Fused Supracyclopentadienyl Ligand Precursors. Synthesis, Structure, and Some Reactions of 1,3-Diphenylcyclopenta[/]phenanthrene-2-one, 1,2,3-Triphenylcyclopenta[/]phenanthrene-2-ol, 1-Chloro-1,2,3-triphenylcyclopenta[/]phenanthrene, 1-Bromo-1,2,3-triphenylcyclopenta[/]phenanthrene, and 1,2,3-Triphenyl-1*H*-cyclopenta[/]phenanthrene

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The photochemical reaction of 1,3-diphenylcyclopenta[*I*]phenanthrene-2-one **5** (phencyclone) with oxygen in acetone leads to the formation of 1,2,3-trihydro-1,2,3-triphenylcyclo-penta[*I*]phenanthrene **7** (9,10-dibenzoylphenanthrene) along with a trace of the lactone 1,4-diphenylcyclo-3-pyran[*I*]phenanthrene-2-one **8**. An independent synthesis of **8** was achieved by the reaction of **5** with FeCl₃ in CHCl₃. The treatment of **5** with phenyllithium yields 1,2,3-triphenylcyclopenta[*I*]phenanthrene-2-ol **9**-OH in good yield. Subsequent reaction of **9**-OH with SOCl₂ or SOBr₂ in pyridine leads to the formation of the halo-analogues 1-chloro-1,2,3-triphenylcyclopenta[*I*]phenanthrene **9**-Cl and 1-bromo-1,2,3-triphenylcyclopenta[*I*]phenanthrene **9**-Br, respectively. Treatment of **9**-OH with HBr in acetic acid affords the rearranged product 1,1,3-triphenylcyclopenta[*I*]phenanthrene-2-one **10** with a trace of **9**-Br. Treatment of **9**-Cl or **9**-Br with zinc in acetic acid affords 1,2,3-tri-phenyl-1*H*-cyclopenta[*I*]phenanthrene **9**-H. 9,10-Phenanthrenediylbis(phenyl)methanone **7** is formed in good yield upon treatment of **9**-OH with HI in acetic acid followed by heating with H₂PO₄. Compounds **7**, **8**, **9**-Cl, **9**-Br, and **10** have been structurally characterized using X-ray crystallography.

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Introduction

Pentaphenylcyclopentadiene was first reported in 1925,^[1] and the first metal complex of the pentaphenylcyclopentadienyl anion was reported in 1964.^[2] The ligand's radical chemistry received considerable early attention^[3–16] and there has been a steady increase in research into metal complexes of the $C_5Ph_5^-$ ligand since the mid-1970s. Almost 60% of all research in this area has been published in the last decade. Substituent variation of the ligand's phenyl rings and the investigation of related perbenzylated and other perary-lated cyclopentadienyl ligand systems have been extensions of this work.^[17–20]

Substituent variation in cyclopentadienyl chemistry has been extended to the study of cyclopentadienyl-related ligands with extended π -systems, such as indenyl and fluorenyl ligands. The first η^5 -indenyl complex, diindenyliron, was reported in 1953,^[21] and the first η^5 -fluorenyl complex, difluorenylzirconium dichloride, was reported in 1965.^[22] However, in comparison with cyclopentadienyl ligands, the ligand chemistry of the indenyl and fluorenyl anions has received relatively little attention. There is some spectroscopic and structural evidence that the binding of a metal to the η^5 -indenyl and η^5 -fluorenyl ligands is weaker than that to a cyclopentadienyl ligand. However, the former compounds appear to have enhanced reactivities, for example, several metallotropic rearrangements of η^5 -indenyl and η^5 -fluorenyl complexes have been reported.

Bulky substituents on the cyclopentadienyl ring often confer greater kinetic stability on metal complexes than is observed for analogues with less sterically demanding ligands. Thus, for example, whereas many cyclopentadienyl and pentamethylcyclopentadienyl complexes are air- and watersensitive, their decabenzyl and decaphenyl analogues can be stored in air, sometimes indefinitely.

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Fig. 1. Structure of 5.



Fig. 2. Structure of 6.

The ligand chemistry of condensed ring analogues of pentaphenylcyclopentadienyl complexes and the effects of the altered electronic and steric demands of the ligands have been examined. The most common route to pentaphenylcyclopentadienyl complexes is either by the conversion of tetracyclone 1 to its hydroxy 2 and halogenated derivatives, which can then be oxidatively added to a low-valent transition metal, or converted to the pentaphenylcyclopentadienyl anion, either directly or by conversion to pentaphenylcyclopentadiene (Scheme 1).

Here, synthetic and structural studies on 1,3-diphenylcyclopenta[*I*]phenanthrene-2-one **5** (phencyclone; Fig. 1), and its derivatives are reported. Early work on the organic and organometallic chemistry of the tetracyclones has been comprehensively reviewed.^[23]

Results and Discussion

The synthesis of the fused ring polycyclic derivative, 1,3-diphenylcyclopenta[*I*]phenanthrene-2-one **5**, was first reported in 1935.^[24] However, difficulties* in preparing a pure product were subsequently noted.^[25–27] Recently, an alternative synthesis of substantially pure phencyclone has been published.^[26] The method involves the base-catalyzed condensation of phenanthrenequinone with 1,3-diphenylacetone under conditions where the temperature was carefully controlled (Scheme 2).

Yields of greater than 80% can be consistently obtained by the procedure described herein. Similar yields have been claimed previously, but the purity of the compound in many of these reports was not well established, as phencyclone was reported to have various colours and to have melting points in the range 245–258°C.^[25–28] In the present study, the crystalline phencyclone is a black compound, with a melting point of 238–240°C after vacuum-drying. The main impurity, found when the reaction was carried out at temperatures above ~70°C or if the basic catalyst



Scheme 1. Preparation of 4.



Scheme 2. Preparation of 5.



Scheme 3. Preparation of 7 and 8.

* A referee has commented (and we concur) that difficulties with the original synthesis can be caused by experimental technique — the phenanthrenequinone purity and/or delays between synthesis steps.





Fig. 3. $ORTEP^{[44]}$ plot (25% probability) of 9,10-dibenzoylphenanthrene (7) viewed (a) along and (b) perpendicular to the plane of the phenanthrene backbone. Atomic numbering is illustrated in Fig. 3(b).

 Table 1.
 Selected bond distances [Å] involving non-hydrogen atoms for 7

 $\frac{\text{Atoms}}{O(1)-C(1)}\\O(2)-C(4)\\C(1)-C(2)\\C(1)-C(5)\\C(2)-C(3)$

C(2)-C(11)

Table 2.	Selected bond	angles [°]	involving	non-hydrogen	atoms
		for '	7		

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	Distance	Atoms	Distance	Atoms	Angle	Atoms	Angle
	1.217(3)	C(3)–C(4)	1.511(3)	O(1)-C(1)-C(2)	119.7(2)	C(2)–C(3)–C(4)	119.7(2)
	1.219(3)	C(3)-C(22)	1.440(3)	O(1)-C(1)-C(5)	121.5(2)	C(2)-C(3)-C(22)	121.4(2)
	1.507(3)	C(4) - C(23)	1.487(3)	C(2)-C(1)-C(5)	118.8(2)	C(4)-C(3)-C(22)	118.9(2)
	1.490(3)	C(11)-C(16)	1.413(3)	C(1)-C(2)-C(3)	119.5(2)	O(2)-C(4)-C(3)	120.5(2)
	1.357(3)	C(16)-C(17)	1.450(3)	C(1)-C(2)-C(11)	119.7(2)	O(2)-C(4)-C(23)	122.3(2)
	1.441(3)	C(17)–C(22)	1.414(3)	C(3)–C(2)–C(11)	120.6(2)	C(3)-C(4)-C(23)	117.2(2)

was added too rapidly,[†] has been assigned in the past as 1,3-dihydro-1,3-diphenylcyclopenta[*I*]phenanthrene-2-one **6** (dihydrophencyclone; Fig. 2).^[24] The dihydrophencyclone isomers **6** are readily detected by ¹H NMR spectroscopy due to the presence of a characteristic resonance at $\delta_{\rm H}$ 5.2 ppm.^[29]

Phencyclone **5** undergoes photooxidation to give 9,10phenanthrenediylbis(phenyl)methanone **7** (9,10-dibenzoylphenanthrene).^[30] The synthesis of **7** has also been achieved by heating phencyclone at reflux in chlorobenzene or xylene in the presence of oxygen, with the mechanism believed to be a stepwise 1,4-addition of ${}^{3}O_{2}$ across the 1,3-diene system of the cyclopentadiene, followed by chelotropic extrusion of CO to form the diketone.^[31] The diketone was formed in the present work as large colourless crystals from the reaction in wet acetone of phencyclone **5** and atmospheric oxygen in direct sunlight. Also formed in this reaction was the lactone 1,4-diphenylcyclo-3-pyran[*I*]phenanthrene-2-one **8** (Scheme 3). The lactone was formed in trace amounts during the photooxidation reaction. When the photooxidation reaction was performed over a longer time, the lactone was not observed, and this may be the result of photochemical decomposition of the lactone. The products were characterized by mass spectrometry, vibrational and ¹H and ¹³C{¹H} NMR spectroscopies, and X-ray crystallography.

The lactone **8** was made independently in near quantitative yield by treating phencyclone **5** with FeCl₃ in chloroform in the presence of water. No mechanistic studies have been undertaken to determine the course of the reaction.

Crystal Structures of 7 and 8

9,10-Dibenzoylphenanthrene 7 crystallized from acetone as discrete molecules. The structure of the compound viewed along, and perpendicular to, the phenanthrene plane is illustrated in Fig. 3. Metric data are collected in Tables 1 and 2. Other crystallographic data have been deposited.

The crystal structure of 7 illustrates the non-planar nature of the phenanthrene moiety, similar to the crystal structures of

[†] Impurities (including a hydrate) have been noted by several authors.^[25–28] We find that reaction in refluxing propanol initially gives the *cis* isomer of 1,3dihydro-1,3-diphenylcyclopenta[*I*]phenanthrene-2-one **6** (dihydrophencyclone), which isomerizes to the *trans* isomer. Sonntag et al.^[28] classify the reaction as an 'isomerization-cyclization' rather than a reduction.



Fig. 4. ORTEP^[44] plot (25% probability) of 1,4-diphenylcyclo-3-pyran[*I*]phenanthrene-2-one 8.

 Table 3.
 Selected bond distances [Å] involving non-hydrogen atoms for 8

Atoms	Distance	Atoms	Distance
O(1A)-C(1A)	1.342(5)	C(1B)–C(5)	1.486(10)
O(2A)–C(1A)	1.215(4)	C(2) - C(3)	1.372(2)
O(1A)–C(2)	1.518(4)	C(3) - C(4)	1.456(2)
O(1B) - C(1B)	1.340(11)	C(4) - C(5)	1.359(2)
O(2B)-C(1B)	1.388(10)	C(2) - C(6)	1.485(2)
O(1B)–C(2)	1.272(5)	C(5)-C(24)	1.474(2)
C(1A)–C(5)	1.353(3)		

the room temperature phase of the parent phenanthrene.^[32–35] The distortion from planarity in phenanthrene has been attributed to the close proximity of the hydrogen atoms at C(15) and C(18). To relieve this steric pressure, the two outer rings of phenanthrene are mutually inclined at an angle of 2.4°. Compound 7 exhibits a greater deviation from planarity, with the two outer rings mutually inclined at 7.3°. The two free phenyl rings, C(5-10) and C(23-28) are disposed on opposite sides of, and at angles of 74.50 and 88.64° to, the phenanthrene backbone. The previously reported structure of $7^{[31]}$ shows no distortion of the phenanthrene moiety and the trans phenyl rings reside at dihedral angles of 79.1(2) and 80.8(2)°, respectively, relative to the phenanthrene ring. All bond distances and angles are otherwise unexceptional, suggesting that the twisting in the phenanthrene backbone does not overly disrupt the π-system.

The crystal structure of 1,4-diphenylcyclo-3-pyran[*I*]phenanthrene-2-one **8** (Fig. 4) shows disorder at the lactone moiety with the carbonyl group showing occupancy of 65 and 35% over the two sites. The structure shows the phenanthrene to be planar, with the lactone puckered out-of-plane. The bond lengths of the phenanthrene system show distinct alternating single and double bonds indicating that it is not aromatic (Tables 3 and 4).

Synthesis of 9-OH

The synthetic routes to the carbinol, 1,2,3-triphenylcyclopenta[*l*]phenanthrene-2-ol **9**-OH (Fig. 5) were not well

Table 4. Selected bond angles [°] involving non-hydrogen atoms for 8

Atoms	Angle	Atoms	Angle
C(1A)-O(1A)-C(5)	121.3(3)	O(1B)–C(2)–C(6)	107.7(3)
O(2A)-C(1A)-O(1A)	119.6(3)	C(3)-C(2)-C(6)	128.21(15)
O(2A)-C(1A)-C(2)	121.3(3)	C(3)-C(2)-C(1A)	117.53(19)
O(1A)-C(1A)-C(2)	118.5(3)	C(6)-C(2)-C(1A)	114.2(2)
C(2)–O(1B)–C(1B)	117.3(6)	C(2)-C(3)-C(4)	118.60(14)
O(1B)-C(1B)-O(2B)	117.2(8)	C(3) - C(4) - C(5)	118.79(14)
O(1B)-C(1B)-C(5)	124.8(7)	C(4)-C(5)-C(24)	128.08(14)
O(2B)-C(1B)-C(5)	116.5(7)	C(24)-C(5)-C(1B)	118.2(4)
O(1B)-C(2)-C(3)	124.1(3)	C(4)-C(5)-C(1B)	113.3(4)



Fig. 5. Structure of 9-OH.

described before this work. Experimental details for the synthesis of this compound were limited,^[36,37] and its characterization was incomplete.

The only published method for the synthesis of **9**-OH is by the room temperature reaction of a suspension of phencyclone **5** in ether with excess phenyllithium, followed by hydrolysis.^[37] The product was reported to be isolated in 42% yield by this method, and was characterized by vibrational, electronic, and ¹H NMR spectroscopy. However, in this study, the main product from these reactions was dihydrophencyclone **6**, identified by vibrational spectroscopy, melting point, and ¹H NMR spectra.^[29] The NMR data for **6** show the presence of both *cis* and *trans* isomers.

The carbinol **9**-OH, prepared according to Scheme 4, is highly soluble in a range of solvents and indefinitely airstable in the dark. Exposure to sunlight for extended periods resulted in the formation of pale yellow products that were not



Scheme 4. Preparation of 9-OH and 6.



Scheme 5. Preparation of 10 and 9-Br.



Scheme 6. Preparation of 9-Cl and 9-Br.

characterized further but may be the **1**-OH isomers, produced by the known photochemical rearrangement.^[37]

1-Halo-1,2,3-triphenylcyclopenta[\]phenanthrene Derivatives

The useful synthetic precursor, 1-bromo-1,2,3,4,5-pentaphenylcyclopentadiene **3**, can be prepared in high yield by the reaction of 1,2,3,4,5-pentaphenylcyclopentadiene-1-ol **2** with hydrobromic acid in glacial acetic acid (Scheme 1).^[38] However, the major product from the corresponding synthesis using 1,2,3-triphenylcyclopenta[*I*]phenanthrene-2-ol **9**-OH was the 1,2-phenyl-shifted compound 1,1,3-triphenylcyclopenta[*I*]phenanthrene-2-one **10** in 70% yield (Scheme 5). The desired product 1-bromo-1,2,3-triphenylcyclopenta[*I*]phenanthrene **9**-Br was obtained in low yield (18%) as a yellow crystalline solid. Both compounds were characterized by vibrational and ¹H and ¹³C{¹H} NMR spectroscopies, mass spectrometry, melting point, elemental analysis, and X-ray crystallography.

A higher yielding synthesis of **9**-Br involved the reaction of 1,2,3-triphenylcyclopenta[*I*]phenanthrene-2-ol **9**-OH with thionyl bromide (Scheme 6) in an identical fashion to the synthesis of the analogous chloro compound **9**-Cl, described below. Using this method, the yield of **9**-Br was 74%.

Diffraction-quality crystals of **10**, prepared as illustrated in Scheme 5, were obtained from chloroform. The structure of the compound is illustrated in Fig. 6. Metric data are collected in Tables 5 and 6. Crystals of **9**-Br suitable for X-ray diffraction were obtained from chloroform. The structure of the compound viewed along, and perpendicular to, the cyclopentadienyl plane is illustrated in Fig. 7. Metric data are collected in Tables 7 and 8.

The preparation of 1-chloro-1,2,3-triphenylcyclopenta[I]-phenanthrene **9**-Cl has been briefly reported.^[36] The compound is prepared in good yield (72%) by the reaction of 1,2,3-triphenylcyclopenta[I]phenanthrene-2-ol **9**-OH with thionyl chloride in dry pyridine (Scheme 6).

Yields are mostly independent of temperature over the range $0-50^{\circ}$ C, but the rigorous exclusion of water is essential. The pale yellow crystals were characterized by vibrational and ¹H and ¹³C{¹H} NMR spectroscopies, mass spectrometry, melting point, elemental analysis, and X-ray diffraction. Crystals suitable for X-ray diffraction were obtained from dichloromethane/hexane. The structure of **9**-Cl is illustrated in Fig. 8. Metric data are collected in Tables 9 and 10.

The crystal structures of **9**-Cl and **9**-Br are very similar. Both compounds crystallize in the same space group. The C–C bond lengths around the cyclopentadienyl moiety are identical. However, the C(4)–C(24) bond length in **9**-Br is slightly shorter than the analogous bond length in **9**-Cl, at 1.463(7) and 1.484(6) Å, respectively.

Synthesis of 9-H

Two synthetic routes to 1,2,3-triphenyl-1*H*-cyclopenta[*I*]phenanthrene **9**-H have been briefly reported.^[36] The first approach involves the reaction of 1,2,3,4,5-pentaphenylcyclopentadiene-1-ol **2** with sulfuric acid and the second proceeds by reduction of 1-chloro-1,2,3-triphenylcyclopenta[*I*]phenanthrene **9**-Cl by the action of zinc in acetic acid. In this study, reaction of 1,2,3,4,5-pentaphenylcyclopentadiene-1-ol **2** with concentrated sulfuric acid for two minutes afforded 1,2,3-triphenyl-1*H*-cyclopenta[*I*]phenanthrene **9**-H in 36% yield as one component of a mixture of about six products (Scheme 7).



Fig. 6. ORTEP^[44] plot (25% probability) of 1,1,3-triphenylcyclopenta[*l*]phenanthrene-2-one 10.

Table 5. Bond distances [Å] involving non-hydrogen atoms for 10

Atoms	Distance	Atoms	Distance
O(1)–C(2)	1.2052(14)	C(1)–C(12)	1.5463(17)
C(1) - C(2)	1.5600(17)	C(3)-C(18)	1.5280(17)
C(1) - C(5)	1.5300(17)	C(4)–C(24)	1.4373(16)
C(2) - C(3)	1.5310(17)	C(24)–C(29)	1.4159(16)
C(3) - C(4)	1.5107(16)	C(29)–C(30)	1.4608(17)
C(4) - C(5)	1.3616(16)	C(30)-C(35)	1.4212(17)
C(1) - C(6)	1.5362(17)	C(5)-C(35)	1.4462(16)

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Atoms	Angle	Atoms	Angle
C(1)-C(2)-C(3)	109.58(10)	C(4)-C(3)-C(18)	115.74(10)
C(1)-C(2)-O(1)	125.54(11)	C(4)-C(3)-C(2)	101.64(9)
C(5)-C(1)-C(6)	114.06(10)	C(3)-C(4)-C(24)	125.16(11)
C(5)-C(1)-C(12)	112.78(10)	C(3)-C(4)-C(5)	112.61(11)
C(6)-C(1)-C(2)	100.16(9)	C(4)-C(5)-C(1)	112.40(10)
C(6)-C(1)-C(12)	113.82(10)	C(1)-C(5)-C(35)	126.94(10)
C(12)-C(1)-C(2)	106.89(9)	C(4)-C(5)-C(35)	120.65(11)
O(1)-C(2)-C(3)	124.87(11)	C(5)-C(4)-C(24)	122.23(11)

The reduction of 1-chloro-1,2,3-triphenylcyclopenta[*l*]-phenanthrene **9**-Cl by zinc in acetic acid produced 1,2,3-triphenyl-1*H*-cyclopenta[*l*]phenanthrene **9**-H as a white crystalline solid in almost 80% yield (Scheme 8).

1,2,3,4,5-Pentaphenylcyclopentadiene **4** is readily prepared by reduction of 1,2,3,4,5-pentaphenylcyclopentadiene-1-ol **2** or 1-bromo-1,2,3,4,5-pentaphenylcyclopentadiene **3** by zinc in acetic acid, or better, by the reaction of 1,2,3,4,5pentaphenylcyclopentadiene-1-ol **2** with hypophosphorus and hydriodic acids in acetic acid. However, hypophosphorus/ hydriodic acid reduction of 1,2,3-triphenylcyclopenta[*I*]phenanthrene-2-ol **9**-OH produces 1,2,3-trihydro-1,2,3triphenylcyclopenta[*I*]phenanthrene **11** as a white crystalline solid in good yield (Scheme 9). The product was characterized by vibrational and ¹H and ¹³C{¹H} NMR spectroscopies, mass spectrometry, melting point, and elemental analysis.

Salts of the pentaphenylcyclopentadienyl and penta-p-tolylcyclopentadienyl anions are remarkably stable, decomposing only slowly in air.^[19,39] Accordingly, the deprotonation of 1,2,3-triphenyl-1*H*-cyclopenta[*I*]phenanthrene **9**-H with butyllithium was attempted at room temperature. The crude product was isolated as a beige powder in good yield which decomposed rapidly on exposure to air.

Conclusions

A series of derivatives of 1,3-diphenylcyclopenta[/]phenanthrene-2-one **5** has been prepared and characterized by elemental analyses, ¹H and ¹³C{¹H} NMR spectroscopy, and, in some cases, single-crystal X-ray diffraction. The ambiguities in some earlier syntheses have been resolved, and the pure compounds are available in good to high yields. Several of these compounds are potential ligand precursors for extremely bulky substituted cyclopentadienyl complexes. Thus, for example, deprotonation of 1,2,3-triphenyl-1*H*cyclopenta[*I*]phenanthrene proceeds analogously to that of pentaphenylcyclopentadiene. The chemistry of the metal complexes will be reported separately.

Experimental

All reactions were carried out under an atmosphere of high purity argon (CIG) or nitrogen (CIG) unless otherwise stated and manipulations were performed using conventional Schlenk techniques.

Reagents

All solvents were distilled under an atmosphere of nitrogen before use. Benzene (Merck), toluene (BDH), tetrahydrofuran (Merck or



Fig. 7. *ORTEP*^[44] plot (25% probability) of 1-bromo-1,2,3-triphenylcyclopenta[*l*]phenanthrene **9**-Br viewed (a) along and (b) perpendicular to the plane of the phenanthrene backbone. Atomic numbering is illustrated in Fig. 7(b).

Table 7.	Selected bond distances [Å] involving non-hydrogen atoms for 9-Br				
Atoms	Distance	Atoms	Distance		

Br(1)-C(1)	1.985(5)	C(4)–C(24)	1.463(7)
C(1)-C(2)	1.514(7)	C(5)-C(30)	1.465(7)
C(1)–C(5)	1.536(7)	C(2) - C(12)	1.435(7)
C(1)–C(6)	1.542(7)	C(3)–C(23)	1.435(8)
C(2)–C(3)	1.364(7)	C(12) - C(17)	1.415(8)
C(3)–C(4)	1.498(7)	C(17)–C(18)	1.426(8)
C(4)–C(5)	1.333(7)	C(18)–C(23)	1.428(8)



Scheme 7. Preparation of 9-H.



Scheme 8. Preparation of 9-H.

Rhone–Poulenc), hexane (Merck), and diethyl ether (Merck) were distilled from sodium benzophenone ketyl. Dichloromethane (Rhone– Poulenc) was pre-dried over calcium chloride and distilled from calcium hydride. Chlorobenzene (Merck) was distilled from calcium hydride. Pyridine (Merck) was pre-dried over potassium hydroxide and distilled from barium oxide. Methanol (Rhone–Poulenc), ethanol (CSR),

 Table 8.
 Selected bond angles [°] involving non-hydrogen atoms for

 9-Br

7-01					
Atoms	Angle	Atoms	Angle		
Br(1)-C(1)-C(2)	110.2(4)	C(2)-C(3)-C(4)	108.1(5)		
Br(1)-C(1)-C(5)	106.7(3)	C(2)-C(3)-C(23)	121.0(5)		
Br(1)-C(1)-C(6)	111.5(4)	C(4)-C(3)-C(23)	130.8(5)		
C(2)-C(1)-C(5)	102.3(4)	C(3)-C(4)-C(5)	109.9(5)		
C(2)-C(1)-C(6)	114.2(5)	C(3)-C(4)-C(24)	126.3(5)		
C(5)-C(1)-C(6)	111.4(5)	C(5)-C(4)-C(24)	123.8(5)		
C(1)-C(2)-C(3)	109.8(5)	C(1)-C(5)-C(4)	109.5(5)		
C(1)-C(2)-C(12)	127.1(5)	C(1)-C(5)-C(30)	122.4(5)		
C(3)-C(2)-C(12)	123.0(5)	C(4)-C(5)-C(30)	127.9(5)		



Scheme 9. Preparation of 11.

propanol (Merck), chloroform (Rhone–Poulenc), acetone (Merck), and glacial acetic acid (BDH) were used as received.

Phenanthrenequinone, 1,3-diphenylacteone, tetraphenylcyclopentadienone, hypophosphorus acid, thionyl chloride, thionyl bromide, hydrobromic acid, acetic anhydride, *n*-butyllithium (1.6 M in hexanes), and tetramethylsilane (all Aldrich), were used as received. Bromobenzene, hydroiodic acid and zinc dust (all Merck) were used as received. Flash silica (240–400 mesh) was obtained from Merck. 1,2,3,4,5-Pentaphenylcyclopentadiene-1-ol was prepared following the procedure described by Field et al.^[38] The crude product, prepared in 93% yield, was analyzed by vibrational spectroscopy and melting point and found to be pure enough for use without further purification.

Instrumentation

¹H NMR (300.13 MHz) and ¹³C{¹H} NMR (75.48 MHz) spectra were recorded on a Bruker DRX300 spectrometer. Spectra were referenced internally to either residual solvent resonances or TMS. Diffuse



Fig. 8. *ORTEP*^[44] plot (25% probability) of 1-chloro-1,2,3-triphenylcyclopenta[*I*]phenanthrene **9**-Cl viewed perpendicular to the plane of the phenanthrene backbone. The atomic numbering is illustrated in Fig. 8(b).

 Table 9.
 Selected bond distances [Å] involving non-hydrogen atoms for 9-Cl

Atoms	Distance	Atoms	Distance
$\overline{\text{Cl}(1)-\text{C}(1)}$	1.824(4)	C(4)–C(5)	1.342(5)
C(1)-C(2)	1.515(6)	C(5)-C(30)	1.471(6)
C(1)–C(5)	1.520(6)	C(2) - C(12)	1.418(6)
C(1)–C(6)	1.535(6)	C(3)-C(23)	1.435(6)
C(2)-C(3)	1.370(6)	C(12)-C(17)	1.413(6)
C(3)–C(4)	1.497(6)	C(17)–C(18)	1.451(6)
C(4)–C(24)	1.484(6)		

Table 10. Selected bond angles [°] involving non-hydrogen atoms for 9-Cl

Atoms	Angle	Atoms	Angle
C(2)-C(1)-C(5)	102.8(3)	C(2)–C(3)–C(4)	108.2(4)
C(2)-C(1)-C(6)	113.3(3)	C(23)-C(3)-C(4)	130.8(4)
C(5)-C(1)-C(6)	111.1(3)	C(5)-C(4)-C(24)	124.9(4)
C(2)-C(1)-Cl(1)	110.8(3)	C(5)-C(4)-C(3)	109.4(4)
C(5)-C(1)-Cl(1)	107.7(3)	C(24)-C(4)-C(3)	125.7(4)
C(6)-C(1)-Cl(1)	110.8(3)	C(4)-C(5)-C(30)	127.0(4)
C(3)-C(2)-C(12)	122.5(4)	C(4)-C(5)-C(1)	109.8(3)
C(2)-C(3)-C(23)	121.0(4)	C(30)-C(5)-C(1)	123.0(3)

reflectance infrared spectra were recorded using a Digilab FTS-40 Fourier-transform spectrometer. Samples were analyzed as homogeneous suspensions in a potassium bromide matrix. The resolution used was 4 cm⁻¹ and, typically, 16 scans were averaged per spectrum. Mass spectra were obtained either using a Kratos MS 902 double-focusing spectrometer with a direct insertion probe and an electron-impact ion source at 200°C (variations as required), 70 eV ionization voltage, and 8 keV acceleration voltage, or by using a matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer with 18 keV acceleration voltage and 21 keV reflection voltage. In the latter case, samples were introduced on a direct insertion probe and data were handled by OPUS software on a DEC VAX station 4000. Elemental analyses were performed by the Australian Microanalytical Service and melting points were recorded on a Reichert hot platform in air and are uncorrected.

Syntheses

1,3-Diphenylcyclopenta[1]phenanthrene-2-one 5 (Phencyclone)

Methanolic KOH (3.0 g, 53 mmol in 30 mL) was added dropwise to a suspension of 1,3-diphenylacetone (20.0 g, 95 mmol) and 9,10-phenanthrenequinone (19.8 g, 95 mmol) in boiling methanol (800 mL). The orange suspension slowly darkened and a black crystalline solid

began to precipitate. The suspension was stirred for a further 15 min at reflux, cooled in an ice bath for 20 min, and the solid separated by filtration. The black crystalline solid was washed with methanol until the washings were colourless, dried under high vacuum (33.4 g, 92%) mp 238–240°C (lit. 245–255°C,^[25] 250–258°C,^[26] 248–250°C^[27]) and used without further purification. ν_{max} (KBr)/cm⁻¹ 3084w, 3056w, 3027w, 1700vs, 1594m, 1494m, 1479m, 1449s, 1344s, 1303s, 1108m, 971w, 805s, 767s, 754vs, 729vs, 719s, 698vs, 637s. $\delta_{\rm H}$ (CDC1₃) 7.80 (d, 2H, ³*J*_{HH} 7.7, 2 × phenanthrene H), 7.53 (d, 2H, ³*J*_{HH} 8, 7.40 (m, 10H, ArH), 7.27 (dd, 2H, ³*J*_{HH} 8, ³*J*_{HH} 8, 2 × phenanthrene H), 6.94 (dd, 2H, ³*J*_{HH} 8, ³*J*_{HH} 8, 2 × phenanthrene H). $\delta_{\rm C}$ (CDCl₃) 148.6 (C=O), 134.5, 133.9, 132.6, 131.7, 130.3, 129.4, 128.9, 128.8, 128.6, 128.5, 126.8, 124.8. *m*/z 382 (100%, M⁺), 354 (90), 352 (37), 327 (18), 175 (28), 168 (13).

9,10-Dibenzoylphenanthrene 7

Phencyclone **5** (0.50 g, 1.31 mmol) was dissolved in acetone and left standing in an open vessel with access to direct sunlight for 48 h until most of the solvent had evaporated. The crystalline material (0.36 g, 71%) mp 202–204°C (lit. $206^{\circ}C$,^[40] $208–209^{\circ}C$,^[41,42] $206.5-207.5^{\circ}C$ [^{43]}) was isolated and recrystallized from acetone. (Found:

C 87.0, H 4.8. $C_{28}H_{18}O_2$ requires C 87.0, H 4.7%). Characterization showed the compound to be 9,10-dibenzoylphenanthrene 7. ν_{max} (KBr)/cm⁻¹ 3087w, 1667vs, 1586m, 1451m, 1304m, 1237vs, 1163m, 1011w, 829m, 764s, 712s, 689s, 613m. δ_{H} (CDCl₃) 8.78 (d, 2H, $^{3}J_{HH}$ 8.4, 2 × phenanthrene H), 7.79–7.64 (m, 8H), 7.50 (ddd, 4H, $^{3}J_{HH}$ 8, $^{3}J_{HH}$ 8, J_{HH} 1), 7.32 (dd, 4H, $^{3}J_{HH}$ 8, $^{3}J_{HH}$ 8). δ_{C} (CDCl₃) 198.3 (C=O), 137.8, 134.2, 134.0, 130.6, 130.3, 128.6, 128.1, 127.6, 127.3, 123.2. *m/z* 386 (35%, M⁺), 309 (32), 281 (32), 252 (45), 105 (100), 77 (88), 51 (11).

1,4-Diphenylcyclo-3-pyran[1]phenanthrene-2-one 8

To a solution of phencyclone 5 (100 mg, 0.26 mmol) in undried chloroform (100 mL) was added FeCl₃ (127 mg, 0.78 mmol). An immediate colour change occurred. The reaction mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum. The residue was purified by flash chromatography on silica, with dichloromethane as eluent. 1,4-Diphenylcyclo-3-pyran[l]phenanthrene-2-one 8 was obtained as an orange crystalline solid upon recrystallization from hot hexane (99 mg, 95%) mp 291-292°C (dec.). (Found: C 85.1, H 4.7. C₂₉H₁₈O₂·3/11CH₂Cl₂ requires C 84.7, H 4.5%). v_{max} (KBr)/cm⁻¹ 3067s, 3026m, 2925m, 2852m, 1706vs, 1520s, 1483m, 1446m, 1348m, 1174s, 1070s, 984s, 933m, 908m, 862w, 797s, 790s, 761s, 752m, 729vs, 705s, 695s. δ_H (CDCl₃) 8.08 (dd, 2H, ³J_{HH} 11, ³J_{HH} 8, 2 × phenanthrene H), 7.79 (m, 2H), 7.52-7.32 (m, 12H), 7.01 (dddd, 2H, J_{HH} 13, ³J_{HH} 7, ³J_{HH} 7, ³J_{HH} 1). δ_H (CDCl₃) 162.6 (C=O), 154.6, 145.8, 136.9, 135.0, 134.2, 131.4, 131.3, 131.1, 131.0, 130.6, 129.4, 129.2, 129.0, 128.6, 128.4, 128.0, 127.3, 126.9, 124.0, 124.0, 120.7, 113.1. m/z 398 (8%, M⁺), 370 (M⁺ – CO, 100), 341 (M⁺ – 2CO, 15), $265 (M^+ - 2CO - Ph, 20).$

Crystals suitable for X-ray diffraction were grown by the slow evaporation of a toluene solution containing $\mathbf{8}$.

1,2,3-Triphenylcyclopenta[1]phenanthrene-2-ol 9-OH

Method 1: Phenylmagnesium bromide, produced from magnesium turnings (0.24 g, 10 mmol) and bromobenzene (1.2 mL, 10 mmol) in ether (40 mL), was added slowly to a suspension of phencyclone **5** (2.5 g, 6.5 mmol) in benzene (150 mL). The resultant translucent red solution was stirred at room temperature for 16 h. Upon exposure to air the reaction mixture turned dark green. The organic phase was washed with H_2SO_4 (1 M, 2 × 50 mL) and water (3 × 100 mL), dried over anhydrous calcium chloride, filtered, and the volume reduced under vacuum until solid began to precipitate. Heptane was added until precipitation was complete. The solid was separated by filtration and washed with heptane until the washings were colourless.

The air-dried pale green solid was dissolved in benzene and loaded onto a flash silica column. Using benzene as eluent three fractions were collected. The first fraction was colourless. The solvent was removed and the residue was recrystallized from dichloromethane/heptane, to give a mixture of the *cis* and *trans* isomers of 1,3-dihydro-1,3-diphenylcyclopenta[/]phenanthrene-2-one $6^{[24]}$ (dihydrophencyclone) as a pale yellow solid which was identified as comprising the known isomers of **6** on the basis of melting point and infrared, mass, and ¹H NMR spectra. The second fraction was dark green and spectroscopically identified as the starting material phencyclone **5**. The third fraction was an intense yellow, which, after removal of the solvent under vacuum and recrystallization from dichloromethane/heptane, afforded 1,2,3-triphenylcyclopenta[/]phenanthrene-2-ol **9**-OH as a fluorescent yellow compound (0.30 g, 10%) mp 221–222°C (lit. 222–223°C, ^[36] 275°C^[37]).

Method 2: A phenyllithium solution (produced from finely chopped lithium wire (1.55 g, 0.223 mol) and bromobenzene (11.4 mL, 0.112 mol) in ether (70 mL) was added slowly to a stirred suspension of phencyclone **5** (4.83 g, 13 mmol) in benzene (300 mL). The resultant translucent red solution was stirred for 1 h. A methanolic KOH solution (3.0 g, 53 mmol in 60 mL) was added dropwise. A bright yellow solid precipitated and the suspension was stirred for 16 h. The volume of the solvent was reduced by approximately half under vacuum. The bright yellow solid was separated by filtration. The crude product was recrystallized from dichloromethane/hexane and

1,2,3-triphenylcyclopenta[*I*]phenanthrene-2-ol **9**-OH was obtained as a fluorescent yellow solid after drying under high vacuum (4.2 g, 72%) mp 222°C (lit. 222–223°C,^[36] 275°C^[37]). ν_{max} (KBr)/cm⁻¹ 3559vs, 3062w, 3028w, 1600w, 1494s, 1449s, 1166w, 1062w, 971w, 918m, 756vs, 730vs, 720s, 703vs. $\delta_{\rm H}$ (CDCl₃) 8.01 (d, 2H, ³*J*_{HH} 8, phenanthrene H), 7.60–7.10 (m, 17H, ArH and phenanthrene H), 6.94 (ddd, 2H, ³*J*_{HH} 8, ³*J*_{HH} 7, ⁴*J*_{HH} 1, phenanthrene H), 6.56 (br s, 2H, phenanthrene H), 2.12 (s, 1H, OH). $\delta_{\rm C}$ (CDCl₃) 147.2, 137.6, 136.4, 134.6, 133.4, 129.8, 129.3, 129.2, 129.0, 128.8, 128.7, 128.2, 127.8, 127.7, 127.6, 124.0. *m/z* 460 (100%, M⁺), 444 (12), 432 (12), 383 (15), 355 (25), 276 (15), 105 (8), 77 (10).

1-Bromo-1,2,3-triphenylcyclopenta[1]phenanthrene 9-Br

Method 1: A suspension of 1,2,3-triphenylcyclopenta[l]phenanthrene-2-ol 9-OH (1.0 g, 2.17 mmol) in glacial acetic acid (75 mL) was heated to 60°C resulting in partial dissolution of the vellow carbinol. A solution of hydrobromic acid (48%, 1.2 mL, 10.8 mmol) in glacial acetic acid (4 mL) was added dropwise to the suspension, resulting in the slow formation of a homogenous orange solution. After stirring at 70°C for 2 h, a flocculent white solid precipitated. Stirring was continued at room temperature for 16 h. Water (30 mL) was added. Dichloromethane (100 mL) was added and the resulting biphasic solution was separated. The organic layer was washed with water $(2 \times 50 \text{ mL})$, 10% Na₂CO₃ (50 mL), dried over Na₂SO₄, and the solvent removed under vacuum to afford a yellow powder. Recrystallization from dichloromethane/hexane afforded the product 1,1,3-triphenylcyclopenta[1]phenanthrene-2-one 10 (695 mg, 70%) mp 271–273°C (dec.) as a white microcrystalline powder. (Found: C 90.3, H 5.5. C₃₅H₂₄O·0.1CH₂Cl₂ requires C 89.9, H 5.2%). v_{max} (KBr)/cm⁻¹ 3084w, 3059m, 3024w, 1748vs (CO), 1600w, 1494s, 1449m, 1034m, 782m, 757vs, 731s, 700s. δ_H (CDCl₃) 8.79 (d, 2H, ³J_{HH} 8), 8.70–7.55 (m, 4H), 7.50–7.40 (m, 3H), 7.35–7.17 (m, 9H), 7.13–7.07 (m, 5H), 5.32 (s, 1H, CH). δ_C (CDCl₃) 212.9 (C=O), 142.0, 139.7, 139.0, 137.6, 135.3, 132.1, 131.7, 130.3, 129.8, 129.4, 129.0, 128.7, 128.6, 128.5, 128.0, 127.7, 127.6, 127.1, 127.0, 127.0, 70.1, 59.0. *m*/*z* 460 (45%, M⁺), 432 (77, M – CO), 354 (M – C₆H₅ – CO), 276 (12), 254 (100), 176 (24).

X-Ray diffraction quality crystals were grown by the slow infusion of hexane into a dichloromethane solution of the compound.

The yellow filtrate from the recrystallization was purified by flash chromatography on silica (40% dichloromethane/60% hexane) to afford 1-bromo-1,2,3-triphenylcyclopenta[*I*]phenanthrene **9**-Br (0.1 g, 18%) mp 238–240°C as a yellow powder. (Found: C 79.3, H 4.3. C₃₅H₂₃Br·0.1CH₂Cl₂ requires C 79.2, H 4.4%). ν_{max} (KBr)/cm⁻¹ 3065m, 3042m, 1568w, 1493s, 1445s, 1034w, 831m, 758vs, 727s, 702vs. $\delta_{\rm H}$ (CDCl₃) 8.80 (dd, 2H, ${}^3J_{\rm HH}$ 7, ${}^4J_{\rm HH}$ 1), 7.81 (dd, 1H, ${}^3J_{\rm HH}$ 8, ${}^4J_{\rm HH}$ 1), 7.66–7.59 (m, 3H), 7.52–7.05 (m, 15H), 6.80 (m, 2H). $\delta_{\rm C}$ (CDCl₃) 152.8, 142.6, 140.1, 137.1, 136.7, 133.8, 132.3, 131.3, 130.9, 130.0, 129.8, 128.5, 128.4, 128.3, 128.2, 127.8, 127.7, 127.4, 127.2, 126.8, 126.7, 126.5, 126.4, 126.2, 126.1, 125.9, 123.6, 123.3, 72.2. *m/z* 524 (3%, M⁺), 443 (100), 363 (98), 340 (30), 301 (18), 289 (27), 165 (30), 206 (28), 182 (45), 80 (23).

Method 2: Thionyl bromide (0.08 mL, 1.09 mmol) was added to a suspension of 1,2,3-triphenylcyclopenta[*I*]phenanthrene-2-ol (**9**-OH) (0.50 g, 1.09 mmol) in pyridine (20 mL). The resulting deep red solution was stirred at room temperature overnight. The solvent was removed under vacuum. The resulting residue was dissolved in dichloromethane (50 mL) and washed with water (2×50 mL), 10% Na₂CO₃ solution (50 mL), and dried over MgSO₄. The solvent was removed under vacuum to afford an orange powder. The residue was purified by flash chromatography on silica (eluting with 40% dichloromethane/60% hexane) to afford 1-bromo-1,2,3-triphenyl-cyclopenta[*I*]phenanthrene (**9**-Br, 0.42 g, 74%).

1-Chloro-1,2,3-triphenylcyclopenta[1]phenanthrene 9-Cl

1,2,3-Triphenylcyclopenta[*I*]phenanthrene-2-ol **9**-OH (0.17 g, 0.37 mmol) was dissolved in pyridine (10 mL) to give a bright yellow/ orange solution. Thionyl chloride (0.03 mL, 0.40 mmol) was added and gradually the solution colour faded. The solution was stirred at

	7	8	9- Br	9- Cl	10
Crystal habit	Colourless prism	Orange prism	Yellow needle	Yellow crystal	Colourless plate
Diffractometer	Rigaku	Brüker	Rigaku	Enraf-Nonius	Brüker
Temperature [K]	294 ± 2	150 ± 2	294 ± 2	294 ± 2	150 ± 2
Empirical formula	C ₂₈ H ₁₈ O ₂	C29H18O2	C35H23Br	C35H23Cl	C35H24O
Formula weight	386.45	398.43	523.47	479.02	460.54
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_1/n$ (#14)	P1 (#2)	P2 ₁ 2 ₁ 2 ₁ (#19)	P2 ₁ 2 ₁ 2 ₁ (#19)	$P2_1/c$ (#14)
a [Å]	10.038(2)	10.4184(19)	14.473(2)	8.743(1)	16.241(5)
b[Å]	15.211(2)	10.5625(19)	19.323(2)	14.459(1)	9.821(3)
c[Å]	13.417(1)	10.624(2)	8.732(3)	19.084(2)	14.979(5)
α[°]	90.00	64.396(3)	90.00	90.00	90.00
β[°]	92.324(9)	72.359(3)	90.00	90.00	101.479(5)
γ [°]	90.00	74.150(3)	90.00	90.00	90.00
V[Å ³]	2047.0(4)	990.9(3)	2442.0(7)	2412.5(3)	2341.5(13)
$D_{\text{calc}} [\text{g cm}^{-3}]$	1.254	1.335	1.424	1.32	1.306
Z	4	2	4	4	4
$\mu [\mathrm{mm}^{-1}]$	0.614 (Cu _K _a)	0.083 (Mo _{Kα})	2.452 ($Cu_{K\alpha}$)	$0.182 (Mo_{K\alpha})$	0.077 (Mo _{Kα})
No. reflections	3382	41660	2106	1644	22525
$N_{\rm ind} (R_{\rm merge})$	3181 (0.02704)	4577 (0.0343)	1762	1327	5547 (0.0502)
Obs. reflections $(I > X\sigma(I))$	2617 (3.0)	3059 (2.0)	1762 (2.5)	1341 (2.0)	3860 (2.0)
$R(F_{\rm o})$	0.0437	0.0490	0.0331	0.029	0.040
R _w	0.0480 (F _o)	$0.1143 \ (F_0^2, \text{all})$	$0.0320 (F_0)$	0.030 (<i>F</i> ₀)	$0.1143 \ (F_{\rm o}^2, {\rm all})$

Table 11. X-ray crystallographic data for compounds 7, 8, 9-Br, 9-Cl, and 10

room temperature for 16h, yielding a pale yellow solid and a pale yellow/green supernatant. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (50 mL) and washed with water $(2 \times 50 \text{ mL})$, 10% Na₂CO₃ solution (50 mL), and dried over MgSO₄. The solvent was reduced in volume under vacuum and hexane was added resulting in the precipitation of the desired product. Filtration and washing with hexane afforded 1-chloro-1,2,3triphenylcyclopenta[/]phenanthrene 9-Cl as a pale yellow powder, which was dried under high vacuum (0.41 g, 77%) mp 257–259°C (lit. 253–254°C^[36]). $\delta_{\rm H}$ (CDCl₃) 8.78 (dd, 2H, ³J_{HH} 8, J_{HH} 11), 7.80 (dd, 1H, ${}^{3}J_{\rm HH}$ 8, ${}^{4}J_{\rm HH}$ 1), 7.61 (m, 3H), 7.48–7.01 (m, 15H), 6.78 (m, 2H). $\delta_{\rm C}$ (CDCl₃) 152.5, 142.4, 141.0, 137.5, 136.7, 133.5, 132.3, 130.9, 130.8, 130.1, 129.8, 128.6, 128.4, 128.1, 127.8, 127.7, 127.4, 127.3, 126.9, 126.8, 126.7, 126.7, 126.3, 126.2, 125.9, 125.7, 123.6, 123.3, 78.5. v_{max} (KBr)/cm⁻¹ 3087w, 3062w, 1594w, 1488s, 1444s, 1069w, 1031w, 875s, 754vs, 740m, 725s, 701vs, 560s. m/z 478 [79%, M - H], 444 (M - Cl, 100), 365 (M - Cl - C₆H₅, 56), 352 (11), 289 (M - Cl - 2C₆H₅, 21), 265 (24), 212 (7), 182 (42).

1,2,3-Triphenyl-1H-cyclopenta[1]phenanthrene 9-H

Method 1: A suspension of 1-chloro-1,2,3-triphenylcyclopenta[1]phenanthrene 9-Cl (0.20 g, 0.42 mmol) and zinc dust (0.11 g, 1.7 mmol) was stirred in acetic acid (20 mL) at 100°C for 2 h. The resulting suspension was cooled to room temperature. Water (50 mL) was added and the resulting solution was extracted with dichloromethane $(3 \times 50 \text{ mL})$. The organic phase was washed with water $(2 \times 50 \text{ mL})$, 10% Na₂CO₃ solution (1×50 mL), and dried over MgSO₄. The solvent was removed under vacuum. The residue was recrystallized from dichloromethane/hexane to afford 1,2,3-triphenyl-1Hcyclopenta[l]phenanthrene 9-H as an off-white microcrystalline powder (0.14 g, 76%) mp 224–225°C (lit. 220–221°C^[36]). (Found: C 94.8, H 5.6. Calc. for C_{35}H_{24} C 94.6, H 5.4%). ν_{max} (KBr)/cm $^{-1}$ 3057m, 3025m, 2926w, 1600w, 1493s, 1443s, 1073w, 1029m, 836w, 755vs, 724s, 714s, 696vs, 559m. $\delta_{\rm H}$ (CDCl₃) 8.71 (dd, 2H, $J_{\rm HH}$ 19, ${}^{3}J_{\rm HH}$ 8), 7.85 (d, 1H, ³J_{HH} 8), 7.65–7.49 (m, 5H), 7.46–7.23 (m, 5H), 7.17–7.00 (m, 10H), 5.45 (s, 1H, CpH). δ_C (CDCl₃) 150.2, 142.9, 141.3, 139.6, 138.5, 135.7, 131.5, 130.9, 129.7, 129.6, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 127.7, 127.6, 126.8, 126.8, 126.6, 126.0, 125.8, 125.6, 125.3, 124.6, 123.5, 123.4, 58.6. *m/z* 444 (100%, M⁺), 365 (11), 289 (16), 265 (6), 183 (8), 165 (4).

Method 2: 1,2,3,4,5-Pentaphenylcyclopentadiene-1-ol 2 (2.0 g, 4.3 mmol) was added to rapidly stirring concentrated sulfuric acid (50 mL), immediately producing an intense purple solution. After 2 min of stirring, the acidic solution was quenched with ice-water yielding a light brown suspension. The soluble organic products were extracted into dichloromethane (100 mL) and the orange/brown extract was washed with saturated sodium hydrogen carbonate solution (2 \times 100 mL), water $(2 \times 100 \text{ mL})$ and saturated sodium chloride solution (100 mL). Analysis of the reaction mixture by TLC with a hexane/dichloromethane (2/1)solvent system showed the presence of at least six different species. The solvent was removed under vacuum. The brown residue was redissolved in hexane and dichloromethane (2/1) and loaded onto a flash silica column. The separation on the column was not as well defined as that on the TLC plate and only two distinct bands were collected. The first fraction, when analyzed by TLC, showed the presence of three compounds. The solvent was removed under vacuum. Fractional crystallization from a dichloromethane/hexane mixture yielded two white compounds, the more insoluble of which was found to be 1,2,3,4,5pentaphenylcyclopentadiene 2 (~ 0.5 g, 26%). The other compound was the desired product, 1,2,3-triphenyl-1H-cyclopenta[l]phenanthrene 9-H (0.7 g, 36%).

The second fraction did not contain any of the desired product and was not analyzed further.

1,2,3-Trihydro-1,2,3-triphenylcyclopenta[]phenanthrene 11

Hydriodic acid (57%, 0.29 mL, 2.16 mmol) was added dropwise to a suspension of 1,2,3-triphenylcyclopenta[*I*]phenanthrene-2-ol **9**-OH (0.25 g, 0.54 mmol) in glacial acetic acid (20 mL) at 50°C. After 10 min, hypophosphorous acid (50%, 0.29 mL, 2.70 mmol) was added dropwise and the solution was refluxed for a further 2 h. The orange colour faded over this period and the colourless solution was cooled and stirred at room temperature for 15 h. The solvent was removed under vacuum. The residue was dissolved in dichloromethane (50 mL), and the organic phase was washed with water (2×50 mL), 10% Na₂CO₃ solution (50 mL), and dried over MgSO₄. The solvent was removed under vacuum to afford the product as an-off white powder. Recrystallization from dichloromethane/methanol yielded the product as an off-white crystalline powder **11** (169 mg, 70%) mp 196–198°C. (Found: C 90.06, H 5.16. $C_{35}H_{26}$.0.3CH₂Cl₂ requires C 89.80, H 5.69%). $\delta_{\rm H}$ (CDCl₃) 8.73 (dd, 2H, $J_{\rm HH}$ 20, ${}^{3}J_{\rm HH}$ 8), 7.88 (d, 1H, $J_{\rm HH}$ 8), 7.69–7.25 (m, 12H), 7.18–7.06 (m, 10H), 5.48 (s, 1H). $\delta_{\rm C}$ (CDCl₃) 150.2, 142.9, 141.3, 139.6, 138.5, 135.7, 131.5, 130.9, 129.7, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 127.7, 127.6, 126.8, 126.6, 126.0, 125.8, 125.6, 125.3, 124.6, 123.4, 1451s, 1156w, 1036w, 780m, 758vs, 727vs, 702vs, 534m. *m/z* 446 (100%, M⁺), 368 (33), 355 (30), 289 (14), 279 (22), 165 (6), 145 (18), 91 (8), 58 (11), 43 (42).

Single Crystal X-ray Diffraction

Crystals were mounted on thin fibres and all measurements were made using either (a) a Rigaku AFC7R 12 kW rotating anode diffractometer and Cu_{Kα} radiation (λ 1.5418 Å), (b) an Enraf-Nonius CAD4 and Mo_{Kα} radiation (λ 0.7107 Å), or (c) a Bruker SMART 1000 CCD and Mo_{Kα} radiation. Radiation was graphite monochromated. Crystallographic data are summarized in Table 11, and *ORTEP*^[44] depictions are provided in Figs 3, 4, 6, 7, and 8. A Gaussian^[45] correction was applied to data from **8**, empirical absorption corrections based on the azimuthal scans of several reflections^[46] were applied to **7** and **9**-Br, and no correction was applied for **9**-Cl and **10**.

The structures were solved by direct methods (*SHELXS*-86^[47] for **7**, **9**-Br, **9**-Cl, *SHELX*-97^[48] for **10**, and *SIR97*^[49] for **8**), and expanded using Fourier techniques using either *DIRDIF*^[50] (**7**, **9**-Br, **9**-Cl) or *SHELX*^[48] (**8** and **10**) and the *teXsan*,^[51] *WinGX*^[52] and *Xtal*^[53] graphical interfaces. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated positions. The ester unit in **8** is disordered about two orientations, with complementary occupancies refined and then fixed at 0.65 and 0.35. The partial-occupancy non-hydrogen sites were modelled with isotropic displacement parameters. The absolute structure of **9**-Cl was determined but not reliably established with the Flack^[54–57] parameter refining to 0.0(1) for the unique dataset; the absolute structure of **9**-Br was established with the Flack parameter refining to 0.00(3).

Crystal structure data have been deposited at the Cambridge Crystallographic Data Centre with deposition numbers CCDC 263929–263933.

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