Pergamon

Tetrahedron Vol. 50, No. 2, pp. 383-401, 1994

0040-4020/94 $6.00+0.00

0040-4020(93)E0103-M

Palladium-Catalyzed Domino Coupling Reactions of Aryl Halides with Norbornene and Norbornene Derivatives – A Simple Route to Polycyclic Aromatic Compounds

Karsten Albrecht[a], Oliver Reiser[a], Martin Weber[b], Burkhard Knieriem[a], and Armin de Meijere[a]*

Institut für Organische Chemie der Georg-August-Universität Göttingen[a], Tammannstrasse 2, D-37077 Göttingen, Germany
Institut für Organische Chemie der Universität Hamburg[b], Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

Abstract: Under palladium-catalysis, norbornene **1**, dicyclopentadiene **10**, norbornenol **13**, and norbornenone **15** react with unsubstituted as well as substituted bromo- and iodobenzenes to give 1 : 3 coupling products with 4-aryl-9,10-dihydrophenanthrene units with up to 70% isolated yields. The structures of two such products **4a** and **4c** were proved by X-ray crystal structure analysis. 2-Bromothiophene **17** reacts with **1** and **10** to yield a mixture of 2 : 1 and 3 : 1 coupling products, while 3-iodopyridine **22a**, 3-iodo-6-methylpyridine **22b** and 4-iodopyridine **25** give only 2 : 1 coupling products with 5,6-dihydro-3,8-phenanthroline and 5,6-dihydro-2,9-phenanthroline units, respectively. Some new mechanistic insights into this interesting four-component domino coupling reaction are presented. The products can easily be transformed by photocyclization/dehydrogenation and/or flash vacuum pyrolysis to a variety of cyclopentadiene-anellated polycyclic aromatic compounds in very high yields. The reported sequence also presents the easiest access to benzo[*e*]pyrene.

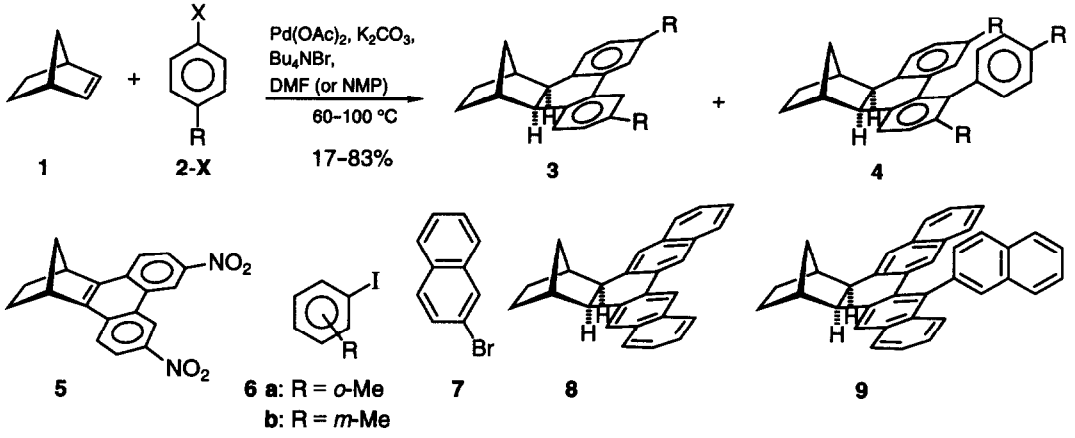
INTRODUCTION

Palladium-catalyzed sequential transformations,[1] in which several new C,C bonds are formed in a single operation, have become a rapidly growing area of research, in which many imaginative new ideas have been tested and realized.[2-7] Such transformations work particularly well for multifold alkene-alkene and alkene-alkyne coupling reactions, in which all the sequential steps occur in an intramolecular fashion, but have also been reported for special intra-inter-intramolecular[8a] and even inter-inter-intramolecular sequences.[8b,9] In most of the latter examples, norbornene **1** has been the olefinic reaction partner, onto which alkynes as well as alkenyl and aryl halides have been coupled.[8-10] Early on, Chiusoli et al. reported a sequential coupling of norbornene with two molecules of iodobenzene **2a-I** (or bromobenzene **2a-Br**) to yield the norbornene-anellated 9,10-dihydrophenanthrene derivative **3a**.[9] As we found later, **1** can also sequentially react with three molecules of an aryl halide **2-X** to give norbornene-anellated 4-phenyl-9,10-dihydrophenanthrene derivatives.[10] We now report on the scope of this interesting four-component domino coupling reaction and some new mechanistic insights.

SCOPE AND LIMITATIONS OF THE FOUR-COMPONENT DOMINO COUPLING

The apparent difference for the two reported coupling modes of norbornene with aryl halides lies in the reaction conditions. While Chiusoli et al. used $Pd(PPh_3)_4$ as a catalyst, and potassium *t*-butoxide as the base in anisole at 130 °C,[9] we applied the protocol developed by Jeffery[11] with $Pd(OAc)_2$ as the catalyst precursor,

potassium carbonate as the base in dimethylformamide (DMF) or *N*-methylpyrrolidone (NMP) at 60–100 °C, and with tetra-*n*-butylammonium bromide[12] as a phase transfer catalyst.[10] Under these conditions, bromo- **2a-Br** and iodobenzene **2a-I** as well as the *para*-substituted aryl iodides **2b,c,d,e-I** with methoxy, fluoro, methyl and chloro substituents gave only the 3 : 1 coupling products **4a-e** (Scheme 1 and Table 1) except for biaryls as by-products in some cases.[13] The *exo*-orientation of the 9,10-dihydrophenanthrene units and the positions



Scheme 1

of substituents in these products were corroborated by the NMR spectroscopic data and rigorously proved by Xray crystal structure analyses for compounds **4a** and **4c** (see Figure 1).[14]

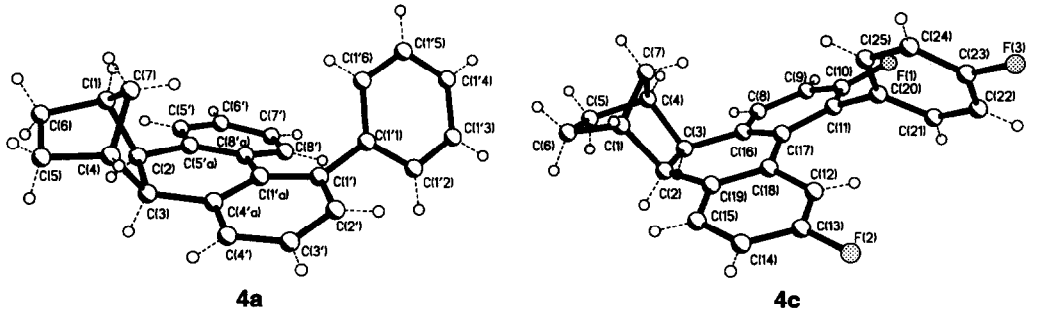


Figure 1. Molecular structures of **4a** and **4c** in the crystals.[14] **4a**: Triclinic crystals of space group $P\bar{1}$, $Z = 2$, unit cell dimensions $a = 9.676(2)$, $b = 9.858(2)$, $c = 10.653(3)$ Å, $\alpha = 117.46(1)$, $\beta = 95.73(2)$, $\gamma = 101.65(1)°$, $V = 861.1(3)$ Å^3. Crystal size $0.2 \times 0.5 \times 0.8$ mm, $T = 293$ K, 2353 reflections collected, final $R_w = 5.5\%$. – **4c**: Triclinic crystals of space group $P\bar{1}$, $Z = 2$, unit cell dimensions $a = 9.714(6)$, $b = 10.199(6)$, $c = 10.809(10)$ Å, $\alpha = 117.47(6)$, $\beta = 95.62(7)$, $\gamma = 101.06(0)°$, $V = 910.9(11)$ Å^3. Crystal size $1.0 \times 1.0 \times 1.0$ mm, $T = 293$ K, 2657 reflections collected, final $R_w = 4.8\%$.

Aryl halides with unsaturated substituents in the *para*-position gave different results.[16] While *p*-bromobenzonitrile **2f-Br** led to both the 2 : 1 and 3 : 1 coupling products **3f** and **4f**, respectively, in poor yields, methyl *p*-iodobenzoate **2g-I** and *p*-iodonitrobenzene **2h-I** gave only the 2 : 1 coupling products **3g** and **3h**, the latter was actually isolated as the dehydrogenated 2 : 1 product **5**, apparently due to the oxidizing ability of *p*-iodonitrobenzene.

With an *ortho* or *meta* methyl substituent on the aryl iodide as in **6a**, **6b**, the 3 : 1 domino products were mixtures of isomers and obtained in only 5 and 33% yield, respectively. Even 2-bromonaphthalene **7** could be coupled with norbornene, albeit the 3 : 1 product **9** was obtained in only 2% yield and the 2 : 1 product **8** in 6%.

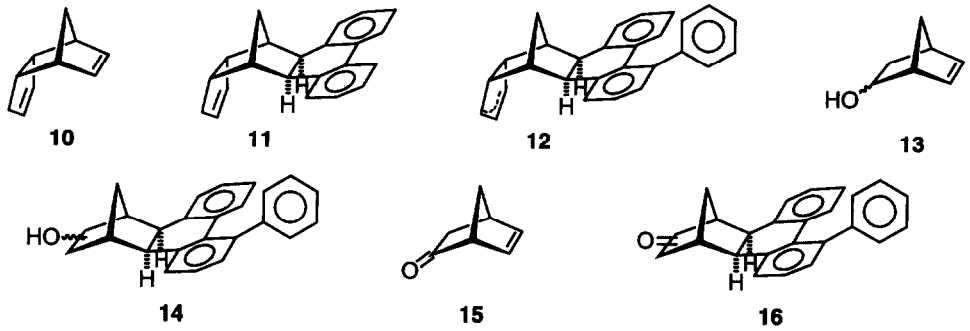
Table 1. Norbornene-Anellated 9,10-Dihydrophenanthrenes **3**, 4-Phenyl-9,10-dihydrophenanthrenes **4**, and Analogous Derivatives (for Details see Scheme 1).

Starting Materials				Reaction Conditions		Conversion	Products and Yields (%)[a]			
Alkene	Aryl Halide	X	R	Temp. [°C]	Time [h]	(%)				
1	**2a**	I	H	65	52	85	**3a**	–	**4a**	83
1	**2a**	Br	H	80	12	100	**3a**	–	**4a**	53
1	**2b**	I	OMe	65 and 80	25 and 30	69	**3b**	–	**4b**	79
1	**2c**	Br	F	75	75	68	**3c**	–	**4c**	48
1	**2d**	I	Me	100	6	100	**3d**	–	**4d**	36[b]
1	**2e**	I	Cl[b]	80	24	100	**3e**	–	**4e**	38[c]
1	**2f**	Br	CN	75	50	35	**3f**	8	**4f**	17
1	**2g**	I	CO_2Me	65	98	60	**3g**	20	**4g**	–
1	**2h**	I	NO_2	75	194	47	**5**	19	**4h**	–
1	**7**	–	–	85	98	36	**8**	18	**9**	6
10	**2a**	I	H	60	24	100	**11**	–	**12**[d]	64
10[e]	**2a**	I	H	60[e]	24	100	**11**	15	**12**	36
13[f]	**2a**	I	H	65	21	76			**14**	66
15[g]	**2a**	I	H	80	24	57			**16**	83[h]

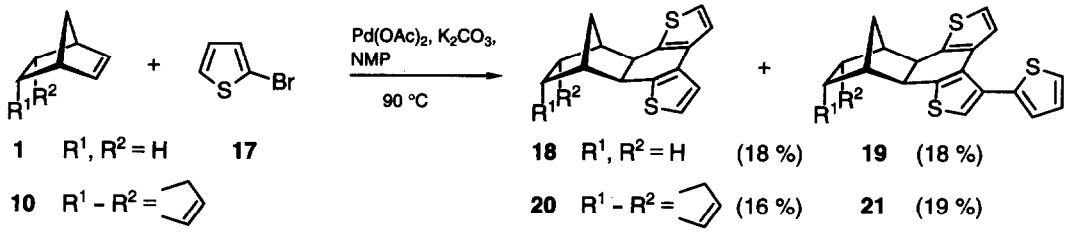
[a] Yields based on the difference between employed and recovered starting material **2-X**. – [b] The NMR data of **4d** appear not be consistent with the positions of the methyl groups as indicated in the formula, but the structure was proved unambigously by X-ray structure analysis. – [c] 4-Chloro-3,5-dideuterioiodobenzene was used. – [d] Mixture of double bond isomers. – [e] Triphenylphosphine (4 equiv. with respect to $Pd(OAc)_2$) was added. – [f] Mixture of *endo*- and *exo*-isomers (3.5 : 1). – [g] Sodium bicarbonate instead of potassium carbonate was used in this case. – [h] An unidentified second 1 : 3 coupling product was isolated in 5% yield.

On the other hand, substituents on the norbornene skeleton had no influence on the reaction mode. The less strained double bond in the anellated five-membered ring of dicyclopentadiene **10** remained untouched while three molecules of iodobenzene **2a-I** were attached to the other double bond. The product **12** was a mixture of isomers with different positions of the double bond in the *endo*-cyclopentene unit. When triphenylphosphine was added to the catalyst cocktail, both the 2 : 1 **11** and 3 : 1 domino products **12** were obtained (15 and 36%, respectively). Norbornenol **13** and norbornenone **15** also gave the corresponding 1 : 3 coupling products **14** and **16**, respectively, in good yields. In order to avoid enolate formation in the case of **15**, the weaker base sodium bicarbonate ($NaHCO_3$) was used instead of potassium carbonate. Because of the better solubility of $NaHCO_3$ in DMF, no phase transfer catalyst Bu_4NBr had to be added.

Heterocyclic aryl halides also underwent domino coupling reactions with norbornene **1** and dicyclopentadiene **10**. 2-Bromothiophene **17** gave both the 2 : 1 and 3 : 1 products **18/20** and **19/21**, respectively, in

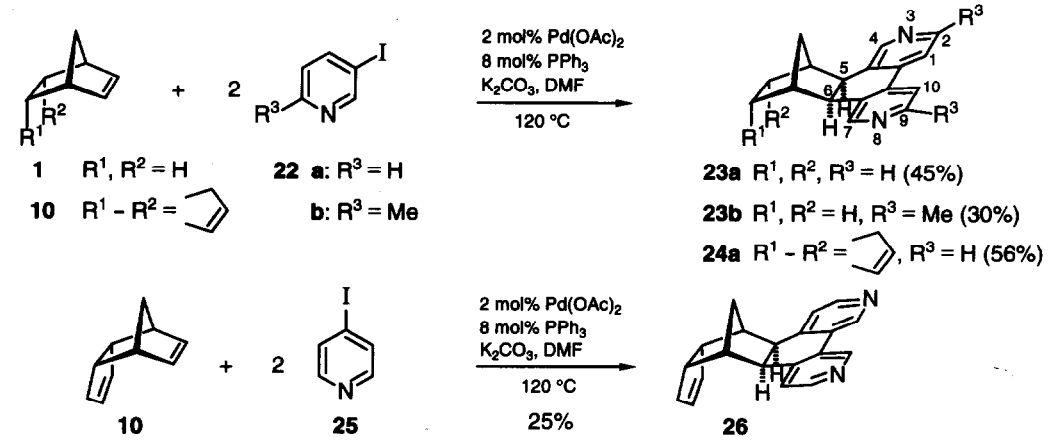


nearly equal yields (see Scheme 2); the conversion of **17** (or 2-iodothiophene) was only 50% even after 20 h at 90 °C. The composition of the product mixture was the same, when the coupling reaction was carried out in the presence of triphenylphosphine.



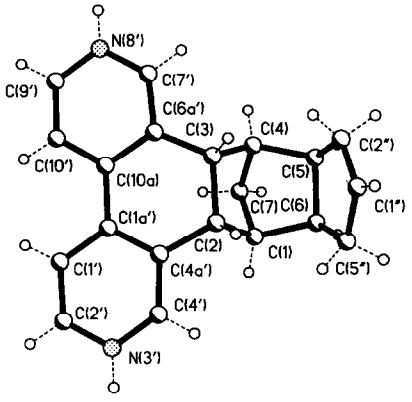
Scheme 2

The domino coupling of iodopyridines **22a,b** and **25** onto norbornene **1** and dicyclopentadiene **10** required even higher temperatures (120 °C) and the presence of triphenylphophine. In all cases, only 2 : 1 coupling products were obtained in up to 56% yield (Scheme 3).



Scheme 3

Unfortunately, the main products from 3-iodopyridines **22a,b** and **1** or **10** were not the ring-anellated 5,6-dihydro-1,10-phenanthrolines, but the 3,8-isomers **23a,b** and **24a**, respectively, with a trace (1%) of the 1,8-isomer being isolated from the reaction of **10** with **22a**. Dicyclopentadiene **10** and 4-iodopyridine **25** gave a single product, namely the ring-anellated 5,6-dihydro-2,9-phenanthroline **26**, but only in 25% yield. The positions of the nitrogen atoms in **24a** and the *exo*-orientation of its dihydrophenanthroline unit were proved by an X-ray crystal structure analysis (see Figure 2).[14]

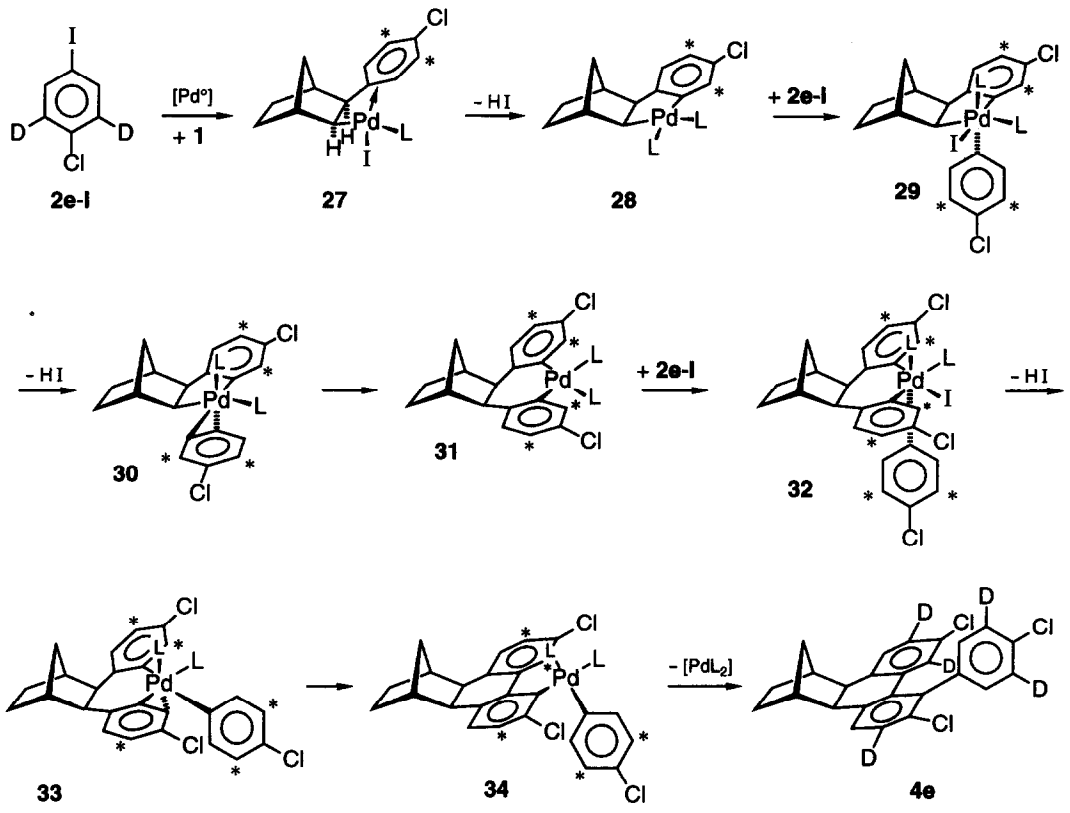


24a

Figure 2. Molecular structure of **24a** in the crystal.[14] Monoclinic crystals of space group *C2/c*, $Z = 8$, unit cell dimensions $a = 20.785(4)$, $b = 15.770(3)$, $c = 11.262(2)$ Å, $\beta = 104.20(3)°$, $V = 3578.7(12)$ Å^3. Crystal size $0.3 \times 0.6 \times 0.1$ mm, $T = 293$ K, 4336 reflections collected, final $R_w = 9.7\%$.

MECHANISTIC ASPECTS OF THE FOUR-COMPONENT DOMINO COUPLING

The previously proposed mechanism[10a] does not account for the positions of the three substituents in 1 : 3 coupling products from norbornene **1** and *p*-substituted aryl iodides, as revealed by the X-ray crystal structure analysis of **4c** (see Figure 1). It is now generally accepted that the catalytic cycle of both the 1 : 2 and 1 : 3 domino coupling reactions involves alternately squaric Pd(II) and octahedral Pd(IV) intermediates.[17,18] But the sequence and regioselectivity of oxidative addition and C,C bond forming (reductive elimination) steps has to be consistent with the structure of **4c**, and the new experimental observation that the doubly labelled 4-chloro-3,5-dideuterioiodobenzene **2e-I** gives a 3 : 1 adduct **4e** with only five deuterium labels remaining in the molecule (see Scheme 4). This indicates that the 4-aryl substituent in the resulting 4-aryl-9,10-dihydrophenanthrene derivative is being attached as the last group onto one of the former deuterium labelled positions *meta* to the iodine and *ortho* to the chlorine in **2e-I**. The whole sequence undoubtedly begins with an *exo-syn*-addition of arylpalladium halide to norbornene,[19] the resulting Pd(II) complex **27** cyclizes by elimination of hydrogen iodide to give the palladacycle **28**,[20] which reacts in another oxidative addition step with **2e-I** to yield the octahedral Pd(IV) complex **29**. The subsequent elimination of hydrogen iodide, in which the proton comes from one of the *ortho*-positions of the aryl ligand, can lead to the aryne-Pd(IV) complex **30**,[21] which can undergo reductive elimination to form the seven-membered palladacycle **31**. In the presence of a triphenylphosphine ligand, the complex of type **31** can apparently undergo further reductive elimination to yield the corresponding norbornene-anellated 9,10-dihydrophenanthrene derivative, as observed for the reaction of dicyclopentadiene **10** with **2a-I** (see above). Eventually, the palladium(II) in **31** can undergo a third oxidative addition of aryl iodide, and the resulting Pd(IV) complex **32**, in a sequence of hydrogen iodide



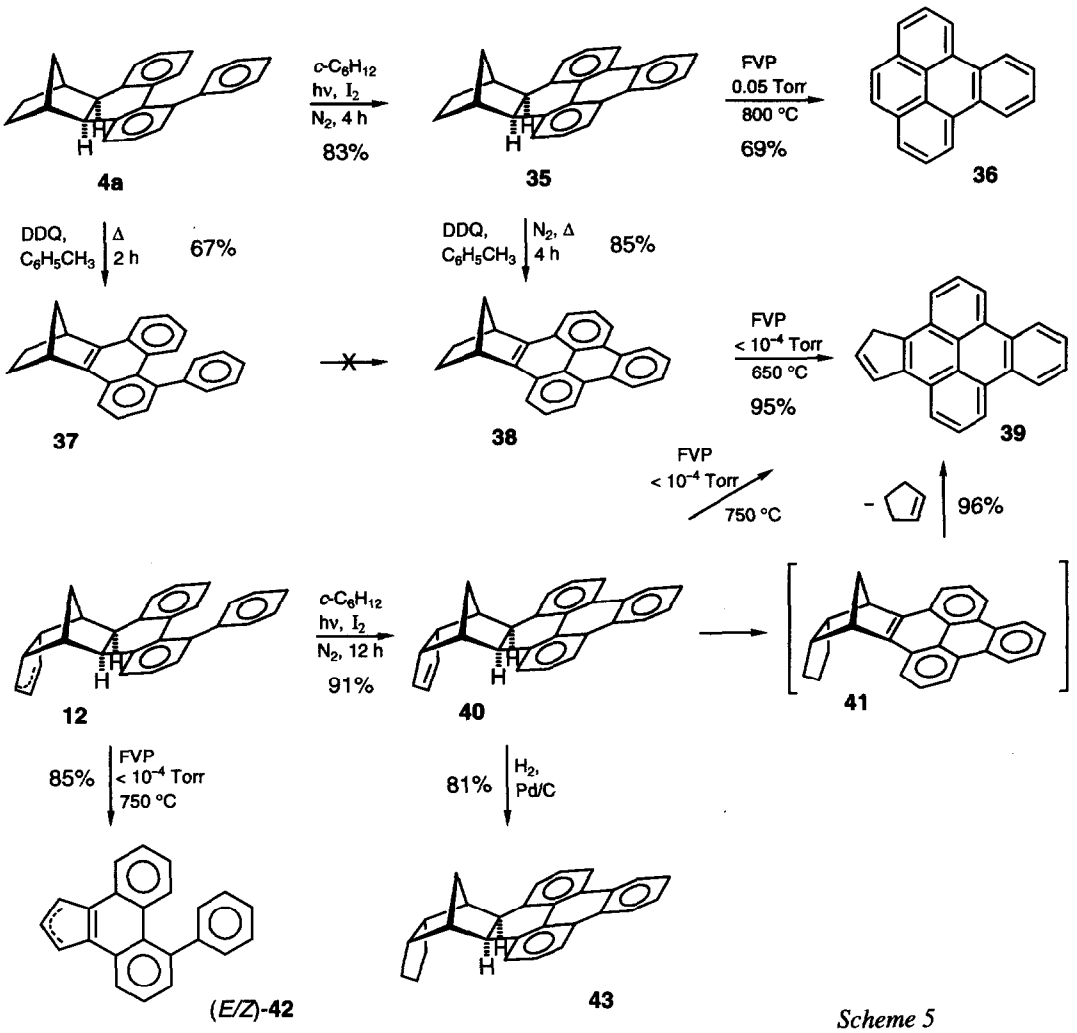
Scheme 4. Proposed mechanism for the four-component domino coupling of norbornene **1** and aryl iodides **2-X** as corroborated by an experiment with doubly labelled 4-chloro-3,5-dideuterioiodobenzene **2e-I** (* indicates the position of deuterium labels in the intermediates).

elimination (deuterium iodide in this particular case) and two subsequent reductive elimination steps with C,C bond formation via the aryne Pd(IV) complex **33**[21] and the Pd(II) complex **34**, reconstitutes the catalytically active Pd(0) species to yield the observed 1 : 3 domino coupling product of type **4e**.

TRANSFORMATIONS OF THE FOUR-COMPONENT DOMINO COUPLING PRODUCTS

The domino coupling products of type **3** and **4** offer an easy approach to a variety of other polycyclic aromatic compounds.[10] As exemplified for **4a**, irradiation in cyclohexane in the presence of iodine results in cyclization with dehydrogenation of the 4-phenyl-9,10-dihydrophenanthrene unit leading smoothly to the norbornene-anellated 4,5-dihydrobenzo[*e*]pyrene derivative **35** (83%, Scheme 5). Further dehydrogenation with dichlorodicyanobenzoquinone (DDQ) leads to the norbornene-anellated benzo[*e*]pyrene **38** (85%). If instead, **4a** is first dehydrogenated with DDQ to compound **37** (67%), the photocyclization/dehydrogenation no longer takes place.

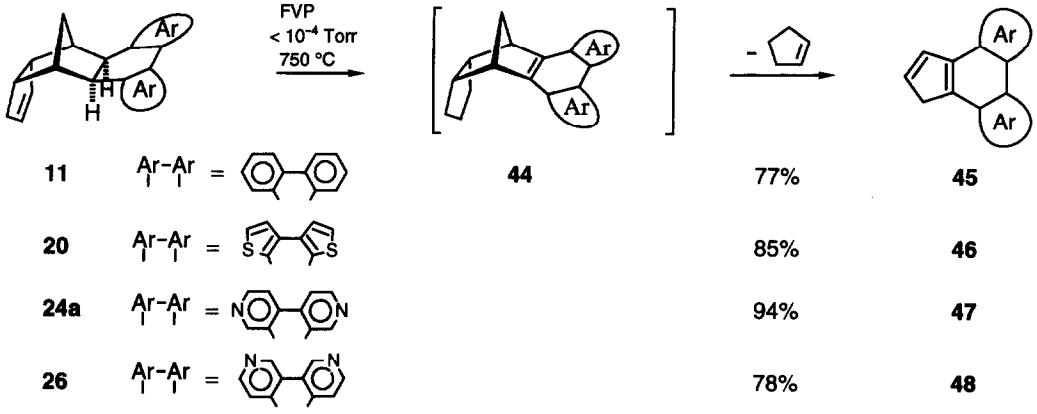
Upon flash vacuum pyrolysis (FVP, sublimation at 0.05 Torr through a 800 °C hot quartz tube)[22] **35** cleanly cleaves off cyclopentene to give benzo[*e*]pyrene **36** (69%). The dehydrogenated compound **38**, under the same pyrolysis conditions, yields 95% cyclopentadieno[*l*]benzo[*e*]pyrene **39** (Scheme 5). A better overall



Scheme 5

yield of this interesting ligand **39** for metal complexes[10b,23] is obtained by photocyclization/dehydrogenation of **12**, the 3 : 1 coupling product of iodobenzene **2a-l** with dicyclopentadiene **10**, and subsequent pyrolysis of **40** (60% overall from **10**), mainly because the dehydrogenation with DDQ is spared. The retro-Diels-Alder reaction[24] of **40** is preceded by an intramolecular transfer of the two bridgehead hydrogens onto the double bond in the *endo*-oriented cyclopentene ring,[25] transforming **40** to **41**, which then easily cleaves off cyclopentene. In fact, cyclopentene was detected as the major volatile by-product in this and analogous pyrolyses, and ($M^+ - C_5H_8$) was also the major fragment ion in all of the mass spectra of **11**, **12**, **20**, **21**, **24a**, **26** and **40**.[26] In a control experiment, **40** was first hydrogenated over palladium on charcoal and the resulting **43** then pyrolyzed, but no retro-Diels-Alder product could be observed.

Consequently, all the domino coupling products obtained from dicyclopentadiene **10** and aryl halides cleanly cleaved to the corresponding cyclopentadiene-anellated oligocyclic arenes. Compound **12** gave a mixture of the two double bond regioisomers (*E*)- and (*Z*)-**42** in 85% yield (Scheme 5). The norbornene-



Scheme 6

annellated 4-phenylphenanthrene **37**, which was obtained by dehydrogenation of **4a**, could also be pyrolyzed to (*E/Z*)-**42**, but aside from the additional step, the overall yield was significantly lower (47 versus 59%). Flash vacuum pyrolysis of dicyclopentadiene derived products **11**, **20**, **24a** and **26** to 9:10-cyclopentadienophenanthrene **45**, 4:5-cyclopentadienobenzo[1,2-*b*:4,3-*b'*]dithiophene **46**, 5:6-cyclopentadieno-3,8-phenanthroline **47** and 5:6-cyclopentadieno-2,9-phenanthroline **48** all proceeded with high yields (77–94%, see Scheme 6).

ACKNOWLEDGEMENTS

This work was supported by the "Volkswagen-Stiftung" and the "Fonds der Chemischen Industrie" as well as the Degussa AG, Hoechst AG and Hüls AG through generous gifts of chemicals. O. R. thanks the "Studienstiftung des deutschen Volkes" for a graduate fellowship. We are indebted to Dr. M. Noltemeyer, Institut für Anorganische Chemie, Georg-August-Universität Göttingen, for carrying out the reported crystal structure analyses, and to S. Beußhausen for his technical assistance.

EXPERIMENTAL PART

^{1}H NMR: Bruker AW 250 (250 MHz), AM 250 (250 MHz), WH 270 (270 MHz), WM 400 (400 MHz), δ = 0 for tetramethylsilane as internal standard, 7.26 for chloroform, 7.15 for [D_5]benzene. – ^{13}C NMR: Bruker AW 250 (62.5 MHz), AM 250 (62.9 MHz), WH 270 (67.9 MHz), WM 400 (100.6 MHz), δ = 77.0 for deuteriochloroform, * = assignment is interchangeable. The multiplicities of ^{13}C NMR signals were generally determined with the help of either DEPT- (Distortionless Enhancement of Polarization Transfer) or APT-techniques (Attached Proton Test) and are designated as follows: CH_3, CH = (+) (DEPT and APT), CH_2 = (–) (DEPT and APT), quaternary C = (–) (APT) or (C_{quat}) (DEPT). – IR: Perkin-Elmer 125, 297, 298, 399, and 1720 FTIR. – MS: Varian MAT CH-7 with Varian Aerograph 1740, MAT 311A, MAT 731 (EI), Finnigan MAT 95, and VG-70-250S Fa. VG Analytical (high resolution). – UV/VIS: Cary 219 (Varian). – Melting points were determined with an Electrothermal melting point app. (Fa. Wagner und Munz, Fa. Büchi) and are uncorrected. – Column chromatography (CC): Merck silica gel 60 (70–230 mesh), Woelm Al_2O_3. – TLC was performed on aluminum sheets with UV fluorescence indicator (E. Merck, Silica Gel 60 F_{254}; Macherey & Nagel, Aluminum Oxide BF_{254}). – Elemental analyses were carried out by Mikroanalytisches Laboratorium, Institut für Organische Chemie, Universität Hamburg, Mikroanalytisches Laboratorium, Institut für Organische Chemie, Universität Göttingen. – HRMS: The molecular composition was determined by high resolution mass spectroscopy with preselective ion peak matching with R ~ 10000 within ± 2 ppm. – X-ray crystal structure analyses: Intensity data were measured with a Siemens Stoe AED 2 diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 71.069 pm), structures were solved with SHELXTL-PLUS.[15]

Further details of these crystal structure investigations are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen. – The following abbreviations will be used: PE = petroleum ether bp 40–80, DMF = *N,N*-dimethylformamide, NMP = *N*-methylpyrrolidone, MTBE = *t*-butyl methyl ether.

Domino Coupling of Aryl Halides and Norbornene

General Procedure 1 (GP 1): To a mixture of 3 mmol of aryl halide, 6 mmol of K_2CO_3, 3 mmol of tetrabutylammonium bromide, and 0.03 mmol of palladium acetate in anhydrous NMP was added at 65–85 °C simultaneously via a syringe pump a solution of 1 mmol of alkene in NMP and a solution of 0.06 mmol of palladium acetate in NMP at a rate of 2–3 mmol of alkene per hour. The reaction mixture was further stirred at this temperature for the stated length of time. The reaction mixture was diluted with 100 ml of dichloromethane and extracted with 5 portions of water (100 ml each), the organic layer was dried over $MgSO_4$, then the solvents were evaporated, and the residue was purified by chromatography and/or recrystallisation.

exo-(4-Phenyl-9,10-dihydrophenanthreno)-2':3',9:10-norbornane (**4a**): According to GP 1, to a mixture of 6.50 g (31.8 mmol) of **2a-I**, 10.27 g (31.9 mmol) of Bu_4NBr, 8.82 g (63.8 mmol) of K_2CO_3 and 24 mg (0.11 mmol) of $Pd(OAc)_2$ in 30 ml of NMP was added at 65 °C during 4.5 h a solution of 1.00 g (10.6 mmol) of **1** in 5 ml of NMP and a solution of 48 mg (0.21 mmol) of $Pd(OAc)_2$ in 5 ml of NMP. The mixture was further heated for 2 d at 65 °C. After standard workup, the crude product was chromatographed on 200 g of silica gel (6 × 15 cm, PE/CH_2Cl_2 9:1): fraction I: (R_f = 0.57) 964 mg of **2a-I** (≙ 85% conversion). – II (R_f = 0.33) 2.41 g (70%, 83% based on conversion of **2a-I**) of **4a**, mp 154–155 °C. – IR (KBr): ν = 3050 cm^{-1}, 2980, 2960, 2880, 1600, 1590, 1440, 1420, 1180, 800, 770, 760, 740, 700. – ^1H NMR (400 MHz, $CDCl_3$, and ^1H-^1H COSY): δ = 1.07 (d, ^2J = 9.6 Hz, 1 H, 7'-H_{syn}*), 1.44 (d, ^2J = 9.6 Hz, 1 H, 7'-H_{anti}*), 1.61–1.75 [m, 4 H, 5'(6')-H], 2.30 (s, 1 H, 1'-H**), 2.45 (s, 1 H, 4'-H**), 3.31 [AB system, δ_A = 3.23, δ_B = 3.39, ^3J = 10.7 Hz, 2 H, 2'(3')-H], 6.66 (dt, ^3J = 10.7, ^4J = 1.3 Hz, 1 H, arene-H), 6.85 (d, ^3J = 8.0 Hz, 1 H, arene-H), 6.98 (t, ^3J = 8.0 Hz, 1 H, arene-H), 7.05 (m, 1 H, arene-H), 7.12 (d, ^3J = 8.0 Hz, 1 H, arene-H), 7.19 (m, 2 H, arene-H), 7.26–7.37 (bs, 5 H, 4-phenyl-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, and DEPT): δ = 29.70 (–, C-5'*), 30.91 (–, C-6'*), 33.23 (–, C-7'), 46.80 (+, C-1'**), 47.17 (+, C-4'**), 49.25 (+, C-2'***), 49.91 (+, C-3'***), 124.73 (+), 126.56 (+), 126.60 (+, rel. intens. 2), 128.68 (+), 128.69 (+), 129.16 (C_{quat}), 129.59 (+), 129.62 (+), 130.41 (+), 131.16 (+), 131.91 (C_{quat}), 138.91 (C_{quat}), 139.64 (C_{quat}), 140.61 (C_{quat}), 145.15 (C_{quat}). – MS (70 eV), *m/z* (%): 322 (100)[M^+], 255 (53), 254 (48)[$M^+ - C_5H_8$], 253 (94)[$M^+ - C_5H_9$], 252 (42)[$M^+ - C_5H_{10}$]. – $C_{25}H_{22}$ (322.4): calcd. C 93.12, H 6.88; found C 93.21, H 6.96%.

exo-[4-(p-Methoxyphenyl)-3,6-dimethoxy-9,10-dihydrophenanthreno]-2':3',9:10-norbornane (**4b**): According to GP 1, to a mixture of 3.73 g (15.9 mmol) of **2b-I**, 5.14 g (15.9 mmol) of Bu_4NBr, 4.40 g (31.9 mmol) of K_2CO_3, and 18 mg (1.5 mol%) of $Pd(OAc)_2$ in 30 ml of NMP was added at 65 °C during 2.5 h a solution of 500 mg (5.3 mmol) of **1** in 5 ml of NMP and a solution of $Pd(OAc)_2$ (24 mg, 2 mol%) in 1 ml of NMP. After stirring for 23 h at 65 °C, the temperature was raised to 80 °C for another 30 h. After standard workup, the crude product was chromatographed on 200 g of silica gel (6 × 15 cm, cyclohexane/CH_2Cl_2 9:1): fraction I (R_f = 0.56): 1.20 g of **2b-I**. – II (R_f = 0.28, PE/CH_2Cl_2 2:1): 1.17 g (54%, 79% based on conversion of **2b-I**) of **4b**, white solid, mp 170 °C. – IR (KBr): ν = 2926 cm^{-1}, 2357, 2330, 1609, 1514, 1461, 1315, 1246, 1175, 1141, 1098, 1043, 942, 910, 864, 821, 783, 761, 736, 703. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.03 (dt, ^2J = 9.8, ^3J = 1.4 Hz, 1 H, 7'-H_{syn}*), 1.47 (dt, ^2J = 9.8, ^3J = 1.4 Hz, 1 H, 7'-H_{anti}*), 1.57–1.72 [m, 4 H, 5'(6')-H], 2.24 (s, 1 H, 1'-H**), 2.34 (s, 1 H, 4'-H**), 3.15 (s, 3 H, OCH_3), 3.17 [AB system; δ_A = 3.09, δ_B = 3.25, ^3J = 9.8 Hz, 2 H, 2'(3')-H], 3.70 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 6.54–6.62 (m, 2 H, arene-H), 6.88–7.01 (m, 2 H, arene-H), 7.11 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H, arene-H), 7.19 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H, arene-H), 7.38 (dd, ^3J = 8.4, ^4J = 2.0 Hz, 1 H, arene-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 29.73 (C-5'*), 30.69 (C-6'*), 32.98 (C-7'), 46.02 (C-1'**), 46.64 (C-4'**), 49.00 (C-2'***), 49.95 (C-3'***), 54.52 (OCH_3), 55.30 (OCH_3), 56.07 (OCH_3), 110.85, 112.84, 114.18, 114.25, 115.30, 127.16, 129.53, 130.69, 131.68, 132.03, 132.15, 132.23, 132.62, 133.11, 155.79, 156.53, 158.43. – MS (70 eV), *m/z* (%): 412 (100)[M^+], 344 (22)[$M^+ - C_5H_8$], 329 (12), 314 (10), 269 (10), 255 (5), 239 (6), 226 (7), 156 (10). – $C_{28}H_{28}O_3$ (412.5): calcd. C 81.52, H 6.84; found C 81.60, H 6.91%.

exo-[4-(p-Fluorophenyl)-3,6-difluoro-9,10-dihydrophenanthreno]-2':3',9:10-norbornane (**4c**): According to GP 1, to a mixture of 5.58 g (31.9 mmol) of **2c-Br**, 10.27 g (31.9 mmol) of Bu_4NBr, 8.81 g (63.7 mmol) of K_2CO_3, and 27 mg (1.1 mol%) of $Pd(OAc)_2$ in 30 ml of NMP was added at 75 °C during 3.5 h a solution of 1.00 g (10.6 mmol) of **1** in 5 ml of NMP and a solution of $Pd(OAc)_2$ (50 mg, 2.1 mol%) in 1 ml of NMP. The mixture was stirred for 72 h at 75 °C. After standard workup, the crude product was chromatographed on 90 g of silica gel (4 × 15 cm, PE/CH_2Cl_2 9:1): fraction I (R_f = 0.58): 1.79 g of **2c-Br**. – II (R_f = 0.32): 1.29 g (32%, 48% based on conversion) of **4c**, pale yellow crystals, mp 165 °C. – IR (KBr): ν = 3057 cm^{-1}, 2904, 1895, 1742, 1606, 1571, 1510, 1467, 1420, 1396, 1328, 1297, 1277, 1221, 1195, 1155, 1128, 1094, 1080, 1015, 967, 922, 883, 820, 783, 765, 734, 702, 683, 666, 645. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.08 (dt, ^2J = 10.0, ^3J = 1.4 Hz, 1 H, 7'-H), 1.56–1.79 [m, 4 H, 5'(6')-H], 2.27 (s, 1 H, 1'-H*), 2.35 (s, 1 H, 4'-H*), 3.21 [AB system, δ_A = 3.14, δ_B = 3.20, ^3J = 9.8 Hz, 2 H, 2'(3')-H], 6.44 (dd, ^3J = 12.8, ^4J = 2.6 Hz, 1 H, arene-H), 6.97–7.25 (m, 6 H, arene-H), 7.33–7.42 (m, 1 H, arene-H). – $C_{25}H_{19}F_3$ (376.4): calcd. C 79.77, H 5.09, F 15.44; found C 79.74, H 5.10, F 15.31%.

exo-[3,6-Dimethyl-4-(p-methylphenyl)-9,10-dihydrophenanthreno]-2':3',9:10-norbornane (**4d**): Under nitrogen a mixture of 1.00 g (10.6 mmol) of **1**, 2.31 g (10.6 mmol) of **2d-I**, 3.41 g (10.6 mmol) of Bu_4NBr, 3.0 g (21.7 mmol) of K_2CO_3, and 50 mg (0.22 mmol) of $Pd(OAc)_2$ in 20 ml of DMF was vigorously stirred at 100 °C. The mixture was filtered, and the residue was washed with 100 ml of CH_2Cl_2. The combined organic layers were extracted with 5 portions of water (100 ml each), dried, and concentrated. The residue was chromatographed on 50 g of silica gel (12 × 3.5 cm, PE) to yield 725 mg of a brown oil (R_f = 0.58), recrystallisation from heptane afforded 470 mg (36%) of **4d**, white needles, mp 123–124 °C. – IR (KBr): ν = 3050 cm^{-1}, 2980, 2960, 2880, 1600, 1590, 1440, 1420, 1180, 800, 770, 760, 740, 700. – ^{1}H NMR (400 MHz, $CDCl_3$,): δ = 1.14 (d, ^2J = 9.1 Hz, 1 H, 7'-H_{syn}*), 1.58 (d, ^2J = 9.1 Hz, 1 H, 7'-H_{anti}*), 1.74–1.80 [m, 4 H, 5'(6')-H], 1.91 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 2.43 (s, 1 H, 1'-H**), 2.47 (s, 1 H, 4'-H**), 2.54 (s, 3 H, CH_3), 3.31 [AB system, δ_A = 3.24, δ_B = 3.38, ^3J = 10.7 Hz, 2 H, 2'(3')-H], 6.66 (s, 1 H, arene-H), 6.91 (dd, ^3J = 7.5, ^4J = 1.1 Hz, 1 H, arene-H), 7.13 (d, ^3J = 8.0 Hz, 1 H, arene-H), 7.15 (dd, ^3J = 7.5, ^4J = 1.1 Hz, 1 H, arene-H), 7.21 (s, 1 H, arene-H), 7.23 (s, 1 H, arene-H), 7.26 (m, 1 H, arene-H), 7.31 (d, ^3J = 8.0 Hz, 1 H, arene-H), 7.39 (d, ^3J = 8.0 Hz, 1 H, arene-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, and DEPT): δ = 20.80 (+, CH_3), 21.11 (+, CH_3) 21.46 (+, CH_3) 30.17 (–, C-5'*), 30.57 (–, C-6'*), 33.17 (–, C-7'), 46.35 (+, C-1'**), 47.17 (+, C-4'**), 49.50 (+, C-2'***), 50.08 (+, C-3'***), 127.25 (+), 128.99 (+), 129.24 (+), 129.49 (+), 129.63 (+), 130.02 (+), 130.14 (+), 131.46 (C_{quat}), 132.45 (C_{quat}), 133.61 (C_{quat}), 134.70 (C_{quat}), 136.09 (C_{quat}), 136.39 (C_{quat}), 137.94 (C_{quat}), 138.85 (C_{quat}), 140.95 (C_{quat}). – MS (70 eV), *m/z* (%): 364 (100)[M^+], 349 (8)[$M^+ - CH_3$], 297 (38), 296 (21)[$M^+ - C_5H_8$]. – $C_{28}H_{28}$ (364.5): calcd. C 92.26, H 7.74; found C 92.31, H 7.76%.

exo-[3,6-Dichloro-2,5,7-trideuterio-4-(4''-chloro-3'',5''-dideuteriophenyl)-9,10-dihydrophenanthreno]-2':3',9:10-norbornane (**4e**): Under nitrogen a mixture of 1.00 g (7.2 mmol) of K_2CO_3, 1.28 g (4.0 mmol) of Bu_4NBr, 15.2 mg (0.07 mmol) of $Pd(OAc)_2$, 200 mg (2.1 mmol) of norbornene (**1**), and 1.53 g (6.4 mmol) of 4-chloro-3,5-dideuterioiodobenzene (**2e-I**) was vigorously stirred for 24 h at 80 °C in a sealed bottle. Subsequently, 100 ml of CH_2Cl_2 was added, the mixture was filtered, and the residue was extracted with 5 portions of water (40 ml each), dried, and concentrated. The residue was chromatographed on 50 g of silica gel (25 × 3.5 cm, PE, R_f = 0.19) to yield 343 mg (38%) of **4e**, colorless crystals, mp 168 °C. – IR (KBr): ν = 2930 cm^{-1}, 2870, 1440, 1365, 1030, 905, 740, 725. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.07 (d, ^2J = 10 Hz, 1 H, 7'-H_{syn}*), 1.37 (d, ^2J = 10 Hz, 1 H, 7'-H_{anti}*), 1.58–1.76 [m, 4 H, 5'(6')-H], 2.26–2.36 [m, 2 H, 1'(4')-H], 3.18 [AB system, δ_A = 3.11, δ_B = 3.26, ^3J = 10.0 Hz, 2 H, 2'(3')-H], 7.05 (s, 1 H, 8-H**), 7.08 (d, ^4J = 2.0 Hz, 1 H, 2''-H***), 7.19 (s, 1 H, 1-H**), 7.32 (d, ^4J = 2.0 Hz, 1 H, 6''-H***). – ^{13}C NMR (62.9 MHz, $CDCl_3$, and APT): δ = 29.85 (–), 30.49 (–), 33.12 (–), 45.93 (+), 46.73 (+), 49.30 (+), 49.93 (+), 126.98 (t, CD, $^1J_{C,D}$ = 26 Hz), 127.81 (t, CD, $^1J_{C,D}$ = 24 Hz), 128.4–129.4 (m, 3 CD), 130.48 (+), 130.62 (–), 130.98 (+), 131.46 (+), 131.70 (+), 132.31 (–), 132.67 (–), 132.73 (–), 133.70 (–), 135.89 (–), 137.65 (–), 138.90 (–), 139.90 (–). – MS (70 eV), *m/z* (%): 429/431 (18/18)[M^+], 318/320 (62/38), 267 (100), 250 (91), 238 (61), 69 (72). – $C_{25}H_{14}D_5Cl_3$: calcd. and found: 429.0856 (HRMS).

exo-(3,6-Dicyano-9,10-dihydrophenanthreno)-2':3',9:10-norbornane (**3f**) *and exo-[3,6-dicyano-4-(p-cyanophenyl)-9,10-dihydrophenanthreno]-2':3',9:10-norbornane* (**4f**): According to GP 1, to a mixture of 2.90 g (15.9 mmol) of **2f-Br**, 5.14 g (15.9 mmol) of Bu_4NBr, 4.40 g (31.9 mmol) of K_2CO_3, and 12 mg (1.0 mol%) of $Pd(OAc)_2$ in 35 ml of NMP was added at 75 °C during 2.5 h a solution of 500 mg (5.3 mmol) of **1** in 5 ml of NMP and a solution of $Pd(OAc)_2$ (24 mg, 2 mol%) in 1 ml of NMP. The mixture was further stirred for 2 d at 75 °C. After standard workup, the crude product was chromatographed on 200 g of silica gel (6 × 15 cm, PE/CH_2Cl_2 9:1): fraction I [R_f = 0.64 (CH_2Cl_2)]: 1.88 g of **2f-Br**. – II [R_f = 0.41 (CH_2Cl_2)]: 66 mg (8% based on conversion of **2f-Br**) of **3f**, mp 219 °C. – IR (KBr): ν = 3078 cm^{-1}, 2955, 2872, 2228, 1918, 1720, 1606, 1572, 1500, 1451, 1403, 1317, 1289, 1207, 1174, 888, 772, 736, 703. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.12 (dt, ^2J = 10.4, ^3J = 1.4 Hz, 1 H, 7'-H_{syn}*), 1.28 (dt, ^2J = 10.4, ^3J = 1.4 Hz, 1 H, 7'-H_{anti}*), 1.64–1.80 [m, 4 H, 5'(6')-H], 2.40 [t, ^3J = 1.4 Hz, 2 H, 1'(4')-H], 3.27 [d, ^4J = 0.8 Hz, 2 H, 2'(3')-H], 7.36 [d, ^3J = 8.0 Hz, 2 H, 1(8)-H], 7.53 [dd, ^3J = 8.0, ^4J = 1.6 Hz, 2 H, 2(7)-H], 8.04 [d, ^4J = 1.6 Hz, 2 H, 4(5)-H]. – ^{13}C NMR (100.6 MHz, $CDCl_3$, and DEPT): δ = 30.17 [–, C-5'(6')], 33.41 (–, C-7'), 45.97 [+, C-1'(4')], 49.69 [+, C-2'(3')], 110.89 [C_{quat}, C-3(6)], 118.66 (C_{quat}, CN), 126.25 (+), 130.74 (C_{quat}), 131.32 (+), 131.63 (+), 142.39 (C_{quat}). – MS (70 eV), *m/z* (%): 296 (38)[M^+], 228 (100)[$M^+ - C_5H_8$]. – $C_{21}H_{16}N_2$: calcd. 296.1313, found 296.1308 (MS). – III [R_f = 0.33 (CH_2Cl_2)]: 127 mg (17% based on conversion of **2f-Br**) of **4f**, mp >230 °C. – IR (KBr): ν = 2955 cm^{-1}, 2872, 2228, 1702, 1606, 1396, 1269, 1181, 841, 736. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.18 (dt, ^2J = 10.4, ^3J = 1.4 Hz, 1 H, 7'-H_{syn}*), 1.32 (dt, ^2J = 10.4, ^3J = 1.4 Hz, 1 H, 7'-H_{anti}*), 1.67–1.84 [m, 4 H, 5'(6')-H], 2.35 (s, 1 H, 1'-H**), 2.46 (s, 1 H, 4'-H**), 3.32 [AB system, δ_A = 3.24, δ_B = 3.40, ^3J = 9.8 Hz, 2 H, 2'(3')-H], 6.89 (d, ^4J = 1.2 Hz, 1 H, arene-H), 7.30–7.36 (m, 3 H, arene-H), 7.43 (dd, ^3J = 8.0, ^4J = 0.8 Hz, 1 H, arene-H), 7.65 (d, ^3J = 8.0 Hz, 2 H, arene-H), 7.75 (d, ^3J = 8.0 Hz, 1 H, arene-H), 7.88 (d, ^3J = 8.0 Hz, 1 H, arene-H). – ^{13}C NMR (100.6 MHz, and DEPT): δ = 29.80 (–, C-5'*), 30.57 (–, C-6'*), 33.49 (–, C-7'*), 46.52 (+, C-1'**), 47.15 (+, C-4'**), 49.24 (+, C-2'***), 50.00 (+, C-3'***), 109.47 (C_{quat}), 113.02 (C_{quat}), 113.13 (C_{quat}), 117.72 (C_{quat}), 118.03 (C_{quat}), 128.85 (+), 129.00 (+), 130.30 (+), 130.64 (+), 130.71 (+), 130.85 (C_{quat}), 130.91 (+), 131.23 (+), 131.40 (+), 132.57 (+), 132.81 (+), 133.16 (+), 133.32 (+), 140.54 (C_{quat}), 143.92 (C_{quat}), 144.74 (C_{quat}), 146.23 (C_{quat}). – MS (70 eV), *m/z* (%): 397 (15)[M^+], 329 (45)[$M^+ - C_5H_8$], 302 (19), 67 (100). – $C_{28}H_{19}N_3$: calcd. 397.1579, found 397.1584 (MS).

exo-(3,6-Methoxycarbonyl-9,10-dihydrophenanthreno)-2':3',9:10-norbornane (**3g**): According to GP 1, to a mixture of 4.17 g (15.9 mmol) of **2g-I**, 5.14 g (15.9 mmol) of Bu_4NBr, 4.40 g (31.9 mmol) of K_2CO_3, and 12 mg (1.0 mol%) of $Pd(OAc)_2$ in 35 ml of NMP was added at 65 °C during 2.5 h a solution of 500 mg (5.3 mmol) of **1** in 5 ml of NMP and a solution of $Pd(OAc)_2$ (24 mg, 2.0 mol%) in 1 ml of NMP. The mixture was further stirred for 96 h at 65 °C. After standard workup, the crude product was chromatographed on 200 g of silica gel (6 × 15 cm, cyclohexane/CH_2Cl_2 5:1): fraction I [R_f = 0.3 (PE/CH_2Cl_2 2:1)]: 1.69 g of **2g-I**. – II [R_f = 0.17 (PE/CH_2Cl_2 2:1)]: 346 mg (20% based on conversion of **2g-I**) of **3g**. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.06 (dt, ^2J = 10.2, ^3J = 1.6 Hz, 1 H, 7'-H_{syn}*), 1.32 (dt, ^2J = 10.2, ^3J = 1.6 Hz, 1 H, 7'-H_{anti}*), 1.62–1.77 (m, 4 H, 5'(6')-H), 2.40 [bs, 2 H, 1'(4')-H], 3.25 [s, 2 H, 2'(3')-H], 3.96 (s, 6 H, CO_2CH_3), 7.12 [d, ^3J = 8.0 Hz, 2 H, 1(8)-H], 7.88 [dd, ^3J = 8.0, ^4J = 1.6 Hz, 2 H, 2(7)-H], 8.60 [d, ^4J = 1.6 Hz, 2 H, 4(5)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, and DEPT): δ = 30.21 [–, C-5'(6')], 33.31 (–, C-7'), 46.09 [+, C-1'(4')], 49.63 [+, C-2'(3')], 52.10 (+, CO_2CH_3), 122.89 (+), 123.86 (+), 128.48 (C_{quat}), 128.93 (+), 130.35 (+), 130.65 (+), 130.88 (C_{quat}), 142.88 (C_{quat}), 167.08 (C_{quat}). – MS (70 eV), *m/z* (%): 362 (100)[M^+], 294 (63), 263 (47).

3,6-Dinitrophenanthreno-2':3',9:10-norbornene (**5**): According to GP 1, to a mixture of 3.97 g (15.9 mmol) of **2h-I**, 5.14 g (15.9 mmol) of Bu_4NBr, 4.40 g (31.9 mmol) of K_2CO_3, and 9 mg (0.8 mol%) of $Pd(OAc)_2$ in 30 ml of NMP was added at 75 °C during 2.5 h a solution of 500 mg (5.3 mmol) of **1** in 5 ml of NMP and a solution of $Pd(OAc)_2$ (24 mg, 2.0 mol%) in 1 ml of NMP. The mixture was further stirred for 8 d at 75 °C. After standard workup, the crude product was chromatographed on 200 g of silica gel (6 × 15 cm, PE/CH_2Cl_2 1:1): fraction I [R_f = 0.72 (CH_2Cl_2)]: 2.09 g of **2h-I**. – II [R_f = 0.59 (CH_2Cl_2)]: 101 mg of 4,4'-Dinitrobiphenyl. – III [R_f = 0.56 (CH_2Cl_2)]: 236 mg (13%, 19% based on conversion of **2h-I**) of **5**, mp >180 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20–1.29 [m, 2 H, 5'(6')-H], 1.84 (dt, ^2J = 8.8, ^3J = 1.4 Hz, 1 H, 7'-H_{syn}*), 2.03 (dt, ^2J = 8.8, ^3J = 1.4 Hz, 1 H, 7'-H_{anti}*), 2.19 [m, 2 H, 5'(6')-H], 4.12 [m, 2 H, 1'(4')-H], 8.20 [d, ^3J = 8.8 Hz, 2 H, 1(8)-H], 8.51 [dd, ^3J = 8.8, ^4J = 2.0 Hz, 2(7)-H], 9.66 [d, ^4J = 2.0 Hz, 2 H, 4(5)-H]. –

^{13}C NMR (100.6 MHz, $CDCl_3$, and DEPT): δ = 26.75 [–, C-5'(6')], 42.42 [+, C-1'(4')], 49.46 (–, C-7'), 120.04 [+, C-4(5)], 121.67 [+, C-2(7)], 125.81 [+, C-1(8)], 129.34 (C_{quat}), 131.51 (C_{quat}), 145.79 (C_{quat}), 1 C_{quat} not observed. – MS (70 eV), *m/z* (%): 334 (8)[M^+], 306 (39), 276 (2), 260 (100).

exo-[4(5)-Phenyl-9,10-dihydrophenanthreno]-2':3',9:10-endo-5':6'-cyclopentenonorbornane (**12**): A mixture of 4.00 g (28.9 mmol) of K_2CO_3, 9.66 g (30.0 mmol) of Bu_4NBr and 67 mg (0.3 mmol) of $Pd(OAc)_2$ in 40 ml of DMF was heated for 30 min to 60 °C; the color of the solution changed from yellow to red. Subsequently, 1.98 g (15.0 mmol) of dicyclopentadiene (**10**) and 9.30 g (45.6 mmol) of iodobenzene (**2a-I**) in 20 ml of DMF were added during 12 h. After further heating for 12 h at this temperature, the mixture was cooled to r. t. and 150 ml of CH_2Cl_2 was added. The mixture was filtered, the filtrate was extracted with 4 portions of water (50 ml each), dried and concentrated. Chromatography on 300 g of silica gel (40 × 4.5 cm, PE) yielded 3.47 g (64%) of **12** (R_f = 0.08). – IR (KBr): ν = 3080 cm^{-1}, 2940, 1480, 1445, 755, 745, 695. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.33 (d, ^3J = 11.0 Hz, 1 H), 1.69 (d, ^3J = 11.0 Hz, rel. intens. 0.5 H), 1.73 (d, ^3J = 11.0 Hz, rel. intens. 0.5 H), 2.22–2.79 (m, 5 H, alkyl-H), 3.22 [AB system, δ_A = 3.07, δ_B = 3.35, ^3J = 9.0 Hz, 2 H, 2'(3')-H], 3.19–3.40 (m, 1 H), 5.77–5.92 (m, 2 H, alkene-H), 6.55–6.68 (m, 1 H, arene-H), 6.80–7.62 (m, 11 H, arene-H). – ^{13}C NMR (62.5 MHz, $CDCl_3$): δ = 33.01, 33.24, 35.88, 36.13, 38.44, 38.99, 41.05, 41.81, 43.31, 43.71, 52.22, 53.11, 53.42, 53.84, 54.19, 124.34, 124.54, 126.55, 126.69, 126.75, 128.08, 128.14, 128.27, 128.39, 128.43, 128.69, 129.06, 129.10, 129.24, 129.30, 129.38, 129.47, 129.65, 129.79, 129.92, 130.08, 130.27, 131.14, 131.28, 131.38, 131.73, 132.11, 132.24, 132.70, 139.31, 139.43, 139.69, 141.04, 141.52, 144.97, 145.09. – MS (70 eV), *m/z* (%): 360 (25)[M^+], 292 (100)[$M^+ - C_5H_8$], 253 (50), 252 (44), 105 (38), 91 (56), 77 (42). – $C_{28}H_{24}$ (360.5): calcd. C 93.29, H 6.71; found C 92.85, H 6.77%; calcd. and found: 360.1878 (HRMS).

exo-9,10-Dihydrophenanthreno-2':3',9:10-endo-5':6'-cyclopentenonorbornane (**11**): A mixture of 2.00 g (14.5 mmol) of K_2CO_3, 4.83 g (15.0 mmol) of Bu_4NBr, 33.2 mg (0.15 mmol) $Pd(OAc)_2$, and 159 mg (0.6 mmol) of PPh_3 in 30 ml of DMF was heated for 20 min to 60 °C. Subsequently, 990 mg (7.5 mmol) of **10** and 3.20 g (15.7 mmol) of **2a-I** in 10 ml of DMF were added during 12 h. After further heating for 12 h at this temperature, the mixture was cooled to r. t. and 100 ml of CH_2Cl_2 was added. The mixture was filtered, the filtrate was extracted with 4 portions of water (50 ml each), dried and concentrated. Chromatography on 200 g of silica gel (20 × 3.5 cm, PE) yielded fraction I (R_f = 0.13): 320 mg (15%) of **11**, mp 96–97 °C. – IR (KBr): ν = 3020 cm^{-1}, 2940, 1445, 755, 730. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (d, ^2J = 12.5 Hz, 1 H, 7'-H_{syn}*), 1.55 (d, ^2J = 12.5 Hz, 1 H, 7'-H_{anti}*), 2.15–2.80 (m, 5 H, alkyl-H), 3.20 [AB system, δ_A = 3.13, δ_B = 3.26, ^3J = 10.2 Hz, 2 H, 2'(3')-H], 3.22–3.35 (m, 1 H), 5.71–5.82 (m, 2 H, alkene-H), 7.02–7.26 (m, 6 H, arene-H), 7.77–7.92 (m, 2 H, arene-H). – ^{13}C NMR (62.5 MHz, $CDCl_3$, and APT): δ = 33.06 (–), 36.00 (–), 37.73 (+), 40.59 (+), 43.40 (+), 52.52 (+), 53.62 (+), 54.90 (+), 121.95 (+), 122.07 (+), 125.93 (+), 125.97 (+), 127.51 (+), 127.55 (+), 129.49 (+), 130.25 (+), 131.19 (+), 131.64 (–), 131.91 (–), 132.70 (+) 138.16 (–), 138.56 (–). – MS (70 eV), *m/z* (%): 284 (22)[M^+], 216 (100), 178 (38). – $C_{22}H_{20}$: calcd. and found 284.1560 (HRMS). – II (R_f = 0.08): 675 mg (36%) of **12**.

exo-[4(5)-Phenyl-9,10-dihydrophenanthreno]-5':6',9:10-norbornan-2-ol (**14**): According to GP 1, to a mixture of 3.35 g (16.4 mmol) of **2a-I**, 5.28 g (16.4 mmol) of Bu_4NBr, 4.53 g (32.8 mmol) of K_2CO_3, and 42 mg (3.5 mol%) of $Pd(OAc)_2$ in 35 ml of DMF was added a solution of 602 mg (6.4 mmol) of **1** in 5 ml of DMF and simultaneously 73 mg (6 mol%) of $Pd(OAc)_2$ in 5 ml of DMF during 3 h. After stirring for 18 h at this temperature and standard workup, the crude product was chromatographed on 200 g of silica gel (6 × 15 cm, PE): fraction I: 796 mg of **2a-I**. – II: 143 mg of biphenyl. – III: 933 mg (66% based on conversion of **2a-I**) of **14**. – IR (KBr): ν = 3306 cm^{-1}, 3055, 2953, 1733, 1667, 1599, 1493, 1439, 1337, 1306, 1181, 1144, 1120, 1090, 1061, 1011, 970, 860, 804, 765, 740, 702, 617, 516. – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.15–1.60 (m, 3 H), 1.80 (bs, 1 H, OH), 2.05–2.25 (m, 3 H), 3.18 (m, 1 H), 3.80–4.00 (m, 1 H), 4.20 (m, 1 H), 6.65 (m, 1 H), 6.80–7.20 (m, 10 H), 7.78 (m, 1 H) – ^{13}C NMR (67.9 MHz, $CDCl_3$, and DEPT): δ = 31.88 (–), 32.26 (–), 32.51 (–), 32.73 (+), 35.48 (+), 36.09 (+), 36.81 (–), 39.19 (–), 39.93 (–), 40.40 (+), 45.89 (+), 46.45 (+), 46.97 (+), 48.26 (+), 49.26 (+), 49.59 (+), 49.87 (+), 55.38 (+), 55.98 (+), 56.18 (+), 73.07 (+), 73.19 (+), 122.06 (+), 122.17 (+), 124.73 (+), 126.17 (+), 126.39 (+), 126.64 (+), 126.90 (+), 126.94 (+), 127.37 (+), 127.71 (+), 127.74 (+), 128.54 (+), 128.87 (+), 129.49 (+), 129.57 (+), 129.70 (+), 129.89 (+),

130.07 (+), 130.40 (+), 130.49 (C_{quat}), 131.60 (C_{quat}), 131.86 (C_{quat}), 137.31 (C_{quat}), 137.49 (C_{quat}), 138.64 (C_{quat}), 140.35 (C_{quat}), 145.00 (C_{quat}). – MS (70 eV), *m/z* (%): 338 (24)[M^+], 262 (82), 253 (14), 252 (11), 244 (19), 229 (13), 215 (23), 179 (37), 178 (100). – $C_{25}H_{22}O$ (338.5): calcd. C 88.72, H 6.55; found C 88.52, H 6.55%.

exo-[4(5)-Phenyl-9,10-dihydrophenanthreno]-5':6',9:10-norbornan-2-one (**16**): A mixture of 1.50 g (13.9 mmol) of bicyclo[2.2.1]hept-5-en-2-one (**15**), 8.50 g (41.7 mmol) of **2a-I**, 5.00 g (59.5 mmol) of $NaHCO_3$, and 71.3 mg (0.32 mmol) of $Pd(OAc)_2$ in 40 ml of DMF was heated for 24 h to 80 °C. After the mixture was cooled to r. t. and 150 ml of CH_2Cl_2 was added, the mixture was filtered; the filtrate was extracted with 4 portions of water (50 ml each), dried and concentrated. The crude product was chromatographed on 200 g of silica gel (30 × 3.5 cm, PE/MTBE 1:1): fraction I (R_f = 0.7): 3.70 g (44%) of **2a-I**. – II (R_f = 0.06): 2.20 g (47%, 83% based on conversion of **2a-I**) of **16**, mp 210–215 °C. – IR (KBr): ν = 2987 cm^{-1}, 2905, 1746, 1597, 1492, 1424, 1404, 1305, 1214, 1165, 1071, 973, 807, 765, 745, 702, 614, 525. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.49–1.59 (m, 2 H), 2.29–2.35 (m, 2 H), 2.73 (s, 1 H), 2.81 (s, 1 H), 3.50 (AB system, δ_A = 3.25, δ_B = 3.73, ^3J = 9.8 Hz, 2 H), 6.66–7.26 (m, 10 H, arene-H), 7.87–7.90 (m, 2 H, arene-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 32.31, 32.52, 39.98, 40.71, 43.80, 44.74, 45.85, 46.43, 48.25, 48.59, 61.73, 62.23, 122.39, 122.48, 125.65, 126.89, 126.95, 127.13, 127.25, 127.36, 128.06, 128.18, 128.51, 128.83, 129.59, 129.85, 129.98, 130.23, 131.05, 131.27, 131.64, 132.17, 133.90, 135.15, 135.93, 139.16, 139.98, 144.54, 216.52, 216.85. – MS (70 eV), *m/z* (%): 336 (33)[M^+], 260 (100), 253 (37), 218 (17), 204 (62), 191 (14), 178 (78). – $C_{25}H_{20}O$ (336.4): calcd. C 89.25, H 5.99; found C 89.22, H 6.13%.

exo-6,7-Dihydropentapheno-2':3',6:7-norbornane (**8**) *and exo-[13-(2''-naphthyl)-6,7-dihydropentapheno]-2':3',6:7-norbornane* (**9**): According to GP 1, to a mixture of 3.30 g (15.9 mmol) of **7**, 5.14 g (15.9 mmol) of Bu_4NBr, 4.41 g (31.9 mmol) of K_2CO_3, and 12 mg (0.05 mmol) of $Pd(OAc)_2$ in 30 ml of NMP was added at 85 °C during 2.5 h a solution of 500 mg (5.3 mmol) of **1** in 5 ml of NMP and a solution of 24 mg (0.1 mmol) $Pd(OAc)_2$ in 5 ml of NMP. The mixture was further heated for 4 d at 85 °C. After standard workup, the crude product was chromatographed on 200 g of silica gel (6 × 15 cm, PE/CH_2Cl_2 9:1): fraction I: (R_f = 0.48) 2.12 g of **7** (≙ 36% conversion). – II (R_f = 0.24): 177 mg (18% based on conversion of **7**) of **8**, mp 168 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.97 (dt, ^2J = 10.0 Hz, 1 H, 7'-H_{syn}*), 1.34 (dt, ^2J = 10.0 Hz, 1 H, 7'-H_{anti}*), 1.73 [bs, 4 H, 5'(6')-H], 2.49 [s, 2 H, 1'(4')-H], 3.44 [s, 2 H, 2'(3')-H], 7.39 [dd, ^3J = 6.2, ^4J = 3.2 Hz, 4 H, 2(3,10,11)-H], 7.33 [dd, ^3J = 6.2, ^4J = 3.2 Hz, 2 H, 1(12)-H*], 7.75 [s, 2 H, 5(8)-H], 7.87 [dd, ^3J = 6.2, ^4J = 3.2 Hz, 2 H, 4(9)-H*], 8.53 [s, 2 H, 13(14)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, and DEPT): δ = 29.19 [–, C-5'(6')], 33.10 (–, C-7'), 45.88 [+, C-1'(4')], 50.63 [+, C-2'(3')], 121.33 (+), 125.43 (+), 125.89 (+), 126.87 (+), 128.10 (+), 128.58 (+), 130.16 (C_{quat}), 132.45 (C_{quat}), 133.39 (C_{quat}), 136.97 (C_{quat}). – MS (70 eV), *m/z* (%): 346 (100)[M^+], 278 (95)[$M^+ - C_5H_8$]. – III (R_f = 0.14): 58 mg (6% based on conversion of **7**) of **9**, mp > 230 °C. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.25 (m, 2 H, 7'-H), 1.76 [m, 4 H, 5'(6')-H], 2.45 (s, 1 H, 1'-H*), 2.52 (s, 1 H, 4'-H*), 3.54 [AB system, δ_A = 3.47, δ_B = 3.61, ^3J = 9.4 Hz, 2 H, 2'(3')-H], 7.35–7.68 (m, 10 H, arene-H), 7.74–8.10 (m, 8 H, arene-H). – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.70 (C-5'*), 30.60 (C-6'*), 33.08 (C-7'), 46.53 (C-1'**), 47.27 (C-4'**), 50.36 (C-2'***), 51.24 (C-3'***), 124.68, 125.20, 125.72, 125.99, 126.02, 126.16, 126.22, 126.96, 127.03, 127.79, 127.87, 128.10, 128.16, 128.22, 128.27, 128.45, 128.48, 128.51, 129.15, 129.40, 129.75, 129.84, 129.95, 130.21, 132.25. – MS (70 eV), *m/z* (%): 472 (100)[M^+], 405 (11)[$M^+ - C_5H_7$].

Palladium-Catalyzed Coupling of Norbornene (1) or Dicyclopentadiene (10) with 2-Bromothiophene (17)

General Procedure 2 (GP 2): Under nitrogen a mixture of 4.0 g (28.9 mmol) of K_2CO_3, 2.0 g (6.2 mmol) of Bu_4NBr and 40.3 mg (0.18 mmol) of $Pd(OAc)_2$ in 40 ml of NMP was heated for 30 min to 60 °C. Subsequently, the temperature was raised to 90 °C and a solution of 2.0 g (12.3 mmol) of 2-bromothiophene (**17**) and 6.2 mmol of an alkene in 20 ml of NMP was added during 8 h. After further heating for 12 h at 90 °C, the mixture was cooled to r. t. and 150 ml of *tert*-butyl methyl ether (MTBE) was added. The mixture was filtered, and the filtrate was extracted with 5 portions of water (40 ml each), dried and concentrated. The crude product was purified by chromatography.

exo-4,5-Dihydrobenzo[1,2-b:4,3-b']dithiopheno-2':3',4:5-norbornane (**18**) *and exo-[1-(2''-thienyl)-4,5-dihydrobenzo[1,2-b:4,3-b']dithiopheno]-2':3',4:5-norbornane* (**19**): According to GP 2, 0.58 g (6.2 mmol) of **1** were allowed to react. Chromatography on 200 g of silica gel (40 × 4.5 cm, PE) yielded: I (R_f = 0.20): 283 mg (18%) of **18**, mp 111 °C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 397 nm (1.70), 376 (1.96), 362 (1.88), 310 (3.42). – IR (KBr): ν = 3080 cm^{-1}, 2940, 2860, 1435, 1080, 845, 708, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.22 (dt, ^3J = 1.0, ^2J = 10.0 Hz, 1 H, 7'-H), 1.50–1.67 (m, 5 H, alkyl-H), 2.46 [bs, 2 H, 1'(4')-H], 3.43 [bs, 2 H, 2'(3')-H], 6.99 (d, ^3J = 5.0 Hz, 2 H), 7.11 (d, ^3J = 5.0 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, and APT): δ = 29.19 (–), 34.68 (–), 45.07 (+), 48.83 (+), 122.61 (+), 123.25 (+), 131.36 (–), 137.99 (–). – MS (70 eV), *m/z* (%): 258 (36)[M^+], 190 (23), 154 (19), 108 (58), 97 (36), 57 (100). – $C_{15}H_{14}S_2$ (258.4): calcd. C 69.72, H 5.46; found C 69.81, H 5.51%; calcd. and found: 258.0536 (HRMS). – II (R_f = 0.18): 248 mg (18%) of **19**, mp 147 °C. – IR (KBr): ν = 3085 cm^{-1}, 2930, 2905, 2850, 1450, 1245, 1220, 835, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.43–1.71 (m, 6 H, alkyl-H), 2.51 [bs, 2 H, 1'(4')-H], 3.44 [bs, 2 H, 2'(3')-H], 6.34 (d, ^3J = 5.3 Hz, 1 H, arene-H), 6.89 (d, ^3J = 5.3 Hz, 1 H, arene-H), 7.05–7.11 (m, 3 H, arene-H), 7.36 (d, ^3J = 5.0 Hz, 1 H, arene-H). – ^{13}C NMR (62.5 MHz, $CDCl_3$, and APT): δ = 29.15 (–), 29.69 (–), 34.64 (–), 44.79 (+), 45.19 (+), 49.05 (+), 49.19 (+), 122.33 (+), 122.95 (+), 123.60 (+), 125.64 (+), 126.97 (+), 127.55 (+), 130.39 (–), 130.59 (–), 130.94 (–), 138.41 (–), 139.28 (–), 139.49 (–). – MS (70 eV), *m/z* (%): 340 (17)[M^+], 248 (100), 203 (21), 85 (27), 71 (39), 57 (68). – $C_{19}H_{16}S_3$ (340.5): calcd. C 67.02, H 4.74; found C 66.95, H 4.84%.

exo-4,5-Dihydrobenzo[1,2-b:4,3-b']dithiopheno-2':3',4:5-endo-5':6'-cyclopentenonorbornane (**20**) *and exo-[1(8)-(2''-thienyl)-4,5-dihydrobenzo[1,2-b:4,3-b']dithiopheno]-2':3',4:5-endo-5':6'-cyclopentenonorbornane* (**21**): According to GP 2, 850 mg (6.4 mmol) of **10** was allowed to react. Chromatography on 200 g of silica gel (40 × 4.5 cm, PE) yielded: I (R_f = 0.13): 283 mg (16%) of **20**, mp 106–108 °C. – IR (KBr): ν = 3050 cm^{-1}, 2950, 1445, 850, 705. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.43 (dt, ^2J = 10.0, ^3J = 1.5 Hz, 1 H, 7'-H_{syn}*), 1.76 (dt, ^2J = 10.0, ^3J = 1.5 Hz, 1 H, 7'-H_{anti}*), 2.34–2.63 (m, 5 H, alkyl-H), 3.07–3.31 (m, 1 H, alkyl-H), 3.39 [AB system, δ_A = 3.37, δ_B = 3.42, ^3J = 12.0 Hz, 2 H, 2'(3')-H], 5.72–5.82 (m, 2 H, alkene-H), 7.00–7.16 (m, 4 H, arene-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, and APT): δ = 32.83 (–), 37.13 (+), 37.45 (–), 40.35 (+), 42.74 (+), 51.86 (+), 52.93 (+), 53.96 (+), 122.63 (+), 122.68 (+), 122.93 (+), 123.13 (+), 131.37 (+), 131.65 (–), 131.85 (–), 132.24 (+), 138.39 (–), 138.55 (–). – MS (70 eV), *m/z* (%): 296 (38)[M^+], 248 (16), 228 (100), 190 (56), 84 (44). – $C_{18}H_{16}S_2$ (296.5): calcd. C 72.93, H 5.44; found C 72.80, H 5.48%. – II (R_f = 0.10): 299 mg (19%) of **21**. – IR (KBr): ν = 3095 cm^{-1}, 2940, 2920, 1610, 1460, 845, 710. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.32 (d, ^2J = 11.0 Hz, 1 H, 7'-H_{syn}*), 1.88 (d, ^2J = 11.0 Hz, 1 H, 7'-H_{anti}*), 2.24–2.81 (m, 5 H, alkyl-H), 3.08–3.21 (m, 1 H), 3.36 [AB system, δ_A = 3.31, δ_B = 3.43, ^3J = 12.0 Hz, 2 H, 2'(3')-H], 5.78–5.87 (m, 2 H, alkene-H), 6.32 (d, ^3J = 7.0 Hz, 1 H, arene-H), 6.86–6.92 (m, 1 H, arene-H), 6.94–7.16 (m, 3 H, arene-H), 7.30–7.41 (m, 1 H, arene-H). – ^{13}C NMR (62.5 MHz, $CDCl_3$, and APT): δ = 32.86 (–), 36.96 (+), 37.42 (–), 37.43 (+), 40.19 (+), 40.59 (+), 42.81 (+), 52.16 (+), 52.96 (+), 54.20 (+), 122.01 (+), 122.24 (+), 123.05 (+), 123.31 (+), 123.32 (+), 123.51 (+), 125.60 (+), 126.95 (+), 127.54 (+), 130.74 (–), 130.94 (–), 130.96 (–), 131.02 (–), 131.08 (–), 131.19 (–), 131.38 (+), 131.49 (+), 132.20 (+), 132.28 (+), 138.53 (–), 139.74 (–), 139.90 (–), 139.96 (–), 140.12 (–). – MS (70 eV), *m/z* (%): 378 (36)[M^+], 310 (100), 272 (42), 227 (30), 195 (20). – $C_{22}H_{18}S_3$ (378.6): calcd. C 69.80, H 4.79; found C 69.45, H 5.12%.

Palladium-Catalyzed Coupling of Norbornene (1) or Dicyclopentadiene (10) with N-Heterocycles

General Procedure 3 (GP 3): Under nitrogen a mixture of 1.90 g (13.7 mmol) of K_2CO_3, 2.20 g (6.8 mmol) of Bu_4NBr, 33.6 mg (0.15 mmol) of $Pd(OAc)_2$, and 157 mg (0.6 mmol) of PPh_3 in 20 ml of DMF was heated at 70 °C for 30 min. Subsequently, a solution of 5.0 mmol of alkene and 10.0 mmol of pyridyl halide in 15 ml of DMF was added during 12 h. The temperature was raised to 120 °C, stirring continued for 24 h. After cooling to r. t. 150 ml of MTBE was added, the solids were removed by filtration, and the solution was extracted twice with 50 ml of 2 N HCl each. The combined aqueous layers were extracted with 50 ml of MTBE, and after addition of solid NaOH (pH = 12), extracted again with 4 portions of MTBE (50 ml each). The combined organic layers from the last extraction cycle were washed twice with 50 ml of water each, dried and concentrated. The residue was purified by chromatography on Al_2O_3 (PE/MTBE/pyridine 10:10:1).

exo-(5,6-Dihydro-3,8-phenanthrolino)-2':3',5:6-norbornane (**23a**): 0.47 g (5.0 mmol) of **1** and 2.10 g (10.2 mmol) of 3-iodopyridine (**22a**) were allowed to react according to GP 3. Chromatography on 80 g of Al_2O_3 (20 × 3.5 cm) yielded 560 mg (45%) of **23a**, R_f = 0.09 (PE/MTBE 1:1), mp 98 °C. – IR (KBr): ν = 3020 cm^{-1}, 2950, 2870, 1575, 1410, 820, 765, 635. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.16 (d, ^2J = 14.5 Hz, 1 H, 7'-H_{syn}*), 1.28 (d, ^2J = 14.5 Hz, 1 H, 7'-H_{anti}*), 1.71–1.75 (m, 4 H, alkyl-H), 2.45 [bs, 2 H, 1'(4')-H], 3.29 [bs, 2 H, 2'(3')-H], 7.62 [d, ^3J = 6.0 Hz, 2 H, 1(10)-H], 8.47 [d, ^3J = 6.0 Hz, 2 H, 2(9)-H], 8.56 [s, 2 H, 4(7)-H]. – ^{13}C NMR (62.5 MHz, $CDCl_3$, and APT): δ = 30.24 (–), 33.37 (–), 42.90 (+), 49.21 (+), 116.15 (+), 133.10 (–), 136.24 (–), 147.80 (+), 152.46 (+). – MS (70 eV), *m/z* (%): 248 (74)[M^+], 207 (20), 180 (100). – $C_{17}H_{16}N_2$ (248.3): calcd. C 82.24, H 6.50, N 11.28; found C 82.17, H 6.57, N 11.33%.

exo-(2,9-Dimethyl-5,6-dihydro-3,8-phenanthrolino)-2':3',5:6-norbornane (**23b**): 0.47 g (5.0 mmol) of **1** and 2.19 g (10.0 mmol) of 3-iodo-6-methylpyridine (**22b**) were allowed to react according to GP 3. Chromatography on 80 g of Al_2O_3 (20 × 3.5 cm) yielded 414 mg (30%) of **23b**, colorless crystals, R_f = 0.12 (PE/MTBE 1:1), mp 155 °C. – IR (KBr): ν = 3005 cm^{-1}, 2940, 2880, 1600, 1575, 860. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.06 (d, ^2J = 14.0 Hz, 1 H, 7'-H_{syn}*), 1.15 (d, ^2J = 14.0 Hz, 1 H, 7'-H_{anti}*), 1.56–1.81 (m, 4 H, alkyl-H), 2.37 [bs, 2 H, 1'(4')-H], 2.58 (s, 6 H, CH_3), 3.23 [bs, 2 H, 2'(3')-H], 7.50 [s, 2 H, 1(10)-H], 8.44 [s, 2 H, 4(7)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, and APT): δ = 26.98 (+), 30.16 (–), 33.21 (–), 42.56 (+), 49.16 (+), 115.38 (+), 130.26 (–), 136.65 (–), 151.76 (+), 156.13 (–). – MS (70 eV), *m/z* (%): 276 (78)[M^+], 247 (18), 235 (28), 208 (100). – $C_{19}H_{20}N_2$ (276.4): calcd. C 82.57, H 7.29; found C 82.61, H 7.27%.

exo-(5,6-Dihydro-3,8-phenanthrolino)-2':3',5:6-endo-5':6'-cyclopentenonorbornane (**24a**): 660 mg (5.0 mmol) of **10** and 2.19 g (10.7 mmol) of 3-iodopyridine (**22a**) were allowed to react according to GP 3. Chromatography on 100 g of Al_2O_3 (30 × 3.5 cm) yielded 800 mg (56%) of **24a**, R_f = 0.11 (PE/MTBE 1:1), mp 170–171 °C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 412 nm (1.51), 377 (1.93), 363 (1.71), 268 (4.12). – IR (KBr): ν = 3020 cm^{-1}, 2940, 2910, 1570, 1405, 815. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.36 [AB system, δ_A = 1.31, δ_B = 1.43, ^2J = 14.0 Hz, 2 H, 7'-H], 2.18–2.24 (m, 2 H), 2.43–2.49 (m, 2 H), 2.61–2.91 (m, 1 H), 3.25 [AB system, δ_A = 3.17, δ_B = 3.32, ^3J = 11.0 Hz, 2 H, 2'(3')-H], 3.20–3.38 (m, 1 H), 5.85–5.98 (m, 2 H, alkene-H), 7.66 [d, ^3J = 8.5 Hz, 2 H, 1(10)-H], 8.48–8.58 (m, 4 H, pyridyl-H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, and APT): δ = 32.99 (–), 34.91 (+), 35.99 (–), 37.68 (+), 43.48 (+), 51.97 (+), 53.65 (+), 54.56 (+), 116.02 (+), 116.12 (+), 131.68 (+), 132.28 (+), 133.56 (–), 133.78 (–), 136.44 (–), 136.72 (–), 146.25 (+), 147.50 (+), 151.85 (+), 152.39 (+). – MS (70 eV), *m/z* (%): 286 (16)[M^+], 218 (100), 180 (38). – $C_{20}H_{18}N_2$ (286.4): calcd. C 83.88, H 6.34, N 9.78; found C 83.52, H 6.77, N 9.69%.

exo-(5,6-Dihydro-2,9-phenanthrolino)-2':3',5:6-endo-5':6'-cyclopentenonorbornane (**26**): 660 mg (5.0 mmol) of **10** and 2.05 g (10.0 mmol) of 4-iodopyridine (**25**) were allowed to react according to GP 3. Chromatography on 100 g of Al_2O_3 (30 × 3.5 cm) yielded 357 mg (25%) of **26**, R_f = 0.11 (PE/MTBE 1:1), mp 158–160 °C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 412 nm (1.51), 377 (1.93), 363 (1.71), 268 (4.12). – IR (KBr): ν = 3044 cm^{-1}, 2960, 2850, 1605, 1595, 1550, 1415, 1350, 845, 705. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.38 (dt, ^2J = 11.0, ^3J = 1.2 Hz, 1 H, 7'-H_{syn}*), 1.45 (dt, ^2J = 11.0, ^3J = 1.2 Hz, 1 H, 7'-H_{anti}*), 2.26–2.81 (m, 5 H), 3.15 [AB system, δ_A = 3.09, δ_B = 3.20, ^3J = 10.0 Hz, 2 H, 2'(3')-H], 3.15–3.35 (m, 1 H), 5.68–5.89 (m, 2 H, alkene-H), 7.03 (d, ^3J = 5.0 Hz, 1 H, 4-H**), 7.07 (d, ^3J = 5.0 Hz, 1 H, 7-H**), 8.41 [d, ^3J = 5.0 Hz, 2 H, 3(8)-H], 9.14 [s, 2 H, 1(10)-H]. – ^{13}C NMR (62.9 MHz, $CDCl_3$, and APT): δ = 33.03 (–), 36.36 (–), 37.07 (+), 39.88 (+), 43.28 (+), 51.99 (+), 53.44 (+), 54.37 (+), 123.82 (+), 124.51 (+), 125.64 (–), 125.88 (–), 131.72 (+), 132.32 (+), 143.58 (+), 143.69 (+), 146.67 (–), 147.02 (–), 148.81 (+), 148.91 (+). – MS (70 eV), *m/z* (%): 286 (18)[M^+], 218 (100)[$M^+ - C_5H_8$], 180 (8). – $C_{20}H_{18}N_2$ (286.4): calcd. C 83.88, H 6.34, N 9.78; found C 82.65, H 6.43, N 9.40%.

4-Phenylphenanthreno-2',3':9,10-norbornene (**37**): A solution of 140 mg (0.43 mmol) of **4a** and 110 mg (0.48 mmol) of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in 20 ml of toluene was refluxed for 2 h. The solution was concentrated, the residue was filtered over 25 g of silica gel (6 × 3.5 cm, PE 60/70) to yield 127 mg (91%) of a colorless oil (R_f = 0.13), which on sublimation (0.01 Torr, 100 °C) afforded 94 mg (67%) of **37**, white solid, mp 123 °C. – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.32 [m, 2 H, 5'(6')-H], 1.88 [AB system, δ_A = 1.76, δ_B = 2.00, ^2J = 8.4 Hz, 2 H, 7'-H], 2.13 [m, 2 H, 5'(6')-H], 4.08 (s, 1 H, 1'-H*), 4.11 (s, 1 H, 4'-H*),

7.08 (t, ^3J = 8.0 Hz, 1 H, arene-H), 7.50 (m, 7 H, arene-H), 7.64 (t, ^3J = 8.0 Hz, 1 H, arene-H), 7.85 (d, ^3J = 8.0 Hz, 1 H, arene-H), 8.01 (d, ^3J = 8.0 Hz, 1 H, arene-H), 8.09 (d, ^3J = 8.0 Hz, 1 H, arene-H). – ^{13}C NMR (67.9 MHz, $CDCl_3$, and DEPT): δ = 27.42 [–, C-5'(6')], 42.28 (+, C-1'*), 42.56 (+, C-4'*), 48.92 (–, C-7'), 123.34 (+, rel. intens. 2), 123.53 (+, rel. intens. 2), 125.41 (+), 125.78 (+), 126.64 (+), 127.99 (C_{quat}), 128.68 (+), 129.07 (C_{quat}), 129.25 (+), 129.36 (+), 129.60 (+), 129.99 (C_{quat}), 141.26 (C_{quat}), 141.57 (C_{quat}), 141.92 (C_{quat}), 146.06 (C_{quat}). – $C_{25}H_{20}$ (320.4): calcd. C 93.71, H 6.29; found C 93.81, H 6.29%.

exo-4,5-Dihydrobenzo[e]pyreno-2',3':4:5-norbornane (**35**): A solution of 910 mg (2.82 mmol) of **4a** and 720 mg (2.84 mmol) of iodine in 1.4 l of cyclohexane was irradiated for 4 h with a 250 W Hg medium pressure lamp and a quartz filter. The solution was concentrated, the residue was filtered over 25 g of silica gel (6 × 3.5 cm, PE/CH_2Cl_2 1:1, R_f = 0.86), and recrystallized from heptane/toluene 10:1 to yield 750 mg (83%) of **35**, yellow crystals, mp 203 °C. – IR (KBr): ν = 3050 cm^{-1}, 3000, 2950, 2850, 1440, 1400, 800, 750. – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.07 (d, ^2J = 10.0 Hz, 1 H, 7'-H_{syn}*), 1.39 (d, ^2J = 10.0 Hz, 1 H, 7'-H_{anti}*), 1.75 [A_2B_2 system, δ_A = 1.72, δ_B = 1.78, ^2J = 9.5 Hz, 4 H, 5'(6')-H], 2.49 [bs, 2 H, 1'(4')-H], 3.49 [bs, 2 H, 2'(3')-H] 7.46 [d, ^3J = 7.7 Hz, 2 H, 3(6)-H], 7.55 [t, ^3J = 7.7 Hz, 2 H, 2(7)-H], 7.60 [XX' part of an AA'XX' system, ^3J = 6.2, ^4J = 3.3 Hz, 2 H 10(11)-H], 8.40 [d, ^3J = 7.7 Hz, 2 H, 1(8)-H], 8.58 [AA' part of an AA'XX' system, ^3J = 6.2, ^4J = 3.3 Hz, 2 H, 9(12)-H]. – ^{13}C NMR (67.9 MHz, $CDCl_3$, and DEPT): δ = 30.31 [–, C-5'(6')], 33.54 (–, C-7'), 46.20 [+, C-1'(4')], 50.38 [+, C-2'(3')], 120.64 (+), 123.51 (+), 126.10 (C_{quat}), 126.70 (+, rel. intens. 2), 128.17 (+), 128.72 (C_{quat}), 129.96 (C_{quat}), 137.65 (C_{quat}). – ^{13}C NMR (67.9 MHz, C_6D_6, and DEPT): δ = 30.47 [–, C-5'(6')], 33.62 (–, C-7'), 46.42 [+, C-1'(4')], 50.60 [+, C-2'(3')], 121.13 (+), 123.91 (+), 126.59 (C_{quat}), 127.26 (+), 128.32 (+), 128.42 (+), 129.48 (C_{quat}), 130.50 (C_{quat}), 137.85 (C_{quat}). – MS (70 eV), *m/z* (%): 320 (90)[M^+], 252 (100)[$M^+ - C_5H_8$]. – $C_{25}H_{20}$ (320.4): calcd. C 93.71, H 6.29; found C 93.69, H 6.26%.

exo-4,5-Dihydrobenzo[e]pyreno-2':3',4:5-endo-5':6'-cyclopentenonorbornane (**40**): A solution of 500 mg (1.4 mmol) of **12** and 355 mg (1.4 mmol) of iodine in 200 ml of cyclohexane was irradiated for 4 h with a 500 W Hg medium pressure lamp and a quartz filter. The solution was concentrated, the residue was chromatographed on 50 g of silica gel (30 × 3.5 cm, PE, R_f = 0.17) to yield 455 mg (91%) of **40**, mp 210 °C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 401 nm (1.83), 376 (2.23), 363 (2.11), 333 (2.92), 264 (4.93). – IR (KBr): ν = 3060 cm^{-1}, 3042, 2920, 2860, 1570, 1480, 1414, 750, 732, 712, 695. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (dt, ^2J = 11.7, ^3J = 1.5 Hz, 1 H, 7'-H_{syn}*), 1.52 (dt, ^2J = 11.7, ^3J = 1.5 Hz, 1 H, 7'-H_{anti}*), 2.31 (bs, 1 H), 2.41–2.82 (m, 4 H), 3.21–3.38 (m, 1 H), 3.44 (d, ^3J = 10.0 Hz, 1 H, 2'-H**), 3.52 (d, ^3J = 10.0 Hz, 1 H, 3'-H**), 5.78–5.81 (m, 2 H, alkene-H), 7.35 (dd, ^3J = 8.0, ^3J = 6.2 Hz, 2 H), 7.52 (d, ^3J = 8.0 Hz, 2 H), 7.58 (dd, ^3J = 6.2, ^4J = 3.3 Hz, 2 H), 8.39 (d, ^3J = 8.0 Hz, 2 H), 8.61 (dd, ^3J = 6.2, ^4J = 3.3 Hz, 2 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, and APT): δ = 33.16 (–), 36.29 (–), 37.89 (+), 40.79 (+), 43.40 (+), 53.33 (+), 53.59 (+), 55.66 (+), 120.35 (+), 123.46 (+), 126.26 (–), 126.54 (–), 126.93 (+), 126.97 (+), 127.56 (+), 127.86 (+), 127.95 (+), 128.01 (–) 128.13 (–), 128.27 (+), 128.56 (+), 128.66 (+), 129.85 (–), 129.90 (–), 131.31 (+), 132.81 (+), 138.18 (–), 138.38 (–). – MS (70 eV), *m/z* (%): 358 (62)[M^+], 290 (100), 252 (53). – $C_{28}H_{22}$ (358.5): calcd. C 93.81, H 6.19; found C 93.72, H 6.17%.

Benzo[e]pyreno-2',3':4,5-norbornene (**38**): A solution of 2.00 g (6.2 mmol) of **35** and 1.44 g (6.3 mmol) of DDQ in 30 ml of toluene was refluxed for 4 h. The mixture was concentrated, and the residue was washed with 200 ml of 5% NaOH (aq.) and recrystallized from heptane to yield 1.68 g (85%) of **38**, yellow crystals, mp 181 °C. – IR (KBr): ν = 3050 cm^{-1}, 2980, 2880, 1600, 1440, 1300, 810, 760, 720. – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.32 [dd, ^2J = 7.3, ^3J = 2.2 Hz, 2 H, 5'(6')-H], 1.82 (d, ^2J = 8.4 Hz, 7'-H_{syn}*), 2.05 (d, ^2J = 8.4 Hz, 7'-H_{anti}*), 2.17 [dd, ^2J = 7.3, ^3J = 2.2 Hz, 2 H, 5'(6')-H], 4.19 [s, 2 H, 1'(4')-H], 7.72 [dd, ^3J = 6.2, ^4J = 3.3 Hz, 2 H, 10(11)-H], 8.04 [t, ^3J = 8.1 Hz, 2 H, 2(7)-H], 8.30 [d, ^3J = 8.1 Hz, 2 H, 3(6)-H], 8.85 [m, ^3J = 6.2, ^3J = 8.1, ^4J = 3.3 Hz, 4 H, 1(8,9,12)-H]. – ^{13}C NMR (67.9 MHz, $CDCl_3$, and DEPT): δ = 27.37 [–, C-5'(6')], 42.40 [+, C-1'(4')], 49.27 (–, C-7'), 119.14 (+), 121.73 (+), 123.72 (+), 125.68 (+), 127.35 (+), 127.41 (C_{quat}), 129.91 (C_{quat}), 130.50 (C_{quat}), 142.11 (C_{quat}), 1 C_{quat} not observed. – MS (70 eV), *m/z* (%): 318 (40)[M^+], 290 (100)[$M^+ - C_2H_4$], 252 (10)[$M^+ - C_5H_6$ = benzo[*e*]pyrene]. – $C_{25}H_{18}$ (318.4): calcd. C 94.30, H 5.70; found C 94.46, H 5.81%.

Aryl Anellated Cyclopentadienes by Flash Vacuum Pyrolysis

General Procedure 4 (GP 4): The specified amount of an alkene was sublimed through a quartz tube (50 × 3 cm, 750 °C) *in vacuo* ($p \leq 10^{-4}$ Torr). The product was collected in the cold zone of the quartz tube.

Cyclopentadieno-9:10-phenanthrene (**45**): According to GP 4, 42 mg (0.15 mmol) of **11** was sublimed at 125 °C during 7 h through the quartz tube to yield 25 mg (77%) of **45**, colorless crystals, mp 106 °C. – UV (CH_2Cl_2): λ_{max} (lg ε) = 366 nm (2.96), 316 (3.76), 303 (3.77), 257 (4.45). – Fluorescence (CH_2Cl_2, excitation at 330 nm): λ_{max} = 448 nm. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.78–3.95 (m, 2 H, 13-H), 6.62–6.82 (m, 1 H, alkene-H), 7.32–7.85 (m, 5 H), 7.89–8.09 (m, 1 H), 8.10–8.25 (m, 1 H), 8.59–8.82 (m, 2 H). – ^{13}C NMR (62.5 MHz, $CDCl_3$, and APT): δ = 38.49 (–), 123.29 (+), 123.46 (+), 123.96 (+), 124.38 (+), 125.21 (+), 125.72 (+), 126.44 (+), 126.76 (+), 127.79 (–), 128.83 (–), 129.65 (–), 130.03 (+), 130.22 (–), 133.76 (+), 138.52 (–), 139.38 (–). – MS (70 eV), *m/z* (%): 216 (100)[M$^+$], 178 (82). – $C_{17}H_{12}$: calcd. and found 216.0939 (HRMS).

4(5)-Phenylcyclopentadieno-9:10-phenanthrene ((*E/Z*)-**42**): According to GP 4, 65.2 mg (0.18 mmol) of **12** was sublimed at 135 °C during 9 h through the quartz tube to yield 45 mg (85%) of (*E/Z*)-**42**, light yellow solid. – IR (KBr): ν = 3025 cm^{-1}, 2920, 1570, 1450, 820, 740. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.84–3.95 (m, 2 H, 13-H), 6.71–6.83 (m, 1 H), 6.95–7.12 (m, 1 H), 7.35–8.25 (m, 12 H, arene-H). – ^{13}C NMR (62.5 MHz, $CDCl_3$, and APT): δ = 39.53 (–), 39.92 (–), 123.33 (+), 123.49 (+), 123.65 (+), 123.85 (+), 123.90 (+), 123.96 (+), 125.53 (–), 125.85 (+), 125.91 (–), 126.17 (+), 126.90 (+), 127.04 (+), 127.12 (+), 127.15 (+), 127.21 (–), 127.28 (+), 128.17 (–), 128.22 (–), 128.50 (–), 128.57 (+), 128.61 (–), 128.72 (+), 128.92 (+), 129.09 (+), 129.16 (+), 129.29 (+), 129.62 (+), 130.01 (+), 130.12 (–), 130.27 (+), 130.80 (–), 133.74 (+), 133.99 (+), 138.54 (–), 138.88 (–), 139.75 (–), 140.98 (–), 141.15 (–), 145.66 (–), 145.71 (–). – MS (70 eV), *m/z* (%): 292 (100)[M$^+$], 276 (16). – $C_{23}H_{16}$: calcd. and found 292.1251 (HRMS).

4:5-Cyclopentadienobenzo[e]pyrene (**39**): *A*: According to GP 4, 560 mg (1.76 mmol) of **38** was sublimed at 150 °C during 6 h through the quartz tube (650 °C) to yield 485 mg (95%) of **39**, light yellow solid. – IR (KBr): ν = 3050 cm^{-1}, 3020, 2990, 1600, 1440, 1370, 1160, 905, 845, 795, 745, 715. – ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.01 (t, ^3J = 1.0 Hz, 2 H, alkyl-H), 6.86 (dt, ^3J = 4.2, ^3J = 1.0 Hz, 1 H, alkene-H), 7.64 (dt, ^3J = 4.2, ^3J = 1.0 Hz, 1 H, alkene-H), 7.73 (dd, ^3J = 7.0, ^4J = 2.0 Hz, 2 H, arene-H), 8.04 (m, ^3J = 6.0, ^4J = 2.0 Hz, 2 H, arene-H), 8.28 (dd, ^3J = 6.0, ^4J = 0.8 Hz, 1 H, arene-H), 8.45 (dd, ^3J = 6.0, ^4J = 0.8 Hz, 1 H, arene-H), 8.87 (m, 4 H, arene-H). – $C_{23}H_{14}$ (290.4): calcd. C 95.14, H 4.86; found C 95.25, H 4.83%.

B: According to GP 4, 40 mg (0.11 mmol) of **40** was sublimed at 150 °C during 2.5 h through the quartz tube (750 °C) to yield 31 mg (96%) of **39**.

Benzo[e]pyrene (**36**): According to GP 4, but at p = 0.05–0.01 Torr, 150 mg (0.47 mmol) of **35** was sublimed at 150–200 °C during 4 h through the quartz tube (800 °C) to yield 104 mg of a mixture of **35** (ca. 10%) and **36** (ca. 90%), which was separated by crystallization from *n*-heptane to yield 82 mg (69%) of **36**.

4:5-Cyclopentadienobenzo[1,2-b:4,3-b']dithiophene (**46**): According to GP 4, 45.6 mg (0.15 mmol) of **20** was sublimed at 130 °C during 7 h through the quartz tube to yield 29 mg (85%) of **46**, mp 128 °C (decomp.). – UV (CH_2Cl_2): λ_{max} (lg ε) = 429 nm (2.39), 307 (3.77), 252 (4.06). – Fluorescence (CH_2Cl_2, excitation at 319 nm): λ_{max} (rel. intens.) = 498 nm (1.0), 477 (0.97). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.75 (dd, ^3J = 5.0, ^4J = 1.0 Hz, 2 H, alkyl-H), 6.71 (dt, ^3J = 5.0, ^3J = 5.0 Hz, 1 H, alkene-H), 7.15 (dt, ^4J = 1.0, ^3J = 5.0 Hz, 1 H, alkene-H), 7.44 (d, ^3J = 5.0 Hz, 1 H), 7.53 (d, ^3J = 5.0 Hz, 1 H), 7.73 (d, ^3J = 5.0 Hz, 1 H), 7.75 (d, ^3J = 5.0 Hz, 1 H). – ^{13}C NMR (62.9 MHz, $CDCl_3$, and APT): δ = 39.36 (–), 122.41 (+), 122.62 (+), 124.35 (+), 125.03 (+), 130.01 (–), 130.29 (+), 132.84 (–), 133.49 (+), 133.61 (–), 134.02 (–), 134.62 (–), 138.21 (–). – MS (70 eV), *m/z* (%): 228 (100)[M$^+$], 91 (39), 71 (83), 55 (37). – $C_{13}H_8S_2$: calcd. and found 228.0067 (HRMS).

5:6-Cyclopentadieno-3,8-phenanthroline (**47**): According to GP 4, 55 mg (0.2 mmol) of **24a** was sublimed at 130 °C during 8 h through the quartz tube to yield 41 mg (94%) of **47**, mp 135 °C (decomp.). –

UV (*iso*-octane): λ_{max} (lg ε) = 441 nm (1.55), 435 (1.55), 429 (1.56), 418 (1.57), 385 (3.37), 365 (3.30), 348 (3.05), 325 (3.67), 313 (3.75), 228 (4.27). – Fluorescence (*iso*-octane, excitation at 313 nm): λ_{max} (rel. intens.) = 433 nm (0.31), 409 (0.82), 388 (1.00). – IR (KBr): ν = 3055 cm^{-1}, 2960, 1445, 800, 760, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.93 (dd, ^3J = 1.7, ^4J = 1.2 Hz, 2 H, 13-H), 6.95 (dt, ^3J = 4.0, ^3J = 1.7 Hz, 1 H, 12-H), 7.57 (dt, ^3J = 4.0, ^4J = 1.2 Hz, 1 H, 11-H), 8.38 (d, ^3J = 6.0 Hz, 1 H, 1-H*), 8.40 (d, ^3J = 6.0 Hz, 1 H, 10-H*), 8.76 (d, ^3J = 6.0 Hz, 1 H, 2-H**), 8.84 (d, ^3J = 6.0 Hz, 1 H, 9-H**), 9.46 (s, 1 H, 7-H***), 9.60 (s, 1 H, 4-H***). – ^{13}C NMR (62.9 MHz, $CDCl_3$, and APT): δ = 39.12 (–), 116.74 (+), 116.79 (+), 123.48 (–), 125.80 (–), 128.56 (+), 131.38 (–), 132.76 (–), 136.08 (+), 138.34 (–), 140.55 (–), 144.19 (+), 145.25 (+), 148.18 (+), 148.29 (+). – MS (70 eV), *m/z* (%): 218 (100)[M^+], 190 (18), 163 (16). – $C_{15}H_{10}N_2$: calcd. and found 218.0843 (HRMS).

5:6-Cyclopentadieno-2,9-phenanthroline (**48**): According to GP 4, 50.3 mg (0.17 mmol) of **26** was sublimed at 150 °C during 7 h through the quartz tube to yield 29 mg (78%) of **48**, yellow solid. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.85 (dd, ^3J = ^4J = 1.0 Hz, 2 H, 13-H), 6.96 (dt, ^3J = 6.2, ^3J = 1.0 Hz, 1 H, 12-H), 7.43 (dt, ^3J = 6.2, ^4J = 1.0 Hz, 1 H, 11-H), 7.80 (d, ^3J = 5.0 Hz, 1 H, 4-H*), 7.96 (d, ^3J = 5.0 Hz, 1 H, 7-H*), 8.77 (d, ^3J = 5.0 Hz, 1 H, 3-H**), 8.83 (d, ^3J = 5.0 Hz, 1 H, 8-H**), 10.10 (s, 1 H, 1-H***), 10.14 (s, 1 H, 10-H***). – MS (70 eV), *m/z* (%): 218 (100)[M^+], 190 (11), 163 (22). – $C_{15}H_{10}N_2$: calcd. and found 218.0843 (HRMS).

REFERENCES AND NOTES

1. For a recent review on sequential reactions in general see: U. Beifuss, L.-F. Tietze, *Angew. Chem.* **1993**, *105*, 137–170; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131–164.
2. (a) B. M. Trost, Y. Shi, *J. Am. Chem. Soc.* **1991**, *113*, 701–703. – (b) B. M. Trost, Y. Shi, *ibid.* **1992**, *114*, 791–792.
3. (a) Y. Zhang, E.-I. Negishi, *J. Am. Chem. Soc.* **1989**, *111*, 3454–3456. – (b) G.-Z. Wu, F. Lamaty, E.-I. Negishi, *J. Org. Chem.* **1989**, *54*, 2507–2508. – (c) Y. Zhang, G.-Z. Wu, G. Agnel, E.-I. Negishi, *J. Am. Chem. Soc.* **1990**, *112*, 8590–8592.
4. (a) N. E. Carpenter, D. J. Kucera, L. E. Overman, *J. Org. Chem.* **1989**, *54*, 5846–5848. – (b) M. M. Abelman, L. E. Overman, *J. Am. Chem. Soc.* **1988**, *110*, 2328–2329. – (c) D. J. Kucera, L. E. Overman, *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, DC, Aug. **1990**.
5. (a) R. Grigg, V. Santhakumar, V. Sridharan, P. Stevenson, A. Teasdale, M. Thornton-Pett, T. Worakun, *Tetrahedron* **1991**, *47*, 9703–9720. – (b) R. Grigg, M. J. Dorrity, J. F. Malone, V. Sridharan, S. Sukirthalingam, *Tetrahedron Lett.* **1990**, *31*, 1343–1346. – (c) R. Grigg, V. Loganathan, V. Santhakumar, V. Sridharan, A. Teasdale, *Tetrahedron Lett.* **1991**, *32*, 687–690.
6. (a) R. C. Larock, B. E. Baker, *Tetrahedron Lett.* **1988**, *29*, 905–908. – (b) R. C. Larock, H. Song, B. E. Baker, W. H. Gong, *ibid.* **1988**, *29*, 2919–2922.
7. (a) F. E. Meyer, P. J. Parsons, A. de Meijere, *J. Org. Chem.* **1991**, *56*, 6487–6488. – (b) F. E. Meyer, A. de Meijere, *Synlett* **1991**, 777–778. – (c) F. E. Meyer, J. Brandenburg, P. J. Parsons, A. de Meijere, *J. Chem. Soc., Chem. Commun.* **1992**, 390–392. – (d) F. E. Meyer, H. Henniges, A. de Meijere, *Tetrahedron Lett.* **1992**, *33*, 8039–8042.
8. (a) S. Torii, H. Okumoto, A. Nishimura, *Tetrahedron Lett.* **1991**, *32*, 4167–4168; P. J. Parsons, M. Stefinovic, P. Willis, F. E. Meyer, *Synlett* **1992**, 864–866. – (b) S. Torii, H. Okumoto, T. Kotani, S. Nakayasu, H. Ozaki, *Tetrahedron Lett.* **1992**, *33*, 3503–3506.
9. M. Catellani, G. P. Chiusoli, *J. Organomet. Chem.* **1985**, *286*, C13–C16. – Review: G. P. Chiusoli, *ibid.* **1986**, *300*, 57–80 and references cited therein.
10. For preliminary reports on this work see: (a) O. Reiser, M. Weber, A. de Meijere, *Angew. Chem.* **1989**, *101*, 1071–1072; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1037–1038. – (b) K. Albrecht, O. Reiser, M. Weber, A. de Meijere, *Synlett* **1992**, 521–523.
11. T. Jeffery, *Tetrahedron Lett.* **1985**, *26*, 2667–2670. – See also: T. Jeffery, *Tetrahedron Lett.* **1990**, *31*, 6641–6644.

12. In most cases, the less expensive tetra-*n*-butylammonium bromide could be substituted for the chloride originally used by Jeffery,[11] with as good results.
13. In the absence of norbornene, the palladium catalyzed aryl aryl coupling can be achieved with yields up to 87%, by raising the reaction temperature to 150 °C. *Cf.* K. Albrecht, M. Weber, A. de Meijere, unpublished results. – M. Weber, *Dissertation*, Universität Hamburg, 1992; K. Albrecht, *Dissertation*, Universität Göttingen, 1993. – This is superior to a recently published palladium-catalyzed aryl aryl coupling which requires the presence of triphenylarsine: M. Brenda, A. Knebelkamp, A. Greiner, W. Heitz, *Synlett* **1991**, *11*, 809–810.
14. Siemens Stoe AED 2 diffractometer, Mo-K_α radiation, structures were solved with SHELXTL-PLUS.[15] Further details of these crystal structure investigations are available on request from the Fachinformationszentrum Energie Physik Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57602, the names of the authors, and the journal citation.
15. G. M. Sheldrick, SHELXTL-PLUS: Program for Crystal Structure Determination, Göttingen 1986.
16. A rate retarding effect of electron-withdrawing substituents in palladium catalyzed aryl halide coupling reactions has been noted. *Cf.* P. J. Harrington, K. A. DiFiore, *Tetrahedron Lett.* **1987**, *28*, 495–498.
17. M. Catellani, G. P. Chiusoli, C. Castagnoli, *J. Organomet. Chem.* **1991**, *407*, C30–C33; M. Catellani, G. P. Chiusoli, *ibid.* **1988**, *346*, C27–C30, and earlier references cited therein. – For a detailed mechanistic study see: J. M. Brown, N. A. Cooley, *Organometallics* **1990**, *9*, 353–359.
18. For a review on the role of Pd(IV) complexes see: A. J. Canty, *Acc. Chem. Res.* **1992**, *25*, 83–90.
19. The primary addition product of phenylpalladium iodide to norbornene, a complex of type **29** with L = PPh_3, has been isolated and fully characterized by X-ray crystal structure analysis. C.-S. Li, C.-H. Cheng, F.-L. Liao, S.-L. Wang, *J. Chem. Soc., Chem. Commun.* **1991**, 710–712.
20. M. Catellani, G. P. Chiusoli, *J. Organomet. Chem.* **1992**, *425*, 151–154, and earlier references cited therein.
21. This is conceived in close analogy to known aryne Pt(II) complexes. *Cf.* M. A. Bennett, H. P. Schwemlein, *Angew. Chem.* **1989**, *101*, 1349–1373; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1296. The frequently formulated possibility (*cf.* B. A. Markies, P. Wijkens, H. Kooijman, A. L. Spek, J. Boersma, G. van Koten, *J. Chem. Soc., Chem. Commun.* **1992**, 1420–1423 and references cited therein) that the *ortho* C–H activation occurs as a consequence of an electrophilic attack of Pd(II) or Pd(IV) on the adjacent arene unit appears to be less likely in this case, as it would have to occur via a highly distorted σ-complex.
22. For reviews on this pyrolysis technique see: (a) E. Hedaya, *Acc. Chem. Res.* **1969**, *2*, 367–373. – (b) U. E. Wiersum, *Rec. Trav. Chim. Pays-Bas* **1982**, *101*, 317–332. – (c) U. E. Wiersum, *ibid.* **1982**, *101*, 365–381. – (d) G. Seybold, *Angew. Chem.* **1977**, *89*, 377–385; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 365–373.
23. For the use of ring-anellated cyclopentadienes as ligands in metal complexes see: (a) L. A. Paquette, K. J. Moriarty, P. Meunier, B. Gautheron, C. Sornay, R. D. Rogers, A. L. Rheingold, *Organometallics* **1989**, *8*, 2159–2167, and references cited therein. – (b) R. L. Haltermann, K. P. C. Vollhardt, *Organometallics* **1988**, *7*, 883–892. – (c) G. Erker, A. A. H. van der Zeijden, *Angew. Chem.* **1990**, *102*, 543–545; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 512. – (d) G. S. Hermann, H. G. Alt, M. D. Rausch, *J. Organomet. Chem.* **1991**, *401*, C5–C9. – (e) G. Erker, R. Nolte, R. Aul, S. Wilker, C. Krüger, R. Noe, *J. Am. Chem. Soc.* **1991**, *113*, 7594–7602.
24. (a) M. Karpf, *Angew. Chem.* **1986**, *98*, 413–429; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 414. – (b) A. Ichihara, *Synthesis* **1987**, 207–222.
25. This intramolecular double hydrogen migration has precedence in polycyclic hydrocarbon chemistry. For related examples see: (a) J.-P. Hagenbuch, B. Stampfli, P. Vogel, *J. Am. Chem. Soc.* **1981**, *103*, 3934–3935. – (b) L. A. Paquette, G. A. O'Doherty, *J. Am. Chem. Soc.* **1991**, *113*, 7761–7762.
26. This fragmentation in the mass spectrometer most probably is a thermal process: H. Budzikiewicz, *Z. Anal. Chem.* **1969**, *244*, 1–6.

(*Received* 6 *August* 1993)