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Selective Transformations of Phenylated Diynes to Polycyclic Compounds by the $RhCl_3$- and $PtCl_4$-Aliquat 336® Ion Pair Catalysts

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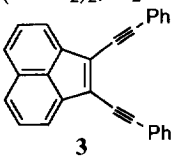
Abstract: The ion pairs generated from methyltricaprylammonium chloride and either $RhCl_3$ or $PtCl_4$ catalyze, under phase transfer conditions, selective cyclorearrangements, as well as intra- and intermolecular addition processes by which discrete polycyclic compounds are formed. The nature of the products depends on the distances between the ethynyl functions and on the catalyst employed.

Transition metal-mediated inter- and intramolecular cycloaddition reactions of alkynes are among the best known methods for the syntheses of many carbocyclic compounds.[1] Müller showed, already by the early 1970's, that diynes react usually in equimolar amounts, with $RhCl(PPh_3)_3$ and with similar complexes, to give metallacyclic compounds that form metal-free polycyclics both by themolysis and by addition of small diynophiles.[2] Recently,[3] we have found that under phase transfer conditions the ion pair generated from methyltricaprylammonium chloride (Aliquat 336®) and $RhCl_3$, and the ion pair generated from the same quaternary ammonium salt and $PtCl_4$ (catalyst **1** and **2**, respectively) catalyze unique cyclorearrangement and oligomerization reactions of some phenylated diynes. In this study we have investigated the one pot transformations of diynes **3-8** by **1** and **2**, that proved these catalytic processes to be of general utility for the facile formation of a wide range of polycyclic aromatics. The nature of the products were shown to depend on the distances and angles between the two alkyne functions in the starting material, as well as on the metal catalysts employed.

RESULTS AND DISCUSSION

In our previous study[3] we observed that while 1,2-bis(phenylethynyl)benzene, 1,2-$C_6H_4(C{\equiv}CPh)_2$ (**9**), is not affected by the ion pair $[(C_8H_{17})_3NMe]^+[RhCl_4(H_2O)_n]^-$ (**1**), it is smoothly converted into 5-phenylindeno[2,1-*a*]indene (**10**) in the presence of the $PtCl_4$-Aliquat 336 catalyst **2**. In this process, which was carried out in a $(CHCl_2)_2/H_2O$ two liquid phase system, one of the phenyl



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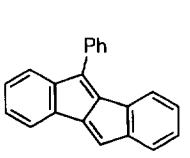
groups took part in the formation of the indenoindene skeleton. We have now found that under the same conditions 1,2-bis(phenylethynyl)acenaphthylene (**3**) (characterized by X-ray diffraction analysis as shown in Fig. 1[4]) *does* react in the presence of **1**, but gives only mixtures of polymers when catalyst **2** is employed. The rhodium catalyst promotes a water assisted reductive dimerization of **3** by which **11** is formed. The structure of **11** has been established by virtue of its elemental analysis, its ^{13}C NMR (which consists of forty eight signals, including two of the tertiary CH and two of the acetylenic atoms), and its mass spectrum (*m/z* 706, $M^{\cdot+}$). In the conversion of **3** into **11** none of the phenyl groups of the starting material takes part in the formation of the product's skeleton. The formation of **11** from **3** can be explained in terms of initial interaction of the diyne with the catalyst coupled with a transfer hydrogenation process[5] to give an intermediate ***a*** (where one L is either Cl or OH[6]) followed by addition of a second molecule of **3**, in a similar fashion as the addition of **1** to 1,8-bis(phenylethynyl)naphthalene (**13**).[3]

It is assumed that the difference in the chemical behavior of **3** and **9** is associated both with the different electronic nature of the C-C bonds that separate the ethynyl groups, and with the



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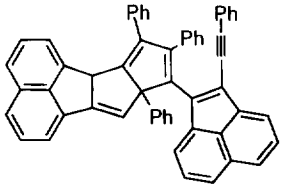

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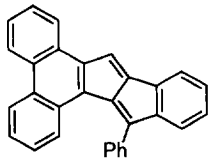

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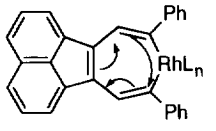
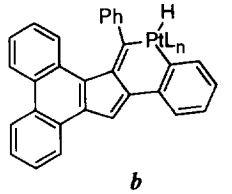
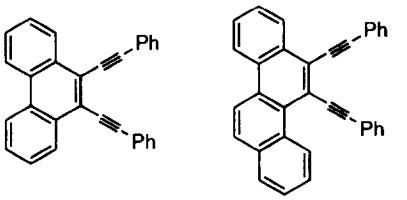


a



b

magnitude of the angles between them. While in **3** the alkyne moieties are attached to a non-aromatic double bond, and the angle between the acetylene functions is according to the X-ray analysis 78°,[4] they are located in **9** on an aromatic carbon atom, forming an angle of only 60°. Thus,



4 **5**

it is understandable why 9,10-bis(phenylethynyl)phenanthrene (**4**) which resembles **9** in this respect, is not affected by **1**, but forms in the presence of **2**, the respective analog of **10**, 9-phenylbenzo-[4,5]pentaleno[9,10-*l*]phenanthrene (**12**). The conversion of **9** to **10** by $PtCl_4$ has been assumed to follow a free radical mechanism.[2] Our studies on the preparation of **10**[3] and **12** by **2** under phase transfer conditions, favor a mechanism which is similar to that of **1**-catalyzed conversion of 1-phenylpropyne into 2,3-dimethyl-1-phenylnaphthalene *via* ortho metallation. This suggests the intermediary of a platinum hydride ***b*** (where one ligand L is Cl) in the formation of **12**.

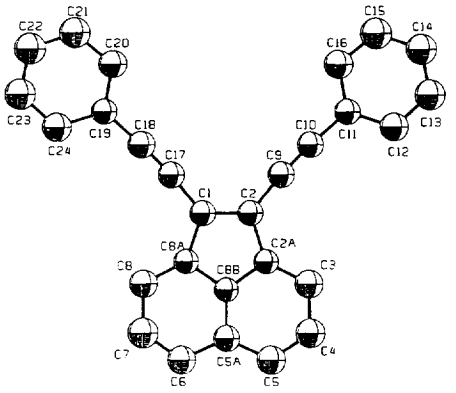


Fig. 1. ORTEP drawing of **3**

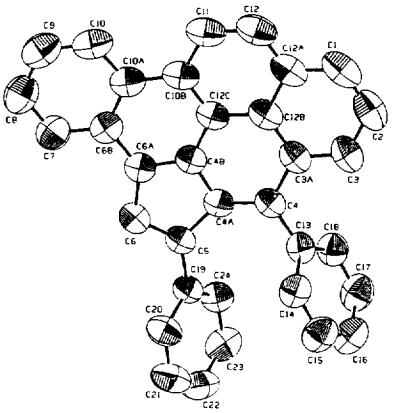
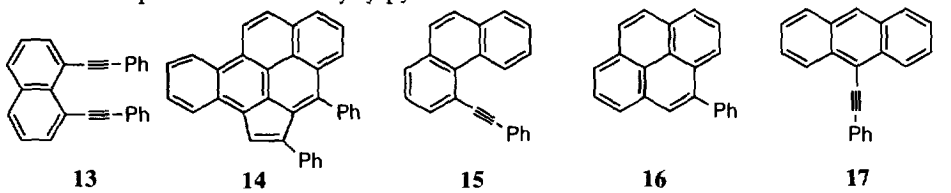


Fig. 2. ORTEP drawing of **14a** (orientation II).

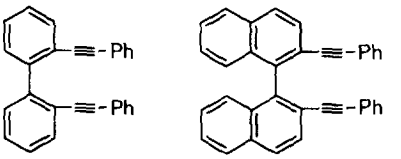
In the light of these results, we expected that the higher benzolog of **4**, 5,6-bis(phenylethynyl)chrysene (**5**) would react in the same manner. In fact, this was not the case. In analogy to **4** it proved refractory to **1**, but in the presence of catalyst **2** compound **14**, with the unknown benzo-[*a*]cyclopenta[*l*,*m*]pyrene skeleton, was obtained. Depending on the solvent used for recrystallization, **14** crystallized with one half molecule of CH_2Cl_2 (**14b**), or as solvent-free crystals (**14a**) when $CHCl_3$ was employed. Both types of crystals were subjected to X-ray diffraction analysis. An ORTEP drawing of **14a** (that has two orientations in the crystal unit) is shown in Fig 2.[4] We assume that the first step in the conversion of **5** to **14** is the cyclization of the phenylethynyl group at position 5 onto carbon 4 of the chrysene moiety. Support in this assumption has been provided by an experiment in which 1-(phenylethynyl)-phenanthrene (**15**) was transformed by **2** to 4-phenylpyrene (**16**). Since, however 9-(phenylethynyl)-anthracene (**17**) proved not to react at all under our

experimental conditions, it seems that the 6-phenylethynyl group cyclizes *during* the reaction of the 5-phenylethynyl group rather than after the formation of the benzo[*a*]pyrene skeleton. It is noteworthy that the formation of cyclopenta-[*c,d*]pyrene, which is a lower benzolog of benzo[*a*]cyclopenta[*l,m*]pyrene has recently been obtained by flash vacuum thermolysis (at 1000°C) and by combustion processes via 4-ethynylpyrene.[7,8]



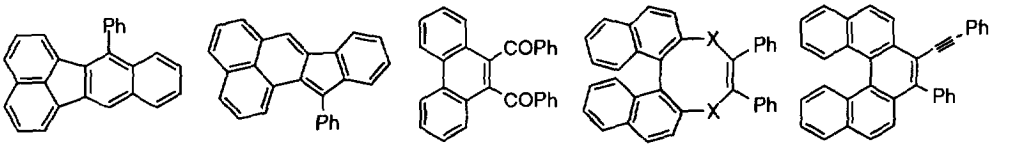
13 **14** **15** **16** **17**

Since 1,8-bis(phenylethynyl)naphthalene (**13**), in which the ethynyl groups are almost parallel to each other, has already been shown to react both in the presence of **1** and **2**, to yield **18** and **19**, respectively,[3] we have not further investigated diynes in which the ethynyl groups are separated by three carbon atoms.



6 **7**

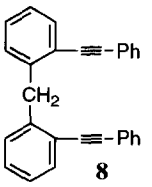
As representative compounds with four atoms separating between the acetylenic functions, we chose 2,2'-bis(phenylethynyl)[1,1'-biphenyl] (**6**) and 2,2'-bis(phenylethynyl)-1,1'-binaphthalene (**7**), in which the ethynyl groups are flexible. Both diynes proved refractory to **1**, but reacted in the presence of **2** under our standard phase transfer conditions. Under exclusion of air **6** formed a labile compound which darkened readily during the workup. This product could however be trapped by oxygen yielding 9,10-dibenzoylphenanthrene (**20**). Thus, in the presence of air, **20** is the only isolable product. This result indicates that the binding between the two acetylene groups has taken place between the two carbon atoms α to the biphenyl moiety. Search for any 6,7-diphenyldibenzo-[*a,c*]cyclooctene-5,8-dione[9] in the reaction mixture (*vide infra*) gave negative results. In spite of the similarity between **6** and **7**, the latter did not yield a dibenzo[*c,g*]phenanthrene derivative. In the



18 **19** **20** **21**, X = CH_2 **23**
22, X = C=O

absence of air, a water-assisted reductive cyclization to 3,6-dihydro[1,2-*a*:7,8-*a*']dinaphthalene (**21**) took place. The structure of this symmetrical hydrocarbon has been established by virtue of its elemental analysis, mass spectrum (*m/z* 458, $M^{\cdot+}$) ^1H NMR (4.62 ppm ABq) and ^{13}C NMR (16 signals including one at 35.15 ppm). Under ambient conditions, the methylene groups were oxidized and consequently **22** was obtained (carbonyl peak at 1680 cm^{-1}; the ^{13}C NMR consisted of 16 signals

including one at 195.67 ppm). Thus, in contrast to **6** the linkage between the two acetylene functions in **7** occurred at the two carbon atoms β to the binaphthyl moiety. We attribute the difference in the type of products obtained from **6** and **7** to the difference in the thermodynamic stability of the planer phenanthrene and of the 5-ring helicene derivative. In respect to the preparation of **7** it is notable that while the compound has been obtained in 80% yield from 2,2'-diiodo-1,1'-binaphthalene[10] and copper(I) phenylacetylide[11] by the mothod described in the literature for **6**,[12] attempts to prepare it by the $PdCl_2(PPh_3)_2$-catalyzed Heck reaction with PhC≡CH, furnished 86% of 3-phenyl-4-(phenylethynyldibenzo[*c*,*g*]phenanthrene (**23**) (two acetylenic signals in the ^{13}C NMR spectrum) (*cf*, also reference 13).



8

1,1'-Methylenebis[2-(phenylethynyl)benzene (**8**) served as an example for a diyne with five carbon atoms separating between the ethynyl functions. The preparation of **8** was accomplished by stepwise double ethynylation of di(2-iodophenyl)methane (**24**)[14] with copper(I) phenylacetylide. Attempts to convert **24** into **8** by the $PdCl_2(PPh_3)_2$-catalyzed Heck reaction gave the expected compound admixed with considerable amounts of the isomeric 9,10-dihydro-9-(1,3-diphenyl-2-propynylidene)anthracene (**26**) whose structure was confirmed by ^1H and ^{13}C NMR as well as by X-ray diffraction analysis (see Fig. 3).[4] We have proven that **26** is formed by a palladium-catalyzed intramolecular cyclization of **25** (which is obviously an intermediate in the synthesis of **8**).

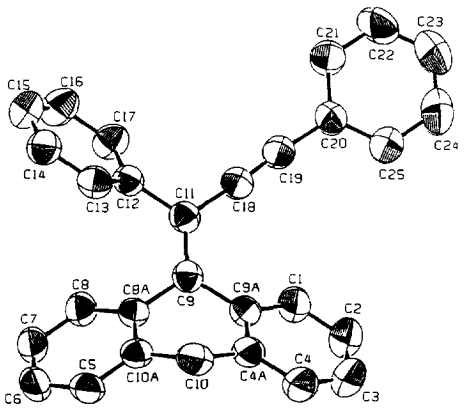


Fig. 3. ORTEP drawing of **26**

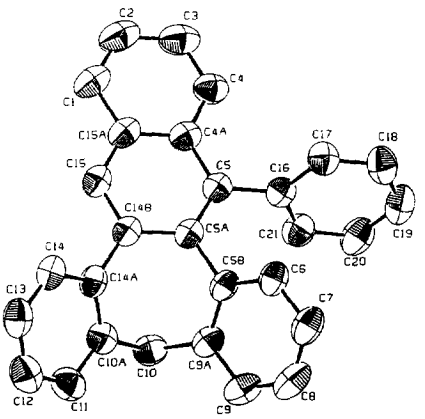
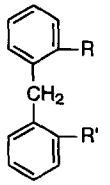
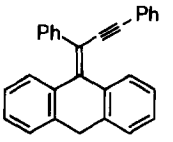
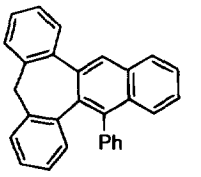


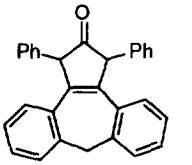
Fig. 4. ORTEP drawing of **27**

Heating of **8** in the presence of **1** under our standard phase transfer conditions resulted in the formation of 5-phenyldibenz[3,4:6,7]cyclohepta[1,2-*b*]naphthalene (**27**). The structure of **27** was confirmed by X-ray diffraction analysis (Fig. 4).[4] It is noteworthy that the ^{13}C NMR shows 29 signals suggesting that all six phenyl ring carbon atoms are located in magnetically different environments.









24: R = R' = I
25: R = I, R' = C≡CPh

26 **27** **28**

In the presence of the platinum catalyst **2**, either no reaction took place (low temperature) or polymeric materials was formed (under vigorous reflux conditions).

While in the rhodium-catalyzed cyclorearrangment of **8** one of the acetylene-bound phenyl groups is involved in the formation of the polycyclic skeleton of **27**, upon conducting of the reaction under 750 psi CO, simple carbonylation across the two triple bonds proved to take place leading to 1,2,3,8-tetrahydro-1,3-diphenyl-8-dibenz[*e*,*h*]azulenone (**28**) (without incorporation of a phenyl group in the skeleton of the product).

Carbonylation of the various diynes (as well as the addition of other small molecules to diacetylenes) by the ion pair catalysts seems not to be an obvious process. Among compounds **3-7** only diyne **4** underwent carbonylation under our standard conditions. [See however the different modes of carbonylation of 1,8-bis(ethynyl)naphthalenes by **1**[5]]. In the presence of **1** (that does not affect **4** by itself) diyne **4** proved to undergo water-assisted reductive double carbonylation yielding lactone **29** (cf., reference 15), as the only isolable product (see Fig. 5).[4] A similar transformation had already been observed when the lower benzolog, **9**, was reacted with CO and **1** under phase transfer conditions.[16] However, in contrast to the reaction of **9**, the carbonylation of **4** took place only on one

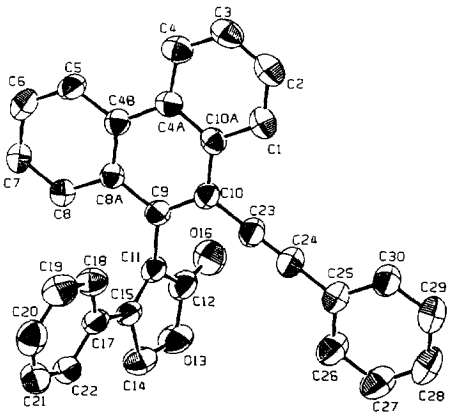


Fig. 5. ORTEP drawing of **29**

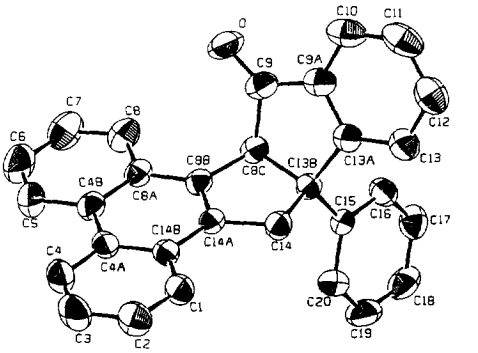
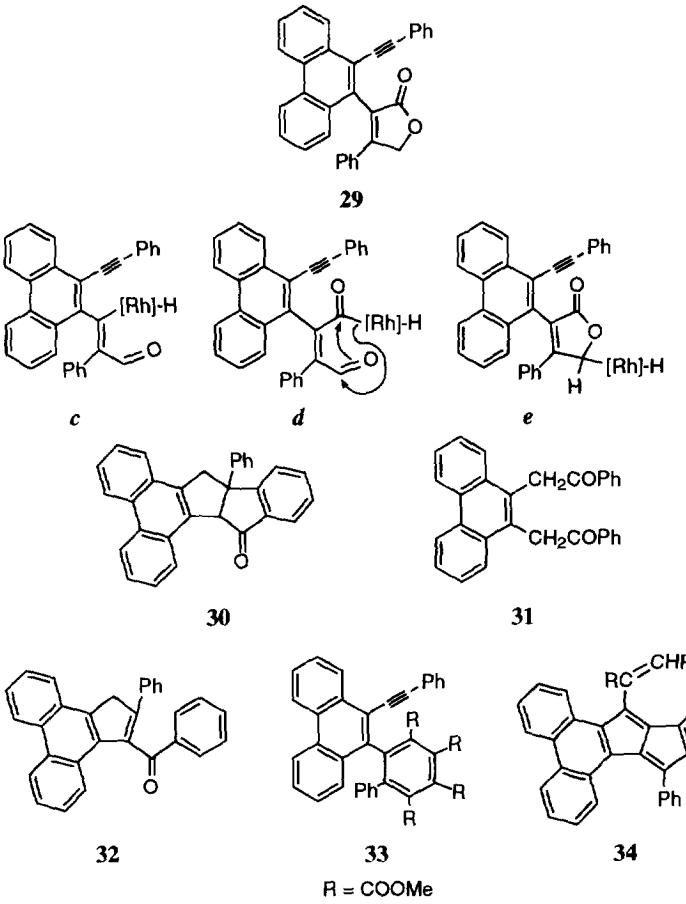


Fig. 6. ORTEP drawing of **30**

ethynyl group rather than between the two triple bonds. A plausible mechanism for the transformation of **4** to **29** includes the initial formation of a formylrhodium complex that may add to one ethynyl bond to form intermediate *c*. Further addition of CO, may lead to ***d*** that upon intra-

molecular ring closure (to form *e*) and reductive elimination yields lactone **29**.



In the presence of the platinum catalyst **2**, **4** could not be carbonylated but yielded **30** (which is formally a rearrangement product of **4** to which the elements of water have been added). The ketone which has been characterized by its IR, ^{13}C NMR elemental and X-ray diffraction analyses (see Fig. 6)[4], is assumed to be formed by platinum-catalyzed hydration of both triple bonds,[17] yielding initially diketone **31**, followed by intramolecular condensation (with elimination of one water molecule) by which a five membered ring is formed. The final steps would then be the transfer of a phenyl proton to carbon 8c (of the final product), cyclization of **32** *via* platinum-mediated ortho metallation, and reductive elimination. Support in this mechanism was provided by an experiment in which the H_2O in the $(CHCl_2)_2/H_2O$ system was replaced by D_2O. Analysis of the product revealed that the proton at C8c and the two hydrogen atoms at C14 were exchanged by deuterium. Although no traces of carbonylation products could be found in this reaction, the formation of **30** was shown to take place only in the presence of CO.

Diyne **4** is also the only one among compounds **3-8** that adds activated alkynes such as

dimethyl acetylenedicarboxylate. In the presence of **1**, the diyne reacted with two molecules of the diester to give the mono-alkyne **33**. Catalyst **2** promoted the addition of one molecule of the acetylenic ester, yielding dimethyl (*Z*)-2-(9-phenylbenzo[4,5]pentaleno[9,10-*l*]phenanthren-9-yl)-2-butenedioate (**34**). Both **33** and **34** were characterized by IR, mass spectrum, ^1H and ^{13}C NMR, as well as by X-ray diffraction analysis (Fig. 7 and Fig. 8),[4] and are assumed to be formed by the routes proposed for similar processes.[16]

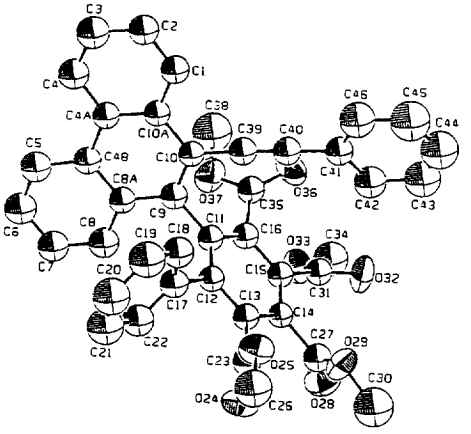


Fig. 7. ORTEP drawing of **33**

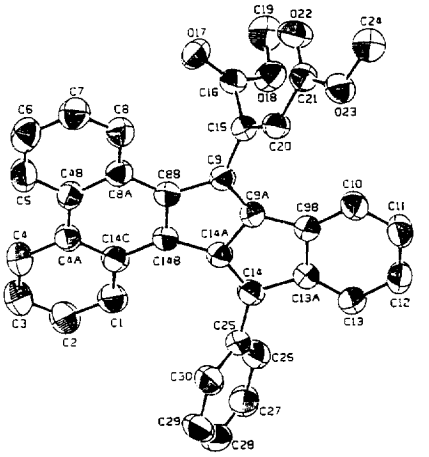


Fig. 8. ORTEP drawing of **34**

EXPERIMENTAL

General Comments. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were taken on a Bruker AMX 400 spectrometer. EIMS were recorded either by direct insertion on a Varian MAT 311 spectrometer or on a Hewlett Packard mass spectrometer model 4989A equipped with an HP gas chromatograph model 5890 series II. All chemicals were reagent grade and were used without further purifications. 2,2'-Bis(phenylethynyl)[1,1'-biphenyl] (**6**)[12,13] and 9-(phenylethynyl)anthracene (**17**)[18] were prepared as previously described.

1,2-Bis(phenylethynyl)acenaphthylene (3). A solution of 3 g (29 mmol) of PhC≡CH in 20 ml of dry THF was added dropwise under Ar to a stirred Grignard solution prepared from 0.7 g (29 mmol) of Mg and 3.16 g (29 mmol) of EtBr in 10 ml of the same solvent. After 30 min at reflux, 2.55 g (14 mmol) of 1,2-acenaphthenedione was added portion wise and the reflux continued for 12 h. The reaction mixture was cooled and decomposed with 10% hydrochloric acid. The crude organic material was dissolved in a minimum amount of MeOH and treated for 4 h with 4 g of $SnCl_2$ in 300 ml of 50% aqueous AcOH at 100°C. The resulting precipitate was washed repeatedly with water and chromatographed on silica gel using a 1:19 mixture of ether-hexane as eluent. Yield of **3** 1.82 g (37%) brick red crystals; mp 154-155°C; 400-MHz ^1H NMR ($CDCl_3$): δ 7.30-7.50 (m, 6), 7.60-7.75 (m,6), 7.80-7.95 (m, 4); 100-MHz ^{13}C NMR ($CDCl_3$): δ 84.74, 100.64, 123.49, 123.69, 126.75, 127.66, 128.24, 128.40, 128.46, 128.61, 128.62, 131.85, 138.58; MS (70 eV, 130°C): *m/z* (rel. intensity) 352 ($M^{\cdot+}$, 100), 252

($C_{20}H_{12}{\cdot}^+$, 37). Anal. Calcd for $C_{28}H_{16}$: C, 95.42; H. 4.58. Found: C, 95.28; H, 4.28.

A suitable crystal for X-ray diffraction analysis was obtained by slow concentration of the eluted solution from the silica gel column. Details of the crystal data, have been deposited at the Cambridge Crystallization Data Centre, 12 Union Road GB - Cambridge, CB2 1EZ (UK).[4] An ORTEP drawing is shown as Fig. 1.

9,10-Bis(phenylethynyl)phenanthrene (4). By the same manner, 3 g (0.14 mmol) of 9,10-phenanthrenequinone was reacted with 3 g (0.29 mmol) of PhC≡CH to give 9,10-bis(phenylethynyl)phenanthrene-9,10-diol [IR (Nujol) 3375, (OH) 2220 cm^{-1} (C≡C); 100-MHz ^{13}C NMR ($CDCl_3$): δ 83.62, 87.16] that was transferred by $SnCl_2$ reduction to 3.9 g (75%) of **4** as colorless needles. Mp 160°C (lit[19] 157°C); 400-MHz ^1H NMR ($CDCl_3$): δ 7.25-7.42 (m, 6), 7.69-7.74 (m, 8), 8.56 (m, 2), 8.68 (m, 2); 100-MHz ^{13}C NMR ($CDCl_3$): δ 87.53, 99.22, 122.71, 123.47, 123.75, 127.39, 127.40, 127.73, 128.49, 128.65, 129.81, 130.70, 131.76.

5,6-Bis(phenylethynyl)chrysene (5) was obtained in 34% yield by the method described above from PhC≡CH and 5,6-chrysenedione. Cream colored needles; mp 187-188°C; 400-MHz ^1H NMR ($CDCl_3$):δ 7.39-7.42 (m, 6), 7.66-7.76 (m, 8), 7.99 (dd, 1, J_o = 7.6 Hz, J_m = 1.3 Hz), 8.04 (d, 1, J = 9 Hz), 8.67 (m, 1), 8.70 (d, 1, J = 9 Hz), 8.74-8.76 (m, 1), 10.43 (d, 1, J = 8.6 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 88.33, 92.22; 99.99; 100.12; 120.92, 121.26, 123.39, 123.57, 123.83, 125.80, 126.69, 127.05, 127.10, 127.17, 127.36, 127.74, 128.20, 128.41, 128.48, 128.51, 128.56, 128.60, 129.11, 129.13, 129.18, 129.82, 131.40, 131.74, 132.48, 133.09; MS (70 eV, 150°C): *m/z* (rel. intensity) 428, ($M{\cdot}^+$, 100), 427 [$M-H)^+$, 32], 426 [$M-2H{\cdot}^+$, 27], 212 ($C_{17}H_8{\cdot}^+$, 21). Anal. Calcd for $C_{34}H_{20}$: C, 95.30; H, 4.70. Found: C, 95.49; H, 4.90.

2,2'-Bis(phenylethynyl)-1,1'-binaphthalene (7). A mixture of 500 mg (0.99 mmol) of 2,2'-diiodo-1,1'-binaphthalene[10], 325 mg (1.96 mmol) of copper(I) phenylacetylide and 5 ml of dry pyridine was heated under Ar for 10 h in an oil bath thermostated at 125°C. The reaction mixture was cooled, digested with excess 10% aqueous HCl and ether. The organic phase was separated, dried and concentrated. The residue was chromatographed on silica gel using a 1:19 mixture of ether-hexane as eluent. The first fraction of 210 mg of unreacted starting material was followed by 136 mg (80% of the reacted diiodo compound) of **7** as colorless crystals. Mp 263-264°C (from a mixture of EtOH and CH_2Cl_2); 400-MHz ^1H NMR ($CDCl_3$): δ 6.72 (d, 2, J = 8.7 Hz), 7.05-7.13 (m, 8), 7.29-7.38 (m, 4), 7.48 (t, 2, J = 8.7 Hz), 7.76 (d, 2, J = 8.6 Hz), 7.95 (t, 4, J = 8.6 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 89.38, 93.47, 121.71, 123.22, 126.45, 126.63, 126.73, 127.79, 127.92, 127.93, 127.98, 128.19, 131.25, 132.66, 132.98, 140.33; MS (70 eV, 130°C): *m/z* (rel. intensity) 454, ($M{\cdot}^+$, 32), 353 ($C_{28}H_{17}^+$, 100), 351 ($C_{28}H_{15}^+$, 32), 350 ($C_{28}H_{14}{\cdot}^+$, 38). Anal. Calcd for $C_{36}H_{22}$: C, 95.12; H, 4.88. Found: C, 95.08; H, 5.03.

3-Phenyl-4-(phenylethynyl)dibenzo[*c,g*]phenanthrene (23). A mixture of 2.0 g (3.95 mmol) of 2,2'-diiodo-1,1'-binaphthalene, 0.85 g (8.3 mmol) of phenylacetylene, 55 mg (7.9×10^{-2} mmol) of $PdCl_2(PPh_3)_2$, 10 mg (2.5×10^{-2} meq) of Cu_2I_2 and 10 mL of Et_3N was stirred under Ar at 60°C for 6 h.

The mixture was digested with excess 10% aqueous HCl. The solid hydrochloride was filtered off and the organic material was extracted (4x) with 50 mL portions of Et_2O. The etheral solution was concentrated and chromatographed on silica gel using a mixture of 98% hexane and 2% ether as eluent. The main fraction of 1.72 g (86%) of a viscous reddish oil proved to be pure **23**. 400-MHz ^1H NMR ($CDCl_3$): δ 6.71 (d, 1, J = 5.6), 7.36-7.64 (m, 15), 7.73 (m, 1), 7.88-8.48 (m, 2), 8.52 (m, 2), 9.15 (d, 1, J = 8.6 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 92.52, 104.02, 121.92, 122.62, 123.09, 124.84, 124.90, 125.45, 125.61, 125.65, 126.64, 127.41, 127.43, 127.61, 128.12, 128.14, 128.33, 128.49, 128.52, 128.66, 128.90, 129.05, 129.53, 131.69, 134.58, 135.04, 136.50, 137.38, 138.23, 138.50, 140.09, 141.03; MS (70 eV, 110°C): *m/z* (rel. intensity) 454, ($M^{\cdot+}$, 18), 354 ($C_{28}H_{18}^{\cdot+}$, 100), 353 ($C_{28}H_{17}^{\cdot+}$, 40), 352 ($C_{28}H_{16}^{\cdot+}$, 31). Anal. Calcd for $C_{36}H_{22}$: C, 95.12; H, 4.88. Found: C, 94.93; H, 5.15.

1-Iodo-2-[(2-phenylethynyl)phenyl]methyl]benzene (25) and 1,1'-Methylenebis-[2-(phenylethynyl)benzene] (8). A mixture of 3.0 g (7.14 mmol) of 1,1'-methylenebis(2-iodobenzene) (**24**)[14], 1.16 g (7.14 mmol) of copper(I) phenylacetylide and 7 ml of dry pyridine was refluxed under N_2 atmosphere for 12 h. The cooled reaction mixture was poured onto excessive 10% aqueous HCl and ether. The etheral solution was dried and concentrated. To the residue of crude monoalkyne was added 1.16 g (7.14 mmol) of PhC≡CCu and 7 ml of pyridine, and the mixture was refluxed for 7 h. After the usual workup and chromatography on silica gel (using hexane with 2-5% ether as eluent) there was obtained in the first fraction 141 mg (5%) of **25** as a colorless oil and 2.076 g (79%) of **8** (colorless oil) in the second fraction.

Compound **25**: 400-MHz ^1H NMR ($CDCl_3$): δ 4.42 (s, 2), 6.97 (m, 1), 7.12 (m, 2), 7.27-7.41 (m, 6), 7.53 (m, 2), 7.65 (m, 1), 7.94 (dd, 1, J_o = 8 Hz, J_m = 1 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 45.22, 87.99, 93.87, 101.40, 123.19, 123.29, 126.36, 127.95, 128.21, 128.25, 128.30, 128.50, 129.15, 130.04, 131.50, 132.14, 139.36, 141.53, 143.10. Anal. Calcd for $C_{21}H_{15}I$: C, 63.98; H, 3.84. Found: C, 64.17; H, 3.90.

Compound **8**: 400-MHz ^1H NMR ($CDCl_3$): δ 4.54 (s, 2), 7.18-7.31 (m, 12), 7.47 (m, 4), 7.57 (m, 2); 100-MHz ^{13}C NMR ($CDCl_3$): δ 38.52, 88.34, 93.59, 123.06, 123.36, 126.14, 128.15, 128.26, 128.52, 129.36, 131.53, 132.16, 142.55; MS (70 eV, 130°C): *m/z* (rel. intensity) 368, ($M^{\cdot+}$, 100), 289 ($C_{23}H_{13}^+$, 19). Anal. Calcd for $C_{29}H_{20}$: C, 94.53; H, 5.47. Found: C, 94.62; H, 5.33.

9,10-Dihydro-9-(1,3-diphenyl-2-propynyliden)anthracene (26). A stirred mixture of 5 g (11.9 mmol) of **24**[14] 2.42 g (23.8 mmol) of PhC≡CH, 166 mg (0.23 mmol) of $PdCl_2(PPh_3)_2$, 20 mg (5×10^{-2} meq) of Cu_2I_2 and 20 ml of Et_3N was heated under N_2 atmosphere at 60°C for 6 h. The reaction mixture was worked up with 10% aqueous HCl and ether, and the organic material was chromatographed on silica gel using hexane with 2-5% ether as eluent. Upon concentration of the eluted material 936 mg (22%) of pure **26** separated. The mother liquor consisted of a concentrated solution of **8** which, however could not be obtained in a pure state free of contamination with **26**. Colorless crystals; mp 133-134°C (from ethyl acetate); 400-MHz ^1H NMR ($CDCl_3$): δ 4.02 (s, 2), 6.83 (m, 2), 7.09 (m, 1) 7.24-7.45 (m, 14), 8.49 (d, 1, J = 7.8 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 37.13, 92.05, 94.89, 119.68, 123.69, 125.07, 125.18, 126.74, 126.80, 126.85, 127.24, 127.35, 127.70, 128.08, 128.13, 128.27, 129.24, 130.22, 131.37, 136.14, 137.10, 137.58, 137.87, 139.82, 140.88, MS (70 eV, 130°C): *m/z* (rel. intensity) 368 ($M^{\cdot+}$, 100), 367 [$(M-1)^+$, 28], 291 ($C_{23}H_{15}^+$, 40), 289 ($C_{23}H_{13}^+$, 33). Anal. Calcd for

$C_{29}H_{20}$: C, 94.53; H, 5.47. Found: C, 94.28; H, 5.14.

A suitable crystal of **26** for X-ray diffraction analysis was obtained by slow recrystallization from EtOAc. Each unit cell proved to consist of two differently oriented pairs of the molecule. Details of the crystal data, have been deposited at the Cambridge Crystallization Data Centre, 12 Union Road GB - Cambridge, CB2 1EZ (UK).[4] An ORTEP drawing is shown as Fig. 3.

1-(Phenylethynyl)phenanthrene (15). To a Grignard reagent prepared from 3.27 g (30 mmol) of C_2H_5Br, 0.72 g (30 mmol) of Mg and 3.06 g (3 mmol) of PhC≡CH in 50 ml of THF was added under N_2, 5.88 g (30 mmol) of 1,2,3,4-tetrahydrophenanthren-1-one. The mixture was refluxed for 12 h, cooled and decomposed with 10% aqueous H_2SO_4. The resutling product was chromatographed on silica gel using hexane as eluent. There was obtained 5.88 g (70%) of 3,4-dihydro-1-(phenylethynyl)phenanthrene as a colorless oil. 400-MHz ^1H NMR ($CDCl_3$): δ 2.39 (m, 2), 2.93 (m, 2), 6.95 (t, 1, J = 5.3 Hz), 7.35-7.59 (m, 8), 7.77 (d, 1, J = 8.2 Hz), 7.85 (dd, 1, J_o = 7.5 Hz, J_m = 1.1 Hz), 9.31 (dd, 1, J_o = 8.3 Hz, J_m = 0.6 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 23.22, 29.38, 90.55, 91.21, 121.03, 124.86, 125.36, 125.46, 126.28, 128.00, 128.19, 128.34, 128.38, 128.55, 129.94, 131.23, 131.67, 133.51, 135.47, 139.43; MS (70 eV, 130°C): *m/z* (rel. intensity) 280, ($M^{\cdot+}$, 100), 279 [$(M-H)^+$, 30], 276 ($C_{22}H_{12}^{\cdot+}$, 21), 265 ($C_{21}H_{13}^+$, 25), 202 ($C_{16}H_{10}^{\cdot+}$, 16). Anal. Calcd for $C_{22}H_{16}$: C, 94.28; H, 5.71. Found: C, 94.43; H, 5.67.

The dehydrogenation of the hydrocarbon was accomplished by heating of 5.04 g (18 mmol) for 3 h with 4.54 g (20 mmol) of DDQ in 150 ml of boiling sodium-dried benzene under N_2 atmosphere. Chromatography on silica gel (using a mixture of 98% hexane and 2% ether as eluent) afforded 2.95 g (59%) of **15**. Mp 109-110°C (from hexane); 400-MHz ^1H NMR ($CDCl_3$): δ 7.23-7.46 (m, 2), 7.61 (m, 1) 7.68-7.86 (m, 7), 7.90-7.97 (m, 2), 7.98 (dd, 1, J_o = 5.9 Hz, J_m = 1.4 Hz), 10.40 (dd, 1, J_o = 9 Hz, J_m = 1.4 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 92.41, 94.88, 119.28, 123.73, 125.54, 125.93, 126.26, 126.61, 126.89, 127.35, 127.86, 128.41, 128.53, 129.72, 129.77, 130.71, 131.34, 133.03, 133.13, 134.83; MS (70 eV, 130°C):*m/z* (rel. intensity) 278 ($M^{\cdot+}$, 48), 277 [$(M-H)^+$, 100],276 [$(M-2H)^{\cdot+}$, 46]. Anal. Calcd for $C_{22}H_{14}$: C, 94.93; H, 5.07. Found: C, 94.66; H, 5.11.

General Procedure for the Transformations of Phenylated Alkynes. Typically, a solution of 39.5 mg (0.15 mmol) of $RhCl_3{\cdot}3H_2O$ (or 50.5 mg of $PtCl_4$) in 2 ml of deionized H_2O was stirred for 15 min with 61 mg (0.15 mmol) of Aliquat 336 in 1.5 ml of $(CHCl_2)_2$. The mixture was heated to reflux and 2 mmol of the appropriate alkyne was added. It was kept at reflux (internal temperature 104°C) under vigorous stirring until the entire starting material was consumed. After cooling, phase separation and workup of the organic layer, the residual material was purified by column chromatography and analyzed.

6b,9a-Dihydro-7,8,9a-triphenyl-9-[2-(phenylethynyl)acenaphthylen-1-yl]pentaleno[1,2-*a*]acenaphthylene (11) was obtained from **3** in the presence of **1** (8 h) in 76% yield as red powder. Mp 291° (dec) (chromatography on silica gel with a 1:9 ether-hexane mixture as eluent; recrystalliztaion from ether-hexane); 400-MHz ^1H NMR (acetone-d_6): δ 5.63 (s, 1), 7.15-7.38 (m, 10), 7.39-7.58 (m, 8), 7.60-7.70 (m, 3), 7.72-7.88 (m, 4), 7.92-8.03 (m, 5), 8.05 (d, 1, J = 7 Hz), 8.46 (d, 1, J = 7 Hz), 8.68 (d, 1, J = 7 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 51.15, 54.17, 84.60, 88.24, 122.84, 123.12,

123.22, 123.59, 125.04, 125.92, 126.01, 126.26, 126.61, 126.80, 126.93, 127.12, 127.31, 127.36, 127.39, 127.57, 127.65, 127.81, 127.96, 128.04, 128.11, 128.15, 128.91, 129.12, 129.64, 131.90, 132.24, 133.09, 133.72, 133.93, 134.15, 134.20, 134.35, 135.11, 135.92, 136.09, 139.74, 140.35, 141.09, 142.36, 142.76, 148.91, 149.73, 157.01. MS (70 eV, 330°C):*m/z* (rel. intensity) 706, ($M^{\cdot+}$, 23), 704 [$(M-2H)^+$, 100). 626 ($C_{50}H_{26}^{\cdot+}$, 23), 623 ($C_{50}H_{23}^+$, 11), 550 ($C_{44}H_{22}^{\cdot+}$, 10), 548 ($C_{44}H_{20}^{\cdot+}$, 10), 274 ($C_{22}H_{10}^{\cdot+}$, 30). Anal. Calcd for $C_{56}H_{34}$: C, 95.15; H, 4.84. Found: C, 95.01; H, 4.46.

9-Phenylbenzo[4,5]pentaleno[9,10-*l*]phenanthrene (12). Reflux of **4** in the $(CHCl_2)_2/H_2O$ system for 12 h in the presence of catalyst **2** afforded [after chromatography on silica gel with hexane (95%) and ether (5%) as eluent] 85% of **12** as green crystals. Mp 222-223°C (from EtOH); 400-MHz ^1H NMR ($CDCl_3$): δ 6.57 (d, 1, J = 7.4), 6.77 (td, 1, J_o = 6.4 Hz, J_m = 1.1 Hz), 6.87 (s, 1) 6.84-6.93 (m, 2) 6.99-7.02 (m, 2), 7.30 (m, 1) 7.48-7.56 (m, 7), 7.87 (m, 1), 8.45 (d, 1, J = 8.4), 8.52 (m, 1); 100-MHz ^{13}C NMR ($CDCl_3$): δ 121.11, 122.55, 123.08, 123.20, 123.22, 123.96, 125.27, 126.15, 126.30, 126.53, 126.73, 127.81, 127.93, 128.01, 128.58, 128.75, 128.92, 129.01, 129.71, 129.95, 131.04, 134.92, 135.55, 145.78, 146.36, 147.39, 149.13, 151.63. MS (70 eV, 140°C): *m/z* (rel. intensity) 378 ($M^{\cdot+}$, 100). Anal. Calcd for $C_{30}H_{18}$: C, 95.21; H, 4.79. Found: C, 95.46; H, 4.95.

4,5-Diphenylbenzo[*a*]cyclopenta[*l,m*]pyrene (14). Reaction of **5** for 7 h in the presence of **2** gave 79% of **14** as intensive red crystals. Mp 164-165°C; 400-MHz ^1H NMR ($CDCl_3$): δ 7.00-7.09 (m, 4), 7.12-7.19 (m, 2), 7.20-7.29 (m, 2), 7.38 (m, 2), 7.75 (s, 1), 7.81-7.88 (m, 2), 7.96 (6, 1, J = 7.7 Hz), 8.29 (dd, 1, J_o =7.3 Hz, J_m = 0.7 Hz), 8.32 (d, 1, J = 9 Hz), 8.41 (d, 1, J = 7.6 Hz), 8.57 (m, 1), 9.04 (d,1, J = 9 Hz), 9.11 (m, 1); 100-MHz ^{13}C NMR ($CDCl_3$): δ 119.96, 122.29, 122.64, 124.29, 124.69, 124.96, 125.34, 125.80, 126.30, 126.36, 126.72, 127.24, 127.37, 127.55, 127.66, 128.06, 128.52, 129.16, 129.32, 130.20, 130.26, 130.30, 131.25, 131.48, 132.20, 135.63, 136.50, 137.33, 142.16, 142.80. MS (70 eV, 150°C): *m/z* (rel. intensity) 428 ($M^{\cdot+}$, 100), 426 [$(M-2H)^{\cdot+}$, 12), 212 ($C_{17}H_8^{\cdot+}$, 15), 175 ($C_{14}H_7^+$), 21). Anal. Calcd for $C_{34}H_{20}$: C, 95.30; H, 4.70. Found: C, 95.02; H, 4.40.

When **14** was recrystallized from a mixture of CH_2Cl_2 and EtOH the compound precipiated as long prisms with one half molecule of CH_2Cl_2 (**14b**). Recrystallization from $CHCl_3$ gave solvent-free **14a**. Both types of crystals were subjected to X-ray diffraction analysis. (The unit cell of **14a** proved to contain two pairs of independently oriented molecules). Details of the crystal data, for both **14a** and **14b** have been deposited at the Cambridge Crystallization Data Centre, 12 Union Road GB - Cambridge, CB2 1EZ (UK).[4] An ORTEP drawing of **14a** is shown as Fig. 2.

Cyclorearrangement of 15. Under the conditions described for the transformation of the diynes, alkyne **15**, was converted into 4-phenylpyrene in 83% yield. Mp 131-132°C (EtOH) (lit[20] 132-133°C); 400-MHz ^1H NMR ($CDCl_3$): δ 7.50 (m, 1), 7.55-7.59 (m, 2), 7.66-7.69 (m, 2), 7.95 (t, 1, J = 7.6 Hz), 8.02 (s, 1), 8.02 (t, 1, J = 7.6 Hz), 8.11 (ABq, 2, $J_{A,B}$ = 9.9 Hz), 8.19-8.22 (m, 4); 100-MHz ^{13}C NMR ($CDCl_3$): δ 123.86, 124.16, 124.82, 124.94, 125.05, 125.15, 125.67, 126.06, 127.22, 127.48, 127.58, 127.76, 128.39, 130.06, 130.39, 130.76, 131.05, 131.30, 139.49, 140.83; MS (70 eV, 130°C): *m/z* 278, ($M^{\cdot+}$, 100).

9,10-Phenanthrenediylbis(phenylmethanone) (20) was obtained in 66% yield when **6** was

refluxed for 24 h in the $(CHCl_2)_2/H_2O$ system in the presence of catalyst **2**. Mp 206°C (lit[21] 206°C); 400-MHz ^1H NMR ($CDCl_3$): δ 7.33-7.37 (m, 4), 7.50-7.54 (m, 4), 7.66 (d, 2, *J* = 8 Hz), 7.72-7.77 (m, 6), 8.81 (d, 2, *J* = 8 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 123.02, 127.24, 127.46, 127.99, 128.44, 128.52, 130.16, 130.53, 133.84, 135.32, 137.65, 198.25; MS (70 eV, 100°C): *m/z* (rel. intensity) 386 ($M\cdot^+$, 100), 309 [$(M-C_6H_5)^+$, 38], 281 ($C_{21}H_{13}O^+$, 40).

3,6-Dihydrocycloocta[1,2-*a*:7,8-*a*']dinaphthalene (21) and **3,6-Dihydrocycloocta-[1,2-*a*:7,8-*a*']dinaphthalene-3,6-dione (22)**. Under N_2 atmosphere the transformation of **7** in the presence of **2** gave (after chromatography on silica gel with hexane as eluent) 52% of **21** as colorless crystals. Mp 152-153°C (from EtOH); 400-MHz ^1H NMR ($CDCl_3$): δ 4.62 (ABq, 4, J_{AB} = 16.3 Hz), 7.10-7.28 (m, 12), 7.49 (t, 2, *J* = 7 Hz), 7.89 (t, 4, *J* = 8 Hz), 8.03 (d, 2, *J* = 9 Hz), 8.36 (d, 2, *J* = 9 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 35.15, 122.76, 125.47, 126.05, 126.08, 126.86, 127.46, 127.47, 128.12, 128.54, 129.74, 130.98, 131.45, 131.74, 133.55, 140.06; MS (70 eV, 130°C): *m/z* (rel. intensity) 458, ($M\cdot^+$, 32), 456 [$(M-2H)\cdot^+$, 21], 454 ($C_{36}H_{22}\cdot^+$, 23), 356 ($C_{28}H_{20}\cdot^+$, 100), 355 ($C_{28}H_{19}^+$, 47), 354 ($C_{28}H_{18}\cdot^+$, 37), 353 ($C_{28}H_{17}^+$, 39), 352 ($C_{28}H_{16}\cdot^+$, 30). Anal. Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.25; H, 5.52.

When the reaction was conducted under ambient atmosphere, and the product was purified by chromatography on silica gel (with hexane containing 8% of ether as eluent) **22** was obtained in 61% yield. Mp 172-173°C (from EtOH); IR (Nujol): 1680 cm^{-1} (C=O); 400-MHz ^1H NMR ($CDCl_3$): δ 7.28-7.37 (m, 6), 7.52-7.59 (m, 4), 7.65 (d, 2, *J* = 8.6 Hz), 7.76 (d, 4, *J* = 8.6 Hz), 7.85 (d, 2, *J* = 9 Hz), 7.92 (d, 2, *J* = 8.6 Hz), 8.48 (d, 2, *J* = 9 Hz); 100-MHz ^{13}C NMR (CDCl3): δ 123.17, 125.24, 127.12, 127.85, 128.03, 128.52, 128.76, 128.84, 129.42, 130.07, 130.52, 132.86, 134.07, 135.42, 138.21, 195.67; MS (70 eV, 170°C): *m/z* (rel. intensity) 486, ($M\cdot^+$, 30), 350 ($C_{27}H_{10}O\cdot^+$, 17], 107 ($C_8H_8\cdot^+$, 100). Anal. Calcd for $C_{36}H_{22}O_2$: C, 88.87; H, 4.56. Found: C, 88.58; H, 4.27.

5-Phenyl-10*H*-dibenz[3,4:6,7]cyclohepta[1,2-*b*]naphthalene (27) was obtained in 82% yield from **8** and the rhodium catalyst **1** (reflux 10 h). Mp 211-212°C (from EtOH); 400-MHz ^1H NMR ($CDCl_3$): δ 3.60 (d, 1, *J* = 12.6 Hz), 3.74 (d, 1, *J* = 12.6 Hz), 6.67 (m, 1); 6.76-6.81 (m, 2), 6.98 (td, 1, J_o = 7.6 Hz, J_m = 1 Hz), 7.13 (td, 1, J_o = 7.6 Hz, J_m = 1 Hz), 7.21 (d, 1, *J* = 7.5 Hz), 7.25-7.37 (m, 4), 7.40-7.56 (m, 3), 7.67 (d, 1, *J* = 7.6 Hz), 7.75 (t, 2, *J* = 8.2 Hz), 7.99 (d, 1, *J* = 8.1 Hz), 8.11 (s, 1); 100-MHz ^{13}C NMR ($CDCl_3$): δ 40.35, 124.70, 125.49, 126.14, 126.15, 126.27, 126.59, 126.67, 126.80, 126.92, 127.14, 127.71, 128.16, 128.40, 128.74, 129.32, 131.22, 131.72, 132.59, 132.67, 133.35, 135.73, 135.93, 137.89, 138.53, 138.87, 139.99, 143.59, 144.01; MS (70 eV, 120°C): *m/z* 368, ($M\cdot^+$, 100). Anal. Calcd for $C_{29}H_{20}$: C, 94.53; H, 5.47. Found: C, 94.54; H, 5.23.

A crystal for X-ray diffraction analysis was obtained by slow recrystallization from CH_2Cl_2-EtOH. Details of the crystal data, have been deposited at the Cambridge Crystallization Data Centre, 12 Union Road GB - Cambridge, CB2 1EZ (UK).[4] An ORTEP drawing is shown as Fig. 4.

1,2,3,8-Tetrahydro-1,3-Diphenyl-8-dibenz[*e,h*]azulenone (28). A mixture of 368 mg (1 mmol) of **8**, 26 mg (0.1 mmol) of $RhCl_3{\cdot}3H_2O$, 40 mg (0.1 mmol) of Aliquat 336, 2 ml of $(CHCl_2)_2$ and 1 ml of H_2O was placed in a glass-lined mini autoclave. The reaction vessel was charged with 750 psi CO, and the mixture stirred at 120°C for 12 h. After cooling, the organic layer was separated, dried,

concentrated and the residue chromatographed on silica gel, using a mixture of 90% hexane and 10% ether as eluent. Yield 250 mg (63%) of **28** as cream colored crystals. Mp 143-144°C (from EtOH): IR ($CHCl_3$): 1670 cm^{-1} (C=O); 400-MHz ^1H NMR (CDCl3): δ 4.00 (ABq, 2, J_{AB} = 12.9 Hz), 5.24 (s, 2), 7.12-7.33 (m, 16), 7.44 (dd, 2, J_o = 8.4 Hz, J_m = 1.3 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 42.09, 61.06, 126.30, 126.66, 127.14, 127.68, 128.42, 128.67, 128.98, 132.47, 136.63, 139.31, 139.46, 211.05; MS (70 eV, 140°C): *m/z* (rel. intensity) 398, ($M^{\cdot+}$, 100), 370 ($C_{29}H_{22}^{\cdot+}$, 57), 355 ($C_{28}H_{19}^{+}$, 9), 293 ($C_{23}H_{16}^{\cdot+}$, 31), 292 ($C_{23}H_{15}^{+}$, 29), 291 ($C_{23}H_{14}^{\cdot+}$, 29), 279 ($C_{22}H_{15}^{+}$,61). Anal. Calcd for $C_{30}H_{22}O$: C, 90.42; H, 5.56. Found: C, 90.70; H, 5.30.

3-Phenyl-4-[10-(phenylethynyl)phenanthren-9-yl]-2-(5*H*)furanone (29). By a similar procedure **4** was carbonylated in the presence of catalyst **1**. Chromatogrpahy of the crude product on silica gel (using a mixture of 35% ether and 65% hexane as eluent) afforeded pure **29**. Yield 54% of colorless crystals; mp 152°C (from EtOH/CH_2Cl_2); 400-MHz ^1H NMR ($CDCl_3$): δ 5.58 (ABq, 2, J_{AB} = 16.8 Hz), 7.11 (m, 1), 7.25-7.48 (m, 9), 7.53 (m, 1), 7.64-7.91 (m, 4), 8.58 (dd, 1, J_o = 8.1 Hz, J_m = 1.5 Hz), 8.78 (d, 2, J = 7.9 Hz); 100-MHz ^{13}C NMR ($CDCl_3$): δ 70.80, 86.14, 99.01, 120.99, 122.74, 122.95, 123.19, 124.76, 125.14, 125.93, 127.06, 127.29, 127.48, 126.60, 127.81, 127.82, 128.38, 128.62, 129.05, 130.35, 130.40, 130.45, 130.65, 131.07, 131.54, 131.55, 158.46, 172.99; MS (70 eV, 140°C): *m/z* (rel. intensity) 436, ($M^{\cdot+}$, 100), 379 ($C_{29}H_{15}O^{+}$, 14). Anal. Calcd for $C_{32}H_{20}O_2$: C, 88.05; H, 4.62. Found: C, 87.81; H, 4.29.

A crystal for X-ray diffraction analysis was obtained by recrystallization from EtOH and CH_2Cl_2. Details of the crystal data, have been deposited at the Cambridge Crystallization Data Centre, 12 Union Road GB - Cambridge, CB2 1EZ (UK).[4] An ORTEP drawing is shown as Fig. 5.

8c,14-Dihydro-13b-phenylbenzo[4,5]pentaleno[10,9-*l*]phenanthren-9-one (30). When in the foregoing procedure catalyst **1** was replaced by catalyst **2**, and the crude product was chromatographed on silica gel (using a 1:4 mixture of ether-hexane as eluent) the resulting compound proved to be **30**. Yield 72%; colorless crystals; mp 183°C (from CH_2Cl_2-EtOH); IR ($CHCl_3$): 1707 cm^{-1} (C=O); 400-MHz ^1H NMR (CDCl3): δ 4.11 (dd, 1, J_1 = 2.3 Hz, J_2 = 14.8 Hz), 4.90 (s, 1), 7.24-7.33 (m, 5), 7.42 (m, 1), 7.59-7.76 (m, 7), 7.82 (m, 1), 8.68-8.74 (m, 3); 100-MHz ^{13}C NMR ($CDCl_3$): δ 47.41, 57.98, 71.00, 122.81, 123.24, 124.53, 124.78, 126.30, 126.36, 126.55, 126.58, 126.73, 126.76, 127.00, 127.24, 128.35, 128.76, 129.25, 129.50, 130.90, 131.00, 132.54, 135.50, 135.74, 136.45, 146.69, 159.65, 203.52; MS (70 eV, 120°C) *m/z* 396, ($M^{\cdot+}$, 100). Anal. Calcd for $C_{30}H_{20}O$: C, 90.88; H, 5.08. Found: C, 90.78; H, 4.97.

A crystal for X-ray diffraction analysis was obtained by slow recrystallization from a mixture of CH_2Cl_2 and EtOH. Details of the crystal data, have been deposited at the Cambridge Crystallization Data Centre, 12 Union Road GB - Cambridge, CB2 1EZ (UK).[4] An ORTEP drawing is shown as Fig. 6.

[2-(Phenylethynyl)phenanthren-1-yl]-2-phenyl-3,4,5,6-benzenetetracarboxylic Acid Tetramethyl Ester (33). A mixture of 378 mg (1 mmol) of **4**, 568 mg (4 mmol) of MeOCOC≡CCOOMe, 26 mg (0.1 mmol) of $RhCl_3.3H_2O$, 40 mg (0.1 mmol) of Aliquat 336, 2 mL of $(CHCl_2)_2$ and 2 ml of

deionized H_2O was stirred at 104°C. After 15 h the mixture was cooled, the phases were separated and the organic material was chromatographed on silica gel, using a 1:1 mixture of hexane and ether as eluent to give 444 mg (67%) of **33** as light yellow crystals. Mp 127-128°C (from CH_2Cl_2-EtOH); IR ($CHCl_3$): 1715 cm^{-1} (C=O); 400-MHz ^1H NMR ($CDCl_3$): δ 3.21 (s, 3), 3.44 (s, 3), 3.90 (s, 3), 3.95 (s, 3), 6.77-6.87 (m, 4), 7.21 (m, 1), 7.29-7.39 (m, 5), 7.42-7.51 (m, 2), 7.55 (m, 1), 7.62-7.68 (m, 2), 8.47 (m, 1), 8.52 (d, 1, J = 8.2 Hz), 8.58 (m, 1); 100-MHz ^{13}C NMR ($CDCl_3$): δ 52.27, 52.40, 53.10, 53.22, 86.79, 100.01, 120.66, 122.41, 122.60, 122.96, 126.74, 126.88, 127.05, 127.17, 127.23, 127.29, 127.48, 127.68, 127.91, 128.42, 128.55, 128.79, 129.37, 129.84, 129.94, 130.47, 130.57, 131.41, 131.71, 135.75, 136.30, 137.83, 141.31, 143.79, 166.25, 166.37, 166.60, 167.31; MS (70 eV, 185°C): *m/z* (rel. intensity) 662 ($M^{\cdot+}$, 100), 603 ($C_{40}H_{27}O_6^+$, 11), 426 ($C_{34}H_{18}^{\cdot+}$, 7). Anal. Calcd for $C_{42}H_{30}O_8$: C, 76.12; H, 4.56. Found: C, 76.39; H, 4.80.

A crystal for X-ray diffraction analysis was obtained by slow recrystallization from EtOAc. Details of the crystal data, have been deposited at the Cambridge Crystallization Data Centre, 12 Union Road GB - Cambridge, CB2 1EZ (UK).[4] An ORTEP drawing is shown as Fig. 7.

(*Z*)-2-(9-Phenylbenzo[4,5]pentaleno[9,10-*l*]phenanthren-9-yl)-2-butenedioic Acid Dimethyl Ester (34). When the rhodium catalyst in the foregoing procedure was replaced by **2** and the molar ratio of **4**:MeOCOC≡COOMe was 1:3, 53% of yellow **34** was obtained after 24 h. Mp 136-137°C (from CH_2Cl_2-EtOH); IR ($CHCl_3$): 1722 cm^{-1} (C=O); 400-MHz ^1H NMR ($CDCl_3$): δ 3.79 (s, 3), 3.91 (s, 3), 6.52 (s, 1), 6.57 (d, 1, J = 7.1 Hz), 6.77 (td, 1, J_o = 7.1 Hz, J_m = 0.9 Hz), 6.81-6.90 (m, 2), 7.02 (m, 1), 7.14 (d, 1, J = 7.1 Hz), 7.31 (m, 1), 7.44-7.54 (m, 7), 8.14 (m, 1), 8.44 (d, 1, J = 8.3 Hz), 8.52 (m, 1); 100-MHz ^{13}C NMR ($CDCl_3$): δ 54.27, 54.76, 122.01, 122.32, 122.47, 122.92, 123.45, 123.98, 124.38, 127.54, 127.83, 128.01, 128.32, 128.50, 128.84, 128.97, 129.07, 131.57, 131.96, 132.14, 132.67, 133.25, 133.97, 134.35, 134.42, 135.76, 136.95, 145.86, 146.37, 147.39, 149.17, 151.63, 165.09, 167.42. Anal. Calcd for $C_{36}H_{24}O_4$: C, 83.31; H, 4.65. Found: C, 82.97; H, 4.54.

A crystal for X-ray diffraction analysis was obtained by slow recrystallization from a mixture of EtOH-CH_2Cl_2. Details of the crystal data, have been deposited at the Cambridge Crystallization Data Centre, 12 Union Road GB - Cambridge, CB2 1EZ (UK).[4] An ORTEP drawing is shown as Fig. 8.

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