **8** and 712 mg (4.00 mmol) of **5** in 10 ml of dry DMF were employed in the palladium-catalyzed reaction, according to the general procedure. The excess of **5** was removed from the crude product mixture at 120 °C/0.5 Torr in a Kugelrohr apparatus. Following flash chromatography [petroleum ether/diethyl ether (100:1), silica gel] a yellow solid crystallized. Recrystallization from dichloromethane/pentane gave 238 mg (45%) of spirocyclic hydrocarbon **9** as a yellow solid of m.p. 234–236 °C. – IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1} (w), 3020 (w), 1599 (m), 1493 (m), 1444 (m), 769 (s), 760 (s), 751 (s), 729 (s), 707 (m), 697 (s), 684 (m), 670 (s), 562 (w), 547 (w). – UV (11.6 μmol/l acetonitrile): λ_{max} (lg ε) = 206 nm (4.92, sh), 230 (4.60, sh), 244 (sh), 268 (4.47), 292 (4.19, sh), 306 (4.09), 362 (3.89). – ^{1}H NMR: δ = 5.56 (s, 1H), 6.48 ("d", J = 7.6 Hz, 1H), 6.54–6.56 (m, 2H), 6.68–6.76 (m, 3H), 6.94–7.07 (m, 6H), 7.13–7.17 (m, 3H), 7.21–7.31 (m, 3H), 7.34–7.44 (m, 4H), 7.59 ("d", J = 7.6 Hz, 2H), 7.78 ("d", J = 7.5 Hz, 1H), 7.89 (dd, J = 7.6, 3.3 Hz, 2H). – ^{13}C NMR: δ = 60.91 (s), 67.32 (d), 119.65 (d), 120.28 (d), 122.46 (d), 124.43 (d), 124.53 (d), 124.74 (d), 125.90 (d), 126.39 (d), 127.06 (d), 127.26 (d), 127.31 (d), 127.48 (d), 127.61 (d), 127.81 (d), 127.95 (d), 128.15 (d), 128.22 (d), 128.30 (d), 128.48 (d), 128.53 (d), 129.15 (d), 133.80 (d), 135.00 (d), 135.87 (s), 138.88 (s), 139.49 (s), 140.61 (s), 141.03 (s), 141.58 (s), 146.67 (s), 148.77 (s), 150.45 (s), 151.51 (s), 155.59 (s). – MS; m/z (%): 533 (44), 532 (100) [M$^+$], 455 (12), 441 (14), 439 (6), 376 (12), 365 (16), 352 (9), 267 (18), 265 (46), 188 (12), 165 (4). – $C_{42}H_{28}$ (532.7): calcd. C 94.70, H 5.30; found C 94.71, H 5.18.

Crystal Data for Compound **9**[7]: Monoclinic, space group $P2_1/n$, a = 909.43(10), b = 1592.87(14), c = 1990.8(2) pm, β = 100.840(10), V = 2.8324 nm^3, Z = 4, D_x = 1.249 mg m^{-3}, λ(Mo-K_α) = 71.073 pm, μ = 0.07 mm^{-1}, T = –130 °C. Data collection and reduction: A pale-yellow prism 0.6 × 0.4 × 0.3 mm was mounted in inert oil. Data were collected to $2\Theta_{max}$ = 50° on a Stoe STADI-4 diffractometer. Of 9152 measured data, 4976 were unique. Structure solution and refinement: The structure was solved by direct methods and refined anisotropically on F^2 using all reflections (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included by using a riding model. The final $wR(F^2)$ was 0.084 for 379 parameters, conventional $R(F)$ 0.040. S = 0.83; max. Δ/ρ = 0.001; max. Δ/ = 173 e nm^{-3}.

Coupling Reactions of Vinylic Bromide **15**: 160 mg (0.56 mmol) of **15** and 399 mg (2.24 mmol) of **5** in 10 ml of dry DMF were employed in the palladium-catalyzed reaction, according to the general procedure. The excess of **5** was removed from the crude product mixture at 120 °C/0.5 Torr in a Kugelrohr apparatus. The residue was then fractionated by flash chromatography (petroleum ether, silica gel).

1st Fraction with R_f = 0.2: 31 mg (14%) of 2,3-diphenylbenzo[4,5]cyclohepta[1,2,3-*de*]naphthalene (**16**) as yellow crystals of m.p. 78 °C. – IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} (w), 3023 (w), 1597 (w), 1577 (w), 1491 (w), 1442 (w), 1384 (w), 1372 (w), 1021 (w), 899 (w), 828 (m), 789 (m), 771 (s), 752 (m), 701 (s), 637 (w), 617 (w), 584 (w), 566 (w). – UV (18.7 μmol/l acetonitrile): λ_{max} (lg ε) = 192 nm (4.78), 202 (4.68, sh), 208 (4.72), 242 (4.70), 254 (4.54), 292 (3.94, sh), 346 (3.92, sh), 362 (3.97), 378 (3.94, sh), 406 (3.76, sh). – ^{1}H NMR: δ = 6.52 (d, J = 12.1 Hz, 1H), 6.56 (d, J = 12.1 Hz, 1H), 7.12–7.19 (m, 9H), 7.20–7.32 (m, 6H), 7.33 (m, 1H), 7.41 (dd, J = 7.9, 1.9 Hz, 1H), 7.58 (s, 1H). – ^{13}C NMR: δ = 125.64 (d), 126.38 (d), 126.43 (d), 126.88 (d), 127.67 (d), 128.10 (d), 129.13 (d), 129.91 (d), 129.96 (d), 130.05 (d), 131.00 (d), 131.25 (d), 131.67 (d), 133.51 (d), 134.61 (s), 134.92 (s), 135.66 (d), 137.31 (s), 137.48 (s), 138.05 (s), 138.99 (s), 139.18 (s), 140.14 (s), 141.58 (s). – MS; m/z (%): 381 (20), 380 (100) [M], 363 (12), 303 (14), 302 (21), 181 (8), 93 (8), 44 (19). – $C_{30}H_{20}$ (380.5): calcd. C 94.70, H 5.30; found C 94.68, H 5.23.

2nd Fraction with R_f = 0.05, further purified by sublimation at 230 °C/0.5 Torr in a Kugelrohr apparatus: 198 mg (64%) of the benzo-annelated sesquifulvalene **17** as red needles of m.p. 272–274 °C. – IR (KBr): $\tilde{\nu}$ = 3157 cm^{-1} (w), 3021 (w), 1590 (w), 1485 (w), 1440 (w), 1029 (w), 798 (w), 772 (m), 716 (m), 698 (s), 564 (w). – UV (14.5 μmol/l acetonitrile): λ_{max} (lg ε) = 210 nm (4.71, sh), 266 (4.42), 304 (4.16, sh), 316 (4.11, sh), 354 (3.93, sh). – ^{1}H NMR: δ = 7.11 (s, 2H), 7.07 ("d", J = 7.8 Hz, 2H), 6.91–7.00 (m, 6H), 6.84–6.90 (m, 8H), 6.80 (td, J = 7.8, 1.1 Hz, 2H), 6.73 (br. s, 8H), 6.57 (td, J = 7.6, 1.0 Hz, 2H). – ^{13}C NMR: δ = 124.83 (d), 126.04 (d), 126.39 (d), 126.56 (d), 126.75 (br. d, 126.91 (d), 127.21 (d), 129.03 (d), 130.37 (d), 130.61 (br. d), 130.95 (d), 133.14 (s), 134.89 (s), 136.00 (s), 137.24 (s), 137.47 (s), 140.13

(s), 146.16 (s), 151.69 (s). – MS; *m/z* (%): 559 (44), 558 (100) [M^+], 481 (22), 403 (11), 291 (8), 201 (17), 191 (11). – $C_{44}H_{30}$ (558.7): calcd. C 94.59, H 5.41; found C 94.59, H 5.36.

The corresponding reaction at higher dilution, using 167 mg (0.59 mmol) of **15** and 104 mg (0.58 mmol) of **5** in 40 ml of dry DMF, i.e. a 1:1 ratio of the coupling components, gave 128 mg (57%) of the yellow hydrocarbon **16** and only trace amounts of the red hydrocarbon **17**.

Coupling Reactions of Vinylic Bromide **23**: 163 mg (500 μmol) of **23** and 356 mg (2.00 mmol) of **5** in 10 ml of dry DMF were employed in the palladium-catalyzed reaction, according to the general procedure. The excess of **5** was then removed from the crude product mixture at 105°C/0.4 Torr in a Kugelrohr apparatus to afford 277 mg of a deep-red residue [TLC, petroleum ether/diethyl ether (50:1), silica gel: R_f = 0.27 (**24**), 0.21 (**26**), 0.14 (**25**), and some more polar products]. The residue was fractionated by flash chromatography [petroleum ether/diethyl ether (100:1), silica gel].

1st Fraction: 72 mg (34%) of the substituted benz[*de*]anthracene **24** as yellow crystals of m.p. 218°C (from dichloromethane/pentane). – IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (w), 3026 (w), 2948 (m), 2870 (w), 1603 (w), 1594 (w), 1489 (w), 1444 (w), 1388 (w), 882 (w), 774 (s), 749 (m), 701 (s), 638 (w). – UV (17.7 μmol/l acetonitrile): λ_{max} (lg ε) = 200 nm (4.92), 230 (4.52, sh), 238 (4.51, sh), 260 (4.52, sh), 266 (4.54), 308 (3.86, sh), 318 (4.06, sh), 328 (4.19, sh), 338 (4.30), 354 (4.27, sh). – ^{1}H NMR: δ = 2.08–2.19 (m, 4H), 2.26–2.34 (m, 2H), 2.40–2.49 (m, 2H), 7.15–7.33 (m, 11H, phenyl-H and 10-H), 7.37 ("t", "*J*" = 7.4 Hz, 1H, 9-H), 7.44 ("dd", "*J*" = 7.1, 7.3 Hz, 1H, 5-H), 7.54 ("dd", "*J*" = 8.4, 1.0 Hz, 1H, 4-H), 7.59 (m, 2H, 6-H and 8-H), 8.13 ("dd", "*J*" = 8.0, 1.3 Hz, 1H, 11-H), 8.19 (s, 1H, 1-H); assignments based on HH-COSY and CH-COSY. – ^{13}C NMR: δ = 27.75 (t), 48.97 (t), 50.91 (s), 121.45 (d, C-1), 122.92 (d, C-8), 123.09 (d, C-11), 124.62 (d, C-4), 126.22 (d), 126.29 (d), 126.51 (d, C-5), 126.70 (d), 126.91 (d, C-6), 127.68 (d), 127.84 (d), 128.18 (d, C-5), 129.76 (s), 130.15 (d), 130.66 (s), 131.55 (d), 132.81 (s), 138.48 (s), 139.46 (s), 142.39 (s), 145.19 (s), 146.46 (s). – MS; *m/z* (%): 424 (6), 423 (34), 422 (100) [M^+], 421 (17), 394 (11), 393 (34), 380 (14), 367 (23), 365 (14), 363 (15), 346 (19), 345 (64), 317 (18), 316 (13), 315 (24), 313 (13), 302 (11), 289 (11), 182 (13). – $C_{33}H_{26}$ (422.6): calcd. C 93.80, H 6.20; found C 93.71, H 6.21.

2nd Fraction: 2.0 mg (0.8%) of the homo-coupling product **26**[2] as red crystals of m.p. 205°C.

3rd Fraction: 17 mg (5.7%) of the substituted cyclopentadiene **25** as slightly yellow needles of m.p. 264–265°C (from 2-propanol). – IR (KBr): $\tilde{\nu}$ = 2929 cm^{-1} (m), 2865 (w), 1661 (m), 1631 (m), 1596 (m), 1488 (m), 1451 (m), 1245 (m), 1213 (w), 1172 (m), 1158 (m), 1142 (m), 1107 (s), 1073 (s), 1039 (s), 1010 (m), 757 (s), 696 (s), 556 (w). – UV (7.3 μmol/l acetonitrile): λ_{max} (lg ε) = 194 nm (5.11), 214 (4.74, sh), 224 (4.54, sh), 228 (4.49, sh), 266 (4.27, sh), 366 (3.96). – ^{1}H NMR: δ = 2.24–2.40 (m, 4H), 2.50–2.58 (m, 2H), 2.62–2.77 (m, 2H), 5.59 (s, 1H), 6.73–6.84 (m, 6H), 6.91–6.94 (m, 2H), 6.97 ("t", "*J*" = 7.3 Hz, 1H), 7.04–7.10 (m, 5H), 7.12 ("t", "*J*" = 7.5 Hz, 1H), 7.16 ("d", "*J*" = 7.7 Hz, 2H), 7.22–7.27 (m, 2H), 7.30 ("t", "*J*" = 8.0 Hz, 1H), 7.37 ("t", "*J*" = 7.7 Hz, 2H), 7.41 ("d", "*J*" = 7.3 Hz, 1H), 7.58 ("d", "*J*" = 8.1 Hz, 1H), 7.60 ("dd", "*J*" = 8.2, 1.0 Hz, 2H), 7.83–7.86 (m, 1H). – ^{13}C NMR: δ = 29.35 (t), 30.01 (t), 48.88 (s), 49.92 (t), 52.98 (t), 53.57 (s), 67.08 (d), 122.35 (d), 125.84 (d), 125.87 (d), 126.36 (d), 126.39 (d), 126.57 (d), 126.68 (d), 127.07 (d), 127.13 (d), 127.33 (d), 127.35 (d), 127.71 (d), 127.87 (d), 128.24 (d), 128.28 (d), 128.34 (d), 128.52 (d), 128.65 (d), 129.65 (d), 132.47 (s), 133.86 (s), 135.78 (s), 135.96 (s), 137.93 (s), 138.63 (s), 139.51 (s), 139.64 (s), 145.19 (s), 145.93 (s), 147.15 (s), 158.90 (s), 162.58 (s). – MS; *m/z* (%): 602 (13), 601 (49), 600 (100) [M^+], 510 (9), 509 (24), 389 (9), 319 (12), 291 (9), 201 (9), 167 (11), 149 (29), 135 (9), 86 (13), 84 (23), 70 (14), 69 (16), 57 (29), 45 (61). – $C_{47}H_{36}$ (600.8): calcd. C 93.96, H 6.04; found C 93.64, H 5.70. – Mol. mass calcd. 600.2817; found 600.2810.

The preliminary investigation of a more polar fraction by NMR and MS indicated a product with a molecular mass of 632, which is derived from 1 equiv. of **24**, 2 equiv. of **5**, and 1 equiv. of oxygen.

The corresponding reaction at higher dilution, using 163 mg (500 μmol) of **23** and 89 mg (500 μmol) of **5** in 40 ml of dry DMF, i.e. a 1:1 ratio of the coupling components, gave 77 mg (36%) of the 1:1 product **24** and 65 mg (53%) of the homo-coupling product **26**.

[1] J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, Wiley, Chichester, **1995**.

[2] G. Dyker, F. Nerenz, P. Siemsen, P. Bubenitschek, P. G. Jones, *Chem. Ber.* **1996**, *129*, 1265–1269.

[3] G. Dyker, J. Körning, F. Nerenz, P. Siemsen, S. Sostmann, A. Wiegand, P. G. Jones, P. Bubenitschek, *Pure Appl. Chem.* **1996**, *68*, 323–326.

[4] D. J. Cardenas, C. Mateo, A. M. Echavarren, *Angew. Chem.* **1994**, *106*, 2529–2531; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2445.

[5] L. J. Silverberg, G. Wu, A. L. Rheingold, R. F. Heck, *J. Organomet. Chem.* **1991**, *409*, 411–420.

[6] Further examples of fulvene formation from vinylic halides and acetylenes: [6a] G. C. M. Lee, B. Tobias, J. M. Holmes, D. A. Harcourt, M. E. Garst, *J. Am. Chem. Soc.* **1990**, *112*, 9330–9336. – [6b] E. Negishi, L. S. Harring, Z. Owczaraczyk, M. M. Mohamud, M. Ay, *Tetrahedron Lett.* **1992**, *33*, 3253–3256.

[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-405633 for compound **9**.

[8] Y. Sugihara, H. Yamamoto, K. Mizoue, I. Murata, *Angew. Chem.* **1987**, *99*, 1283–1285; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1247.

[9] [9a] H. Prinzbach, D. Seip, L. Knothe, W. Faiist, *Liebigs Ann. Chem.* **1966**, 34–56. – [9b] H. Prinzbach, D. Seip, L. Knothe, W. Faiist, *Helv. Chim. Acta* **1967**, *50*, 1669–1692. – [9c] B. Pullman, M. A. Pullman, E. D. Bergmann, M. H. Berthod, E. Fischer, Y. Hirshberg, D. Lavie, E. Mayot, *Bull. Soc. Chim. Fr.* **1952**, 73–78.

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