287. Transition-Metal Complexes with Bidentate Ligands Spanning *trans*-Positions

I. The Synthesis of 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene, a Ligand Promoting the Formation of Square Planar Complexes

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(22. IX. 76)

Summary. The bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**) was synthesized from 2,11-dimethyl-benzo[*c*]phenanthrene (**3**) *via* the corresponding bromomethyl derivative **9**. **3** was obtained from the cyclization with boron trifluoride etherate of 1,1-di-(*p*-methylphenethyl)-epoxyethane (**7**), which was prepared from 1,5-di(*p*-tolyl)-pentan-3-one (**6**).

1. Introduction. – Square planar complexes are very numerous and they have been the object of intensive study [1]. The interest in these complexes is mainly due to one basic feature: they are coordinatively unsaturated and, therefore, undergo with relative ease a variety of reactions which are of theoretical and practical interest.

The academic chemist's interest in square planar complexes has been mainly directed towards gaining an understanding of the factors determining their formation [2], the study of their optical spectra [3], the assignment of the order of *d*-energy levels [4], the kinetics of nucleophilic substitution reactions [5] and the development of a theoretical treatment to explain the *trans*-effect [6]. There has also been, on the part of academic and industrial chemists, active study of processes of potential or actual interest in the field of catalysis [7].

If one considers the formation of square planar complexes in general terms, one can make the following rough generalization: they are formed only when, in the molecule, there occurs some particular 'circumstance' which destabilizes or even prevents the formation of species of higher coordination numbers. The 'circumstance' could arise through the operation of either electronic or steric factors. Most important among the former is the presence of a metal ion with a d^8-electron configuration [2] and among the latter the presence of a bulky ligand [5]. Square planar complexes are also frequently obtained using chelating agents giving complexes in which there is extensive electron delocalization [8] [9]. Although many series of complexes of ligands of the latter type have been prepared, the information obtained from their study cannot be directly related to the electron occupancy of the *d*-orbitals of a

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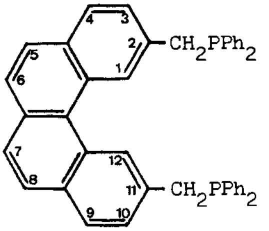
metal ion, *i.e.*, its 'spectroscopic oxidation state' [10] may be significantly different from its formal oxidation state.

One way to obtain a wide range of square planar complexes while preventing extensive delocalization of metal *d*-electrons is by the use of a fairly 'innocent' ligand [10] of rigid structure which places 'inert' organic matter above and below the plane of the complex. One such ligand could be 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**).



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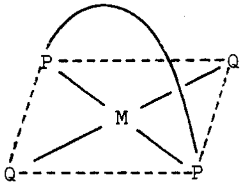

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Using data from the X-ray structure determination of benzo[*c*]phenanthrene [11] and standard interatomic distances [12] one can obtain a reasonable geometric model for ligand **1**. The hydrocarbon moiety and the two phosphorus atoms are sufficiently flexible to allow the formation of complexes of the type *trans*-[MQ_2(**1**)] (**2**) (Q = charged or uncharged ligand, 'ionic' charges have been omitted for clarity) with a wide range of metal ions. Examination of molecular models of complexes of type **2** shows that: (1) the space above the coordination plane, defined by the metal and donor atoms, is largely occupied by the polynuclear hydrocarbon and the two methylene groups and, therefore, should not be available for the formation of another coordinate bond and (2) the space below the coordination plane is, in part, taken up by the four terminal benzene rings restricting the size of the ligand that could bind to the metal atom from this side of the coordination plane. Thus, in the absence of significant distortions from regular structure of the organic ligand and/or of the coordination polyhedron, the ideal geometry of the complexes formed by ligand **1** is *trans*-square planar. Also square pyramidal complexes *trans*-[MQ_2L(**1**)] could easily be formed if the ligand L does not have a *van der Waals* radius much greater than that of a bromine atom. It is, obviously, possible for ligand **1** to form mononuclear complexes with coordination polyhedra other than those mentioned above. Linear, two-coordinate complexes should be easily formed and the steric considerations developed above for square planar complexes should also apply to T-shaped, three-coordinate species. Furthermore, it appears to be possible to construct models of complexes in which the P-M-P bond angle is as small as 120° although this appears to cause deviations from standard bondlengths and angles. It is also possible to imagine the formation of a variety of irregular coordination polyhedra. The extent of their occurrence, however, will be established only by an extensive investigation of the coordination chemistry of ligand **1**. The general conclusions that can be reached at this stage are that ligand **1** should induce the preferential formation of quadratic complexes with the two phosphorus atoms in *trans*-positions and that their *cis*-arrangement, *i.e.*, P-M-P bond angles close to 90°, appears to be prevented by overlap of terminal phenyl substituents.

It is also possible to construct molecular models in which each phosphorus atom of ligand **1** is bound to a different metal atom, *i.e.*, it is acting as a bridging group. In these cases many of the above geometric constraints do not apply.

In view of the wide ranging interest in square planar complexes and because of the unusual features that complexes of ligand **1** might possess, a synthetic route for this ligand was developed.

Benzo[*c*]phenanthrene itself, and many of its alkyl derivatives, have been prepared over the past two decades during the course of investigations into the carcinogenic nature of polycyclic aromatic hydrocarbons. The synthetic routes commonly employed to prepare benzo[*c*]phenanthrenes have been reviewed by *Clar* [13].

The first objective of this study was the synthesis of 2,11-dimethylbenzo[*c*]phenanthrene (**3**). As its preparation does not appear to have been reported in the literature and as the methods used for the preparation of the other recorded isomers [13–15] could not be readily modified to yield the 2,11-isomer as the only product, a route related to that described by *Burditt et al.* [16] for the preparation of benzo[*c*]-phenanthrene was used.

2. Results and Discussion. – 2,11-Dimethylbenzo[*c*]phenanthrene (**3**) was prepared following the synthetic route outlined (*Scheme*). All intermediates in these syntheses have been fully characterized, and their analytical and spectral data are in all cases consistent with the formulations shown.

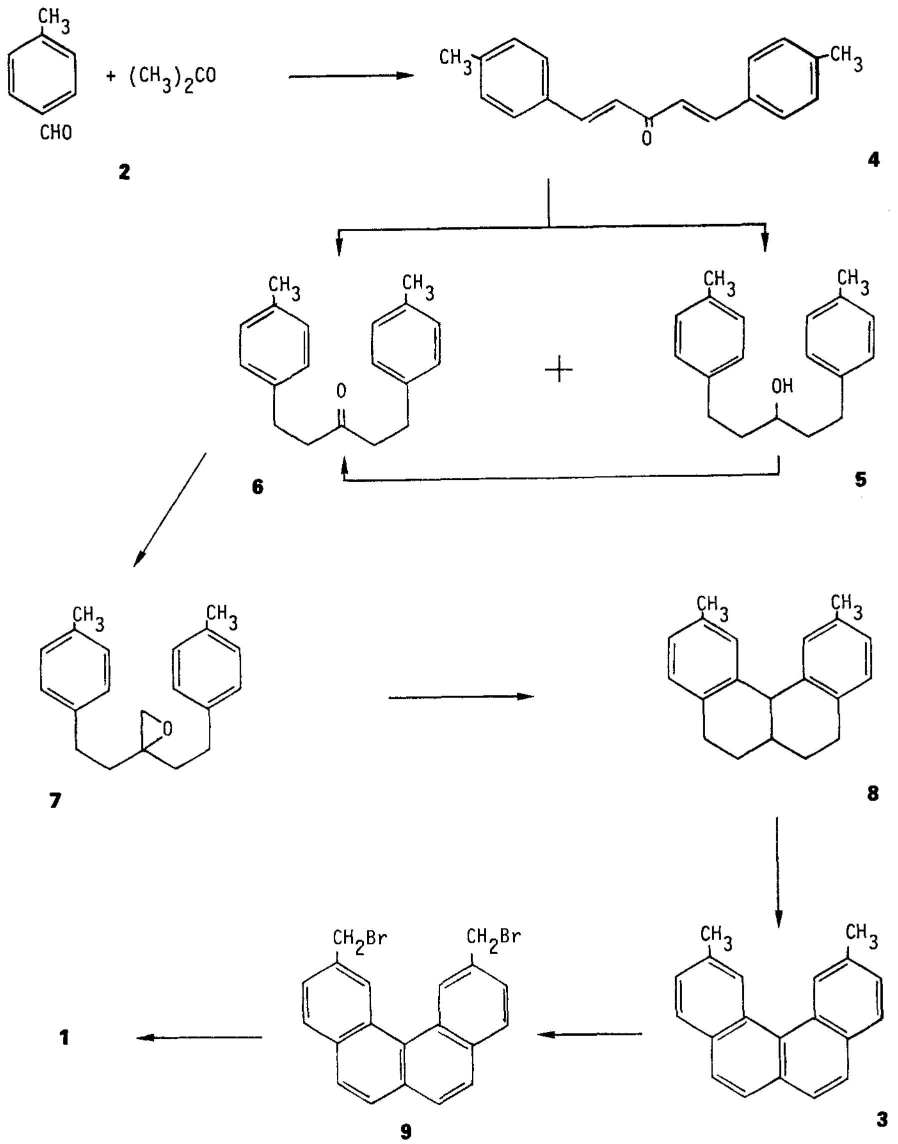
As previously reported [17], the base-catalysed condensation of a *p*-substituted benzaldehyde with acetone proceeded in good yield provided that a sufficiently large volume of solvent was used to prevent the intermediate benzylidene-acetone from precipitating from solution.

Specific hydrogenation of the double bonds in benzylidene-acetones has been reported with *Raney* nickel [18], platinum oxide [16] and palladium on carbon [19] and the latter was used for the reduction of compound **4**, although the ketone **6** thus obtained contained moderate amounts of the alcohol **5**.

As previously reported for the platinum oxide system [16], addition of acetic acid to the reaction mixture effectively prevented side reactions due to the base-catalysed condensation of the product with the starting material. This alcohol/ketone mixture was re-oxidized with chromic acid, following the procedure of *Brown & Garg* [20] to give ketone **6** as the sole product. Ketone **6** was converted to epoxide **7** by reaction with dimethylsulfoxonium methylide [21]. This procedure was both more convenient and more efficient than the traditional two-stage process, which was also investigated, in which a *Wittig* reaction is used to convert the ketone first to an olefin, which is then oxidized by a peracid to the epoxide [22]. The opening of a terminal epoxide ring by boron trifluoride etherate is known to be a facile process [23] [24] and the cyclised hydrocarbon **8** was consistently obtained in good yield by treatment of the epoxide **7** with boron trifluoride etherate in benzene solution [25] at 25°.

The three principal methods currently in use for the aromatization of cyclic hydrocarbons were tried, *i.e.*, with metal catalysts [26], sulfur (or selenium) [27] or high-potential quinones [28], and the latter was used for the aromatization of **8**. It

Scheme



was found that 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [29] [30] gave consistently higher yields of benzo[*c*]phenanthrene (**3**) than were obtained with tetrachloro-1,4-benzoquinone, provided that short reaction times [28] and small volumes of solvent [30] were employed. As with all reactions with halogenated quinones, the aromatization process was not free from side reactions, but pure **3** could be obtained with reasonable ease by chromatography.

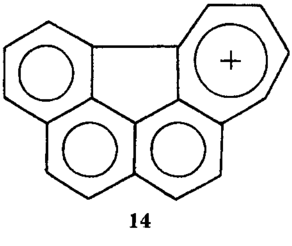
The bromination of **3** with N-bromosuccinimide using reaction conditions similar to those employed by *Peter* & *Jenny* [14] in the bromination of 3,10-dimethylbenzo-

[*c*]phenanthrene gave bromination products which showed ^{1}H-NMR. resonances due to the presence of significant amounts of species containing the $-CHBr_2$ and $-CH_3$ groups ($\delta = 6.92$ and 2.59 ppm, respectively). The use of higher temperatures and shorter reaction times, however, minimized these side reactions. The pure dibromide **9** was obtained by recrystallization of the crude product.

Reaction of dibromide **9** with lithium diphenylphosphide occurred rapidly at 0° to give diphosphine **1** which was purified by recrystallization from acetone. Although the pure, solid diphosphine was not susceptible to aerial oxidation, purification of the crude diphosphine in air gave bis(phosphineoxide) **13**. Consequently, work-up of the crude product was always carried out in a nitrogen atmosphere.

The ^{1}H-NMR. spectra of compounds **3** and **9** can be analysed on the basis of the assignments made by *Bartle* & *Jones* [31] for benzo[*c*]phenanthrene, but those of compounds **1** and **13** are less resolved in the aromatic region because of the presence of the phosphorus atoms and of the terminal phenyl groups. All the above compounds, however, clearly show a resonance to low field of the main aromatic region, which is also present in the parent hydrocarbon and which has been assigned to the sterically-strained protons in the C(1) and C(12) ring positions [31]. Coupling of phosphorus with the methylene protons was only observed for bis(phosphineoxide) **13** ($^2J_{P-H} =$ 14 Hz), the methylene proton resonance in diphosphine **1** appearing as a broad singlet which was not resolved at 90 MHz.

The mass spectrum of compound **3** reflects the high stability of the fully aromatized ring system in that the parent ion is the most intense peak in the spectrum; **3** decomposes by loss of the methyl groups to give the cations $[C_{18}H_{10}]^+$, *m/e* 226 and $[C_{18}H_{10}]^{2+}$, *m/e* 113. In contrast, the derivatives having substituents $-CH_2X$ ($X =$ $-Br$, $-PPh_2$, $-P(O)Ph_2$) show much less intense parent ion peaks and apparently decompose by loss of X, their spectra showing a very intense peak corresponding to the ion $[C_{20}H_{16}]^+$, *m/e* 256. Additionally, compound **3** and its derivatives **9**, **1** and **13** all decompose to give the cation $[C_{19}H_{11}]^+$, *m/e* 239, which has also been observed in the mass spectra of 1-methyl and 3-methylbenzo[*c*]phenanthrene [32] and has been suggested as having the structure **14**.



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Experimental Part

Melting points (m.p.) were determined using a *Thomas* 'Unit-melt' apparatus and are uncorrected. Infrared spectra (IR.) were recorded as nujol mulls or KBr discs on a *Perkin Elmer* 337 IR. spectrophotometer (absorption band in cm^{-1}). The 60 MHz ^{1}H-NMR. spectra were run on a *Perkin Elmer* R 12 spectrometer, chemical shifts (δ) being given in ppm with respect to an internal TMS standard. High resolution spectra (^{1}H, ^{13}C and ^{31}P) were obtained at 90 MHz on a *Bruker*

HX90 spectrometer using the deuterium resonance of $CDCl_3$ as an internal lock. The ^{13}C chemical shifts are in ppm. downfield with respect to an internal TMS standard while the ^{31}P chemical shifts are in ppm relative to an external H_3PO_4 standard. Shifts to higher fields are denoted as negative and those to lower field as positive. Mass spectra (MS.) were obtained at 70 eV on a *CEC* 21-110B mass spectrometer [*m/e*-values (rel. intensity)]. Elemental analyses were performed by *Galbraith* Laboratories, Knoxville, Tenn. 37921.

Abbreviations: RT. = room temperature, i.V. = *in vacuo*.

The scale given in the synthetic steps below is that of the batch size typically employed. Generally, the synthetic intermediates were purified only to the extent necessary for the success of the subsequent stage of synthesis and the yields quoted refer to materials of such a purity.

Di-(p-*methylbenzylidene*)*-acetone* (**4**). 100 g *p*-tolualdehyde (0.83 mol) was added dropwise to a stirred solution of 46.6 g of potassium hydroxide (0.83 mol) and 48.4 g of acetone (0.83 mol) in 2 l of ethanol and 1.6 l of water. The reactions mixture was stirred for 30 min then another 100 g (0.83 mol) *p*-tolualdehyde was added dropwise and the mixture stirred for further 2 h. Filtration gave **4** as a yellow solid which was washed with 3.0 l of water and dried for two days at 100°; yield 192 g (89%). An analytically pure sample was obtained by recrystallization of the crude product from ethyl acetate. M.p. 175–177° (lit. 173–174.5° [33]). – ^1H-NMR. ($CDCl_3$): 6.8–7.8 (*m*, 12, phenyl H's+vinyl H's); 2.35 (*s*, 6, CH_3). – MS.: 262 (100, M^+), 263 (26, M^+ (^{13}C)). – IR: (KBr disc): 1640*s* ($\rangle C{=}O$), 1617*s* ($C{=}C$).

1,5-Di-(p-*tolyl*)*pentan-3-one* (**6**). 380 g **4** (1.45 mol) suspended in 2.5 l of ethyl acetate containing 50 ml of glacial acetic acid was stirred with 40 g of a 5% Pd/C catalyst in a hydrogenator pressurized to 4.1 atm of hydrogen at RT. Hydrogen uptake began immediately and was apparently complete within 30 min, although the mixture was stirred in the hydrogenator for a total of 2 h, to ensure complete reaction. The resulting mixture was filtered and the straw-colored filtrate was evaporated to dryness on a rotary evaporator. The residue, on cooling, gave 306 g of a white solid which generally consisted of a mixture of 75–80% ketone **6** and 20–25% of alcohol **5**, the actual amount of alcohol **5** in the mixture being estimated by ^1H-NMR. The mixture above was redissolved in 750 ml of ether and a solution of 29.7 g (0.1 mol) of sodium dichromate and 22.7 ml of conc. sulfuric acid in 150 ml of water was added dropwise to the stirred solution at 0°. (This corresponds to the addition of an 8–9% excess of dichromate over the amount required to oxidize the amount of alcohol present in that sample). The mixture was stirred overnight. The ether layer was separated, washed with 5% aqueous potassium hydroxide and water until neutral and dried over magnesium sulfate. Evaporation of the solution gave the 267 g (70%) of **6** as a white solid. Recrystallization from *n*-hexane gave an analytically-pure sample of **6**, m.p. 53.5–54°. – ^1H-NMR. ($CDCl_3$): 6.92 (*s*, br., 8, phenyl H's); 2.3–2.85 (*m*, 8, methylene H's); 2.22 (*s*, 6, CH_3). – MS.: 266 (52, M^+), 267 (11, M^+ (^{13}C)). – IR. (KBr disc): 1710*s* ($\rangle C{=}O$).

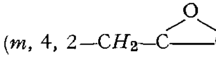
$C_{19}H_{22}O$ (266.38) Calc. C 85.67 H 8.32% Found C 85.92 H 8.47%

1,5-Di-(p-*tolyl*)*-pentan-3-ol* (**5**). Multiple recrystallisations from *n*-hexane of a sample of the alcohol/ketone mixture prepared as described above gave pure **5** as a white crystalline solid, m.p. 94–95°. – ^1H-NMR. (CCl_4): 6.90 (*s*, br. 8, phenyl H's); 3.48 (*qui*, $^3J_{H-H}$ = 6 Hz, 1, CHOH); 2.60 (*t*, $^3J_{H-H}$ = 7.5 Hz, 4, –CH_2CH_2CHOH); 2.25 (*s*, 2CH_3, 6); 1.71 (*q*, $^3J_{H-H}$ = 7 Hz, 4, 2–CH_2CH_2CHOH); 1.20 (*s*, 1, –CHO*H*). – MS.: 268 (9, M^+), 269 (2, M^+ (^{13}C)). – IR. (KBr disc): 3340*s*, 3270*s* (O–H).

$C_{19}H_{24}O$ (268.40) Calc. C 85.08 H 8.96% Found C 85.02 H 9.01%

1,1-Di-(p-*methylphenethyl*)*-epoxyethane* (**7**). Dimethylsulfoxide (DMSO) was dried by refluxing over calcium hydride at *ca.* 5 Torr (using a nitrogen bleed) for several hours and was freshly distilled from calcium hydride immediately before use. All handling of DMSO solutions and the subsequent steps were carried out under nitrogen.

200 ml of DMSO was slowly added to a vigorously-stirred mixture of 6.60 g (0.275 mol) of sodium hydride and 60.5 g (0.275 mol) of trimethylsulfoxonium iodide at 0°. After 30 min, the evolution of hydrogen appeared complete and the mixture was allowed to warm to RT. and then stirred for a further 30 min to ensure complete reaction. To the dimethylsulfoxonium methylide reagent thus prepared, was added a solution of 53.3 g (0.20 mol) of **6** in 200 ml of DMSO.

The resulting mixture was stirred at 25° for 30 min and then at 60° for 1 h. After cooling to RT., the reaction mixture was poured into water (1.0 l) and the aqueous solution extracted with chloroform (3 × 200 ml). The combined chloroform extracts were filtered and washed with 4 × 250 ml of water then filtered again and dried over magnesium sulfate. The dessicant was filtered off and washed with 4 × 150 ml of chloroform and the combined filtrate and washings evaporated i.V. to give the product **7** as a viscous yellow oil: yield 46.2 g (83%). Vacuum distillation of the crude product gave a pure sample of **7** in the form of a pale yellow oil: b.p. 185–187°/1.4 Torr. – ^{1}H-NMR. (CCl_4): 6.97 (*s*, br., 8, phenyl H's); 2.4–2.7 (*m*, 6, 2 benzyl-CH_2 + terminal CH_2); 2.23 (*s*, 6, 2 CH_3); 2.0–1.6 (*m*, 4,  $2{-}CH_2{-}\overset{O}{C}{-}CH_2$). – MS.: 281 (1.5, M^+ (^{13}C)), 280 (5, M^+).

$C_{20}H_{24}O$ (280.41) Calc C. 85.65 H 8.64% Found C 85.49 H 8.65%

2,11-Dimethyl-5,6,6a,7,8,12b-hexahydrobenzo[c]*phenanthrene* (**8**). The reaction was performed under nitrogen. 192 g (170 ml) of boron trifluoride etherate was added dropwise to a stirred solution of 50 g (179 mol) of **7** in 420 ml of dry benzene. The reaction vessel was cooled in an ice bath during the addition, and the temperature of the reaction mixture maintained below 25°. When addition was complete, the reaction mixture was stirred at RT. for 5 h and then 450 ml of water was slowly added, the temperature again being kept below 25° by use of an ice bath. The organic layer was separated, washed with 5% aqueous sodium hydroxide and water until neutral, dried over magnesium sulfate, and evaporated i.V. to give a yellow-brown oil which solidified on standing: yield 47 g. An analytically pure sample, a white crystalline solid, was obtained by chromatography on an alumina column with *n*-pentane and subsequent recrystallization from *n*-hexane: m.p. 71–72°. – ^{1}H-NMR. (CCl_4): 6.83 (*s*, br., 4, H—C(3), H—C(4), H—C(10), H—C(11)); 6.76 (*s*, br., 2, H—C(1), H—C(13)); 3.74 (*d*, *J* = 5 Hz, 1, H—C(14)); 2.65 (*t*, *J* = 7 Hz, 4, 2H—C(5) + 2H—C(9)); 2.22 (*s*, 6, 2 CH_3); 1.2–2.1 (*m*, 5, 2H—C(6), 2H—C(8), H—C(7)). – MS.: 263 (24, M^+ (^{13}C)), 262 (100, M^+).

$C_{20}H_{22}$ (262.40) Calc. C 91.55 H 8.45% Found C 91.33 H 8.54%

It proved to be unnecessary to use analytically pure **8** for the next step. Sufficient purification of the crude material was achieved as follows: The crude product was dissolved in 200 ml of *n*-pentane, the solution slurried with activated charcoal, filtered and then stirred with alumina. Filtration and evaporation of the *n*-pentane i.V. gave **8** as a pale yellow solid: yield 37 g (78%).

2,11-Dimethylbenzo[c]*phenanthrene* (**3**). The reaction was carried out under nitrogen. Benzene was dried over lithium aluminum hydride and freshly distilled before use. 92.6 g (0.408 mol) of solid 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were slowly added to a vigorously stirred suspension of 35.4 g (0.135 mol) of **8** in 20 ml of benzene. When half of the DDQ had been added, the reaction mixture became very viscous and a further 200 ml of benzene were added before completing addition of the remaining DDQ. The stirred mixture was then refluxed vigorously for 4 h and filtered hot, the solid residue being washed 6 × 50 ml of benzene. The combined filtrate and washing were evaporated i.V. to give the crude product as a dark brown solid. The crude material was chromatographed on an alumina column, **3** being eluted with a ether/*n*-pentane 5:95 giving a white solid which was recrystallized from *n*-hexane to give pure **3** as colorless needles: yield 14.7 (42%), m.p. 133–134°. – ^{1}H-NMR. ($CDCl_3$): 8.79 (*s*, br., 2, H—C(1) + H—C(12)); 7.2–7.85 (*m*, 8, aromatic H's); 2.57 (*s*, br., 6, 2 CH_3). – MS.: 257 (23, M^+ (^{13}C)), 256 (100, M^+), 239 (30, $[C_{19}H_{11}]^+$), 226 (16, $M^+ - 2CH_3$), 119.5 (15, $[C_{19}H_{11}]^{2+}$).

$C_{20}H_{16}$ (256.35) Calc. C 93.71 H 6.29% Found C 93.42 H 6.21%

2,11-Bis(bromomethyl)benzo[c]phenanthrene (**9**). The reaction was carried out under nitrogen. 2.05 g (8 mmol) of **3** and 2.95 g (16.6 mmol) of N-bromosuccinimide (NBS) were suspended in 40 ml of carbon tetrachloride and the stirred suspension heated until refluxing vigorously (bath temperature *ca.* 100°). Bromination was then initiated, if necessary, by the addition of 0.2 g of dibenzoyl peroxide in 1.0 ml of chloroform and the mixture was vigorously refluxed for a further 30 min. The hot reaction mixture was filtered and evaporated to give the crude product as a white solid. Material of sufficient purity for use in subsequent diphosphine synthesis ($\geq$ 90% pure) was obtained by a single recrystallization of the crude product from benzene/carbon tetrachloride 1:9, the crystals being thoroughly washed with diethyl ether and dried i.V.; yield 1.80 g (54%). Analytically pure **9** was obtained as a white crystalline solid by recrystallization of the crude product *twice* from benzene/carbon tetrachloride 1:9: yield 1.20 g (36%), m.p. 154–155° (dec.). – ^{1}H-NMR. ($CDCl_3$): 9.02 (*s*, br., 2, H—C(1)+H—C(12)); 7.5–8.0 (*m*, 8, aromatic H's); 4.74 (*s*, 4, methylene H's). – MS.: 416 (10, M^+ (^{81}Br ^{81}Br)), 414 (19, M^+ ^{79}Br ^{81}Br)), 412 (10, M^+ (^{79}Br ^{79}Br)), 335 (68, $M^+ - {}^{79}$Br), 333 (65, $M^+ - {}^{81}$Br), 256 (100, $[C_{20}H_{16}]^+$), 239 (70, $[C_{19}H_{11}]^+$), 226 (29, $M^+ - 2CH_2Br$).

$C_{20}H_{14}Br_2$ (414.15) Calc. C 57.99 H 3.41 Br 38.61% Found C 57.87 H 3.64 Br 38.81%

2,11-Bis(diphenylphosphinomethyl)benzo[c]*phenanthrene* (**1**). The reaction and work-up were carried out under nitrogen. All solvents were degassed and freshly distilled before use. Lithium diphenylphosphide was prepared by the addition of 4.0 ml of a 2.2M solution (8.8 mmol) of *n*-butyllithium in *n*-hexane to a stirred solution of 1.60 g (1.50 ml) diphenylphosphine (8.6 mmol) in 15 ml of THF at 0°. The bright orange solution of lithium diphenylphosphide formed was allowed to warm to RT. and then was added dropwise to a stirred solution of 1.29 g (3.1 mmol) of **9** in 10 ml of THF at 0°, until the addition of one drop caused the reaction mixture to retain a deep orange-red coloration. The resulting solution was stirred at 25° for 30 min and then evaporated to dryness i.V. The sticky residue was redissolved in 25 ml of methylene chloride. This solution was washed with 6 × 20 ml of water, to remove the lithium bromide formed in the reaction, dried over magnesium sulfate and then concentrated i.V. to a volume of *ca.* 2.0 ml. 60 ml of diethyl ether was then slowly added to precipitate the crude diphosphine as a cream solid which was filtered off, washed with 20 ml of ether and dried i.V. The crude product was redissolved in 80 ml of hot acetone and crystallized by gradually concentrating the resultant solution in a stream of nitrogen. **1** was obtained as colorless crystals which were washed with 5 ml of acetone and dried at 80°/$1 \cdot 10^{-5}$ Torr for five days: yield 0.85 g (44%), m.p. 173–176°. – ^{1}H-NMR. ($CDCl_3$): 8.91 (*s*, br., 2, H—C(1)+H—C(12)); 6.8–8.0 (*m*, 28, other aromatic H's); 3.64 (*s*, br., 4, methylene H's). – ^{13}C-NMR. ($CDCl_3$): 126–139 (*m*, aromatic C's); 36.7 (*d*, $^1J_{P-C} = 16$ Hz, methylene C's). – (^{1}P-NMR. ($CDCl_3$): –8.7 (*s*). – MS.: 625 (8, M^+ (^{13}C)), 624 (18, M^+), 439 ($M^+ - P(C_6H_5)_2$), 256 ^{3}100, $[C_{20}H_{16}]^+$), 239 (40, $[C_{19}H_{11}]^+$), 226 (13, $M^+ - 2CH_2P(C_6H_5)_2$).

$C_{44}H_{34}P_2$ (624.71) Calc. C 84.60 H 5.49 P 9.92% Found C 84.26 H 5.30 P 10.04%

2,11-Bis(oxydiphenylphosphinomethyl)benzo[c]*phenanthrene* (**13**). A solution of 0.5 g (0.8 mmol) **1** in 30 ml of acetone was treated at 0° with 10 ml of 30% hydrogen peroxide2)*.* On warming to RT., the product began to precipitate and, after stirring overnight to complete precipitation, was filtered off and dried i.V. Recrystallization from chloroform/toluene afforded **13** as a white crystalline solid: yield 0.28 g (54%), m.p. 291–292°. – ^{1}H-NMR. ($CDCl_3$): 9.37 (*s*, br., 2, H—C(1) +H—C(12)); 7.0–8.2 (*m*, 28, other aromatic H's); 4.10 (*d*, $^2J_{P-H} = 14$ Hz, 4, methylene H's). – ^{31}P-NMR. ($CDCl_3$): +29.7 (*s*). – MS.: 657 (10, M^+ (^{13}C)), 656 (20, M^+), 455 (6, $M^+ - (C_6H_5)_2PO$), 256 (21, $[C_{20}H_{16}]^+$), 239 (11, $[C_{19}H_{11}]^+$), 226 (10, $M^+ - 2CH_2P(O)(C_6H_5)_2$). – IR. (KBr disc): 1183*s* (P=O).

$C_{44}H_{34}P_2O_2$ (656.71) Calc. C 80.48 H 5.22 P 9.43% Found C 80.91 H 5.44 P 9.36%

The authors are indebted to Prof. *S. Bank* and Prof. *H. Kwart* for much valuable advice with the development of this work.

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2) The use of H_2O_2 in acetone solution mentioned in this preparation *is in fact to be avoided. Such a mixture is potentially explosive* and becomes particularly dangerous after the solvent has been evaporated. During the course of subsequent work on related compounds a violent explosion of the oily residue occurred after the acetone had been evaporated. It was later discovered that the explosive nature of acetone/H_2O_2 mixtures has been observed elsewhere *e.g.*, see *A. D. Brewer*, Chem. in Britain *1975*, 355.

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