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

Part XVIII[1])

Crystal and Molecular Structure of the Ligands 2,11-Bis(di-R-phosphinomethyl)benzo[*c*]phenanthrene (R = Phenyl, *tert*-Butyl) and a Comparison of their Conformation in a Variety of Complexes

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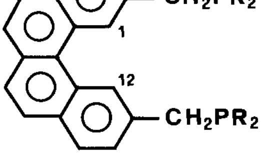
The X-ray crystal structures of 2,11-bis(di-R-phosphinomethyl)benzo[*c*]phenanthrenes (R = Ph, *t*-Bu) are reported. Both ligands have the same conformation and the substitution of a Ph by a *t*-Bu group does not cause significant changes in the tetracyclic aromatic unit which shows the same distortions as the parent hydrocarbon. The conformations and structural features of the two ligands and 18 complexes containing these ligands as well as of one compound with a ligand with Et substituents are compared. It is pointed out that *1*) the conformations of the free ligands differ significantly from those of their complexes, *2*) in all the complexes characterized to date, these ligands act as chelating agents, and *3*) the ligands adopt two different conformations in the complexes, one of them appearing to be more flexible than the other.

Introduction. – The ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1a**) was originally designed to cause the preferential formation of square-planar complexes of the type [MX_2(**1a**)], (M = d^8 metal, X = anion) in which the chelating diphosphine spans *trans*-positions [2]. At a later stage, the related ligands 2,11-bis-[di(*tert*-butyl)phosphinomethyl]benzo[*c*]phenanthrene (**1b**) and 2,11-bis(diethylphosphinomethyl)benzo[*c*]phenanthrene (**1c**) were also synthesized.



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[1]) Part XVII: [1].

The X-ray structures of several complexes of **1a** have confirmed that the ligands are indeed able to span *trans*-positions in complexes of square-planar or related geometries, *i.e.* the P–M–P bond angles are close to 180° [2–5]. In addition, the ligands can also chelate metal ions with other geometries in which the P–M–P angle, α, shows values lower than 180° [5–10]. In the trigonal complex [AgCl(**1a**)] [6], for instance, this angle is 141°, in the similar complex [CuCl(**1a**)] [6] it is 131°, and in the pseudo-tetrahedral complex [HgCl$_2$(**1a**)] [9] it is 126°. When the P–M–P angle, α, is very different from 180°, the presence of *t*-Bu instead of Ph groups produces a widening of this angle as shown in the series of complexes [AgX(**1a**)] [10] and [AgX(**1b**)] [8]. The widening is greater, when weak donor anions are used, *i.e.* 20° for X = ClO$_4$ and 2° for X = Cl [8]. On the other hand, a widening of the P–M–P angle in the same group of metals occurs on increasing the atomic number Z as shown in the series [MCl(**1a**)] (M = Cu, Ag, and Au) in which the P–M–P angles are 131, 141, and 178°, respectively [6].

In these complexes, the ligand occurs in two quite different conformations. In one group of compounds, the C(19)–P(1) and C(20)–P(2) vectors are pointing to the same side of the mean benzo[*c*]phenanthrene plane, these are called P-type complexes (P for parallel, *Fig. 1*). In the other group, these vectors point to opposite sides of this plane, these complexes are called A-type (A for antiparallel, *Fig. 1*).

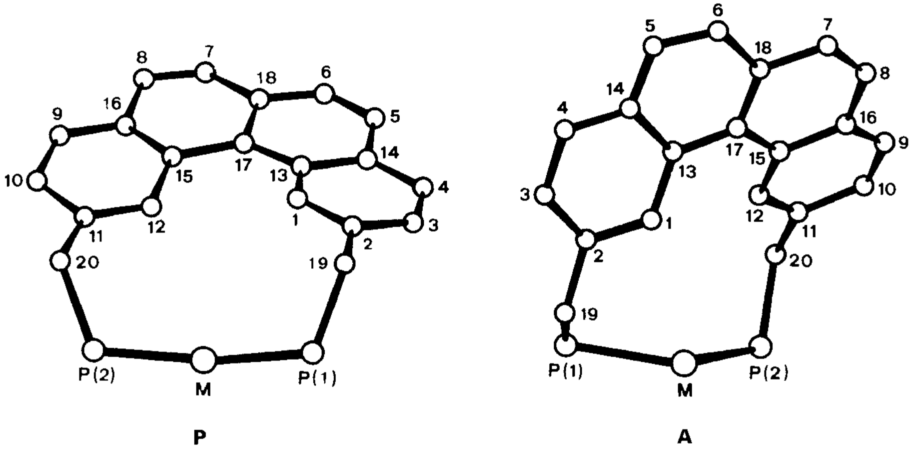

Fig. 1. *View of a P-type and an A-type complex*

To further probe the conformational flexibility of these complexes, the crystal and molecular structures of the free ligands **1a** and **1b** were determined by X-ray diffraction methods and compared to their complexes. The complex [Ag(ClO$_4$)(**1c**)] [11] was also included in the comparison.

Results and Discussion. – *Figs. 2* and *3* show the molecular structures of the ligands **1a** and **1b**. To discuss the basic features of these ligand systems and the changes occurring on complex formation, we have defined a series of structural parameters listed in *Table 1.* These are discussed below. Tables of atomic coordinates, anisotropic displacement parameters, distances, and angles have been deposited *(Cambridge Crystallographic Data Centre)*.

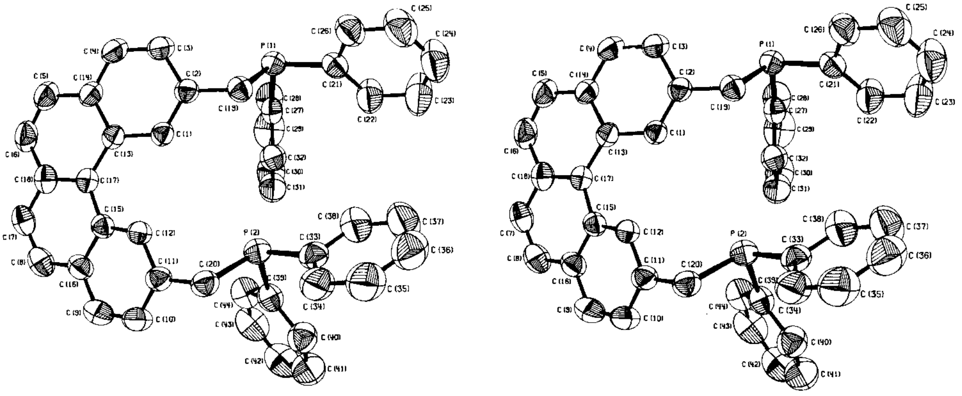

Fig. 2. *An ORTEP view of 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene* (**1a**)

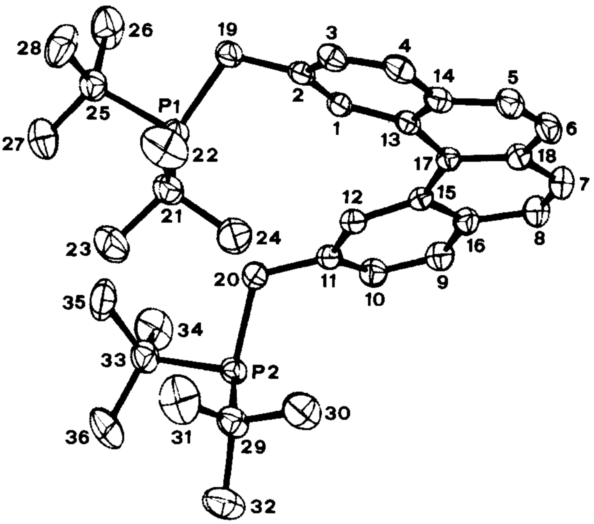

Fig. 3. *An ORTEP view of 2,11-bis[di(*tert*-butyl)phosphinomethyl]benzo[*c*]phenanthrene* (**1b**)

Deviation of the Tetracyclic Moiety from Planarity. Significant deviations from planarity are found both in the free ligands and their complexes. They are due to the proximity of the H-atoms at C(1) and C(12) as already found in the parent hydrocarbon benzo[*c*]phenanthrene [12]. The effect of H_1H_{12} overlap can be gleaned from the 'tilt' angle β, which is defined as the dihedral angle between two planes pl_1 and pl_2 (the planes pl_1 and pl_2 are the best planes through the ring atoms C(1), C(2), C(3), C(4), C(13), C(14), and C(9), C(10), C(11), C(12), C(15), C(16), respectively). The 'tilt' angle, β, between these planes is 21.6° for **1a**, 26.9° for **1b**, and 27.3° for the parent hydrocarbon (**HC**). The reasons for the difference in 'tilt' angle values between **1a**, **1b**, and **HC** which are *ca.* 6°, are not obvious and may possibly be related to packing forces.

Complex formation can induce large changes in tilt angles. It is noteworthy that for P-type compounds, the β-values fall in the range 17–27°, while for the complexes of A-type they range from 28 to 36°, all except one of them being $\geqslant 32°$.

Ligand Conformations. The conformations of the ligands can be described in terms of the torsion angles, w_1, w_2, w_3, and w_4. These are defined as follows: $w_1 = w\{C(1)–C(2)–C(19)–P(1)\}$, $w_2 = w\{C(2)–C(19)–P(1)–M\}$, $w_3 = w\{C(12)–C(11)–C(20)–P(2)\}$, $w_4 = w\{C(11)–C(20)–P(2)–M\}$, $0° \leqslant w_i < 360°$. In the free ligands, w_2 and w_4 are not defined. Instead, an estimate of the torsion angle for the P lone pair, which may be considered as a pseudo-ligand, is given. It is assumed that this lone pair lies on the plane bisecting the R–P–R angle (**1a**: R = Ph, **1b**: R = *t*-Bu) in a position completing a coordination polyhedron about P and including it. The torsion angle w_2 for **1a** was estimated from the sum Σ and difference Δ of $w\{C(2)–C(19)–P(1)–C(21)\}$ and $w\{C(2)–C(19)–P(1)–C(27)\}$ as follows: If $|\Delta| < 180°$, $w_2 = \Sigma/2 \pm 180°$; if $|\Delta| > 180°$, $w_2 = \Sigma/2$. Analogous considerations apply to w_4 of **1a** and to **1b**. For comparison purposes, all molecules were transformed to correspond to a left-handed helix conformation of the benzo[*c*]phenanthrene backbone (*Fig. 1* shows a P-type complex with a left-handed helix conformation and an A-type complex with a right-handed one).

Table 1. *Geometrical Parameters Suitable for the Description of* **1a** *and* **1b** *and their Complexes*

Compound	α(P–M–P) [°]	Torsion angles [°][a]				Conformation[b]	Tilt angle β[°][c]	d(P(1)··P(2) [Å]	Ref.
		w_1	w_2	w_3	w_4				
1a	–	64	–	–118	–	P	22	5.71	
1b	–	57	–	–131	–	P	27	6.09	
[AuCl(**1a**)]	175.7	86	–64	–43	76	P	27	4.61	[6]
[PdCl$_2$(**1a**)]	175.7	82	–70	–45	67	P	23	4.64	[4]
[RhCl(CO)(**1a**)]	174.7	81	–70	–44	66	P	24	4.62	[4]
[IrCl(CO)(**1a**)]	173.9	79	–71	–51	65	P	17	4.61	[5]
[IrCl$_3$(CO)(**1a**)]	170.7	93	–65	–59	74	P	24	4.81	[5]
[RuCl(CO)(NO)(**1a**)]	167.4	88	–70	–49	71	P	18	4.78	[3]
[Ag(ClO$_4$)(**1c**)]	167.6	84	–65	–49	75	P	18	4.75	[1][d]
	164.8	81	–56	–59	73	P	22	4.71	[1][d]
[HgI$_2$(**1a**)]	146.0	90	–88	–45	89	P	26	4.77	[9]
[Ag(Cl$_3$Sn)(**1a**)]	142.2	84	–56	–48	48	P	19	4.61	[10]
[Ag(ClO$_4$)(**1a**)]	151.5	84	–67	57	–73	A	36	4.67	[10]
[Ag(NO$_3$)(**1a**)]	148.6	81	–64	65	–75	A	36	4.65	[10]
[AgBr(**1a**)]	141.3	71	–58	64	–75	A	36	4.60	[12b]
[AgCl(**1a**)]	140.8	82	–64	63	–78	A	36	4.58	[10]
[CuCl(**1a**)]	131.9	82	–63	43	–68	A	28	4.08	[6]
[HgCl$_2$(**1a**)]	125.6	92	–57	51	–80	A	32	4.44	[9]
[Ag(ClO$_4$)(**1b**)]	161.5	71	–60	68	–69	A	36	4.72	[8]
[AgCl(**1b**)]	142.6	73	–58	62	–74	A	33	4.63	[8]
[AgBr(**1b**)]	141.6	71	–58	64	–75	A	34	4.62	[8]

[a] Torsion angles are defined as $w_1 = w\{C(1)–C(2)–C(19)–P(1)\}$, $w_2 = w\{C(2)–C(19)–P(1)–M\}$, $w_3 = w\{C(12)–C(11)–C(20)–P(2)\}$, $w_4 = w\{C(11)–C(20)–P(2)–M\}$.

[b] See text.

[c] The angle between best planes through C-atoms C(9), C(10), C(11), C(12), C(15), C(16), (pl$_1$) and through C(1), C(2), C(3), C(4), C(13), C(14), (pl$_2$).

[d] Two molecules in the asymmetric unit.

A-Type complexes show characteristic w angles of 80, –60, 50, and –75°, respectively *(Table 1)*. Corresponding P–M–P angles, α, range from 126 to 162°. The typical w angles of P-type complexes are 85, –70, –50, and 70°, respectively, the corresponding P–M–P angles range from 142 to 176°. On the whole, large P–M–P angles are associated with P-type conformations and small P–M–P angles with A-type conformations. In the range between 142 and 162°, both conformation are found.

By comparison, the conformations of the free ligands are quite different from those of the P-type complexes; w_1 is $\sim 25°$ smaller, w_3 is $\sim 75°$ smaller in **1a** and **1b** than in the metal complexes, while w_4 even changes sign.

Analysis of the conformational angles indicates an intrinsic difference in conformational flexibility. A-Type conformations may be considered as slightly distorted C_2-symmetric structures with $w_1 = w_3 = w_{1,0} \approx 70°$ and $w_2 = w_4 = w_{2,0} \approx -65°$ (*e.g.* [Ag(ClO$_4$)(**1b**)], *Fig. 1*). Loss of the C_2 axis occurs in two symmetrically and energetically equivalent ways and produces $w_1 = w_{1,0} + \Delta_1$, $w_2 = w_{2,0} + \Delta_2$, $w_3 = w_{1,0} + \Delta_3$, $w_4 = w_{2,0} + \Delta_4$, or $w_1 = w_{1,0} + A_3$, $w_2 = w_{2,0} + \Delta_4$, $w_3 = w_{1,0} + \Delta_1$, $w_4 = w_{2,0} + \Delta_2$. Thus, from a set of observed torsion angles $w_i = w_{i,0} + \Delta_i$ a symmetry related set is obtained. A scatter plot of an expanded set of w_1's and w_3's for A-type conformations shows a continuous unimodal distribution centered about C_2-symmetric conformations (*Fig. 4*, right).

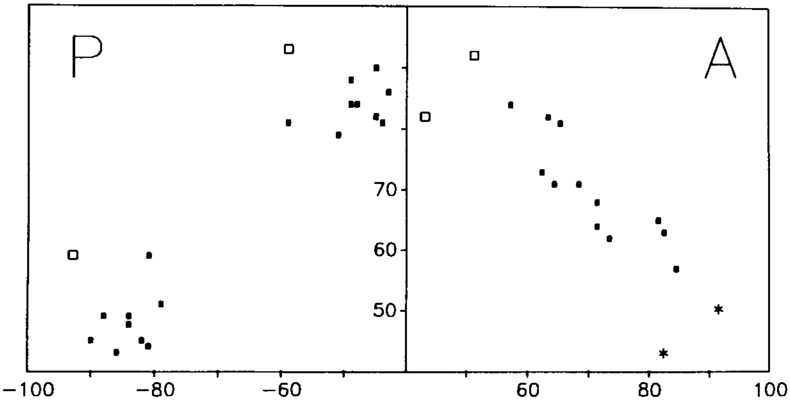

Fig. 4. *Scatterplot of* w_1 (vertical) vs. w_3 (horizontal) *for A- and P-type conformations.* Note that both plots show diagonal mirror lines. Filled squares indicate the main clusters of points in the seven-dimensional space of structural parameters *(Tables 1* and *2)*. Open squares and stars outliers.

The P-type conformations may be considered as distorted C_s-symmetric structures. Loss of the symmetry plane occurs in two equivalent ways and produces enantiomeric conformations characterized by $w_1 = w_{1,0} + \Delta_1$, $w_2 = w_{2,0} + \Delta_2$, $w_3 = -w_{1,0} + \Delta_3$, $w_4 = -w_{2,0} + \Delta_4$ or $w_1 = w_{1,0} - \Delta_3$, $w_2 = w_{2,0} - \Delta_4$, $w_3 = w_{1,0} - \Delta_1$, $w_4 = -w_{2,0} - \Delta_2$, respectively. Due to severe crowding of the H-atoms between C(1) and C(12), distortions from C_s symmetry are more pronounced than distortions from C_2 symmetry for A-type conformations. Clusters of enantiomeric conformation are clearly separated in a scatterplot of w_1 *vs.* w_3 (*Fig. 4*, left).

The shapes of the two distributions indicate that changes either of anion or of metal cation affect the ligand conformations of P-type complexes much less than those of the A-type complexes *(Fig. 4)*. The elongated shape of the distribution of A-type complexes may be considered to map the pathway for conformational interconversion. From this observation and from the structural correlation principle [13], we conclude, qualitatively, that A-type structures are conformationally more flexible than P-type structures. In an NMR experiment at sufficiently low temperatures, the CH_2 protons in complexes with the flexible A-type conformation would, thus, be expected to give an *AB*-type spectrum, while the more rigid P-type conformation should give an *AA'BB'*-type spectrum. Attempts were made to observe this behaviour by recording the spectrum of [$PdCl_2$(2,11-bis(diphenylarsinomethyl)benzo[*c*]phenanthrene)]. Complexes of the latter ligand were chosen, *1)* as they are fully analogous to those of ligand **1a** [14], and *2)* to obtain simpler spectra because of the absence of $^{31}P,^{1}H$ coupling. As reported earlier [14], at room temperature the CH_2 protons give rise to a sharp *singlet* at 4.27 ppm. This resonance shows a significant broadening at 223 and becomes extremely broad at 188 K. At 178 K, it becomes even broader and shows four weak maxima at *ca.* 3.7, 4, 4.2, and 4.7 ppm. Solubility problems prevented further lowering of the temperature. Although these results cannot be considered as conclusive, they are consistent with the hypothesis outlined above.

Finally one might ask, whether there are other correlations among the parameters in *Table 1*. If there are such correlations, do they shed light on the factors determining which conformation is preferred? Principal component analysis [15] on an extended set of structural parameters, specifically on the correlation matrix of w_1, w_2, w_3, w_4, α, β, and $d(P\cdots P)$ shows some trends *(Table 2)*.

Table 2. *Results of Factor Analysis on Correlation Matrices*

a) *A-Type complexes*			
Factor	1	2	
Eigenvalue	3.22	2.60	
% correlation	46	37	
Eigenvectors			
α	0	0.53	
β	0	0.59	
$d(P\cdots P)$	0	0.60	
w_1, w_2, w_3, w_4	0.5	0.10	
	0.5	−0.04	
	0.5	0.10	
	0.5	0.04	
b) *P-Type complexes*			
Factor	1	2	3
Eigenvalue	2.95	1.99	1.09
% correlation	42	29	15
Eigenvectors			
α	0	0.08	0.93
β	0.58	0	0
$d(P\cdots P)$	0	−0.55	−0.24
w_1, w_2, w_3, w_4	0.57	−0.05	−0.06
	0.10	0.59	−0.18
	0.57	0.05	0.06
	0.10	−0.59	0.18

A principal component analysis on the A-type conformations shows two principal factors, the first involves only w_1 to w_4 and reflects the deformation from C_2 symmetry; it affects all w's about equally. The second factor correlates α, β, and $d\,(\mathrm{P}\cdots\mathrm{P})$. It shows that β increases as α increases, a trend that is independent of the conformational angles w_1, w_2, w_3, and w_4. For compound [Ag(ClO$_4$) (**1b**)], α is 162°, and β is 36°, ~ 8° larger than in the parent hydrocarbon benzo[*c*]phenanthrene. A further increase of α would most likely imply a corresponding increase in β and, therefore, in the strain energy of the hydrocarbon backbone. Thus, for angles $\alpha > 160°$ and $\beta > 36°$, the alternative P-type conformation is adopted.

Principal component analysis on the 20 P-type conformations shows correlation between w_1, w_3, and β, and between w_2, w_4, and $d\,(\mathrm{P}\cdots\mathrm{P})$. Significantly, α does not correlate strongly with any of the other variables. We conclude that conformations P can accomodate a large range of bond angles α.

In summary, for $\alpha > 160°$ strain in the hydrocarbon backbone prevents adoption of conformation A and, therefore, the conformation P is preferred. For $\alpha < 140°$, conformation A is clearly preferred. In the range $140 < \alpha < 160°$ the crude analysis presented above cannot distinguish between A- and P-type conformations. An attempt at such a distinction would have to include additional structural parameters, *e.g.* the bond angles at C(2), C(11), C(19), C(20), P(1), P(2) and the conformational angles of the Ph and *t*-Bu groups at the P-atom.

Experimental. – *2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene* (**1a**) was prepared and crystallized as described in [2], while *2,11-bis[di(*tert*-butyl)phosphinomethyl]benzo[*c*]phenanthrene* (**1b**) was prepared as described in [16] and crystallized from MeOH/benzene solutions.

Table 3. *Crystal Data, Intensity Measurements, and Refinement for the Compounds* **1a** *and* **1b**

Compound	**1a**	**1b**
Formula	$C_{44}H_{34}P_2$	$C_{36}H_{50}P_2$
Mol.-wt.	624.70	544.74
a [Å]	11.067	12.476(1)
b [Å]	13.794	16.800(2)
c [Å]	11.485	16.437(2)
α [°]	92.1	90.0
β [°]	105.0	107.80(1)
γ [°]	92.8	90.0
V [Å^3]	1689	3280.1(6)
Z	2	4
Density (calc.) [g·cm^{-3}]	1.23	1.10
Space group	$P\bar{1}$	$P2_1/a$
Crystal dimensions [mm^3]	0.3 × 0.3 × 0.35	0.38 × 0.25 × 0.17
Radiation	Mo*Kα*	Cu*Kα*
μ [cm^{-1}]	1.35	12.6
Diffractometer	*Hilger-Watts Y290*	*Syntex P2$_1$*
Scan mode	$2\Theta, w$	w
Scan range [°]	1	0.9
Background measurements	1/4 of scan time at each end of scan range	1/2 of scan time at ±0.5° from the center of scan
2 Θ limits [°]	0–48	3–116
Observations, total No.	5224	5237
No. unique data $F_0^2 > 3\sigma(F_0^2)$	4159	4491
Final No. of variables	517	344
Final R, R_w	0.036	0.0574, 0.0840

Data Collection and Determination of Structures. A summary of crystal data and details concerning the measurements are given in *Table 3*.

Ligand **1b**. Cell constants from fifteen independent reflections measured on a *Syntex P2₁* diffractometer and refined by a least-square process. Monitoring of three standard reflections, measured every hundred reflections, indicated no decay during the data collection. Intensities were corrected for *Lorentz* and polarization effects. Atomic scattering factors and anomalous dispersion terms were taken from [17]. The structure was solved by direct methods with the CAOS program which takes into account also higher-order phase relationships [18]. P- and C-atoms were refined anisotropically by full-matrix least-square procedures; the function minimized was $\Sigma w(|F_0| - |F_c|)^2$ with weights of the type $w = a + F_0 + F_0^2$, where a and b are of the order of $2F_0$ (min) and $2/F_0$(max), respectively [19]. Contribution of H-atoms in fixed positions with isotropic thermal parameters of the nearest C atom (d(C–H) = 1 Å, – (C–C–H) = 109.05 or 120°). The positions of the H-atoms were updated after refinement. Convergence was reached at $R = 0.057$ ($R_w = 0.084$).

Ligand **1a**. Data collection was performed some 15 years ago. Some details, especially e.s.d.'s of the cell constants, are lost. Intensities were corrected for *Lorentz* and polarization effects. Atomic scattering factors and anomalous dispersion were taken from [17]. The structure was solved by direct methods and refined in two blocks (XRAY72 [20]), P- and C-atoms with anisotropic, H-atoms with fixed isotropic displacement parameters (B(benzo[*c*]phenanthrene) = 6.3, $B(CH_2) = 6.0$, B(Ph) = 7.8 $Å^{-2}$). The function minimized was $\Sigma(|F_0| - |F_c|)^2/\sigma^2(F_0)$. The final R value was 0.036.

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