

Fig. 2. Stereoscopic view of the unit cell in the crystal $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Tc}(\text{O})(\text{C}_6\text{H}_3\text{NO}_4)_2]$ (b axis vertical, c axis horizontal).

The average value of the N(3)—C bonds in the cation is 1.521 (8) Å, and the average angle around N(3) is 109.5 (5)°. All the values are shown in the supplementary material. The terminal C atoms have very high thermal factors, especially C(28), resulting in high standard deviations. The average C—C distance is 1.50 (1) Å, and the n -butyl chains are flattened as shown by the large angular values. The average angle N(3)—C—C is 116.2 (5)° and C—C—C of the n -butyl chains is 113.8 (8)°.

The packing of the molecules in the crystal is shown in Fig. 2. No hydrogen bonding is expected in this crystal. The n -butyl groups of the cations are arranged in a flat cross (except one terminal C atom), with the cross parallel to the base of the square pyramid.

The infrared absorption band at 983 cm^{-1} was assigned to the stretching $\nu(\text{Tc}=\text{O})$. This value can be compared to the values obtained in a series of $[\text{TcOX}_4]^-$ ions as compiled by Davison *et al.* (1987). The authors have found a slight correlation between the Tc=O bond distances and the absorption band

$\nu(\text{Tc}=\text{O})$. As the bond distance increases, the absorption band decreases in energy. When X is Cl, the Tc=O bond is 1.610 (4) Å with $\nu(\text{Tc}=\text{O})$ at 1016 cm^{-1} (Cotton, Davison, Day, Gage & Trop, 1979), while when X is S, the bond is longer (~1.67 Å) (Davison *et al.*, 1987; Rochon, Melanson & Kong 1992) and the vibration was found around 950 cm^{-1} . There is only one example where X is O and the $\nu(\text{Tc}=\text{O})$ was reported at 970 cm^{-1} with a Tc=O bond distance of 1.648 (5) Å (Davison *et al.*, 1987). We have found a bond length of 1.634 (4) Å and $\nu(\text{Tc}=\text{O})$ at 983 cm^{-1} , which is in good agreement with these authors.

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Structure of Ni^{II}, Pd^{II} and Pt^{II} Complexes with the Bidentate Ligand 2,11-Bis(diethylphosphinomethyl)benzo[*c*]phenanthrene

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Abstract. {2,11-Bis(diethylphosphinomethyl)benzo[*c*]phenanthrene-*P,P'*}dichloronickel(II), $[\text{Ni}(\text{C}_{28}\text{H}_{34}\text{P}_2)\text{Cl}_2]$, $M_r = 562.14$, orthorhombic, *Pbcn*, $a =$

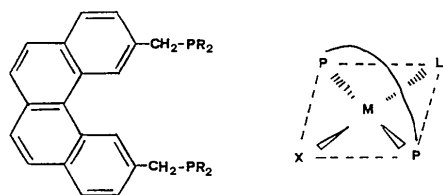
16.197 (6), $b = 16.886$ (4), $c = 9.693$ (2) Å, $V = 2651$ (1) Å³, $Z = 4$, $D_x = 1.408$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 10.7$ cm⁻¹, $F(000) = 1176$, $T =$

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295 K, final $R = 0.057$ for 969 observed unique reflections. {2,11-Bis(diethylphosphinomethyl)benzo[*c*]phenanthrene-*P,P'*}dichloropalladium(II), [Pd(C₂₈H₃₄P₂)Cl₂], $M_r = 609.83$, orthorhombic, *Pbcn*, $a = 16.256(5)$, $b = 16.847(3)$, $c = 9.844(2)$ Å, $V = 2696(1)$ Å³, $Z = 4$, $D_x = 1.504$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 10.1$ cm⁻¹, $F(000) = 1248$, $T = 295$ K, final $R = 0.055$ for 1044 observed unique reflections. {2,11-Bis(diethylphosphinomethyl)benzo[*c*]phenanthrene-*P,P'*}dichloroplatinum(II), [Pt(C₂₈H₃₄P₂)Cl₂], $M_r = 696.52$, orthorhombic, *Pbcn*, $a = 16.283(4)$, $b = 16.863(4)$, $c = 9.823(2)$ Å, $V = 2697(1)$ Å³, $Z = 4$, $D_x = 1.715$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 55.9$ cm⁻¹, $F(000) = 1376$, $T = 295$ K, final $R = 0.054$ for 1338 observed unique reflections. The three isomorphous complexes have square-planar coordinated metal atoms, with the P atoms in *trans* positions. The ligand assumes a conformation generally found in complexes with this type of ligand, based on the benzo[*c*]phenanthrene backbone, when the P—M—P angle is smaller than 160°.

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 *trans*-[MX₂(1a)] ($M = d^8$ metal, $X = \text{anion}$) in which the chelating diphosphine spans *trans* positions (DeStefano, Johnson & Venanzi, 1976). Lately, the related ligands 2,11-bis[di(*tert*-butyl)phosphinomethyl]benzo[*c*]phenanthrene, (1b) (Kapoor & Venanzi, 1977), and 2,11-bis(diethylphosphinomethyl)benzo[*c*]phenanthrene, (1c) (Baumgartner, 1980), have also been synthesized to gain additional information about the effect of electronic and steric effects on structural parameters. Thus the complexes *trans*-[MCl₂(1c)] with $M = \text{Ni}^{\text{II}}$, Pd^{II} and Pt^{II} were prepared (Baumgartner, 1980) and their crystal structures determined as it was of interest to compare differences in coordination parameters of square-planar complexes of the three metals.



(1a) $R = \text{Ph}$, (1b) $R = \text{'Bu}$, (1c) $R = \text{Et}$

Experimental. Crystals of the three isomorphous compounds were obtained from a chloroform/acetone 2:1 solution. Crystals of dimensions $0.08 \times 0.12 \times 0.25$ mm, $0.10 \times 0.12 \times 0.20$ mm and $0.08 \times 0.15 \times 0.25$ mm were used for data collection for the

Ni, Pd and Pt complexes, respectively. Syntex *P2*₁ diffractometer; graphite-monochromated Mo *K* α radiation; unit-cell dimensions determined using 15 reflections ($20 \leq 2\theta \leq 26^\circ$). 3560 (Ni complex), 3700 (Pd complex), 3785 (Pt complex) total reflections were collected with 0.8° scan range in ω -scan mode up to $\theta_{\text{max}} = 28^\circ$, and with $0 \leq h \leq 21$, $0 \leq k \leq 22$, $0 \leq l \leq 13$. Three standards (400, $\bar{1}11$, $\bar{5}\bar{5}\bar{4}$) were measured every 100 reflections and showed no significant change; data processed to yield values of I and $\sigma(I)$ (Bachechi, Zambonelli & Marcotrigiano, 1977); in the estimation of $\sigma(I)$ the uncertainty factor was $p = 0.013$, 0.005 and 0.002 as calculated from the variance of the standard reflections (McCandlish, Stout & Andrews, 1975). Corrections were made for Lorentz, polarization and shape anisotropy (North, Phillips & Mathews, 1968). Of 3560, 3700 and 3785 unique reflections, 969, 1044 and 1338 reflections were considered observed [$I > 3\sigma(I)$], for the Ni, Pd and Pt complexes, respectively. Structures solved by Patterson and Fourier methods and refined by full-matrix least squares (on F), function $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F_o)$, minimized. Heavier atoms, C(19) and the C atoms of the ethyl groups were refined with anisotropic thermal parameters; H atoms were included at calculated positions with fixed coordinates and isotropic thermal parameters. 105 parameters were refined. For Ni, Pd and Pt complexes respectively, data/parameters = 9.2, 9.9, 12.7; convergence at $R = 0.057$, 0.055, 0.054; $wR = 0.036$, 0.041, 0.071; $S = 2.39$, 2.10, 0.26; maximum $\Delta/\sigma = 0.20$, 0.12, 0.02. Final difference maps showed no peaks exceeding $0.30 \text{ e } \text{\AA}^{-3}$. All calculations performed on an HP 2100 MX minicomputer (CNR Research Area, Rome) using local programs (Cerrini & Spagna, 1977). Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic parameters of non-H atoms are given in Table 1.*

Discussion. A perspective view of *trans*-[NiCl₂(1c)] with the numbering scheme is shown in Fig. 1. A selection of bond distances and angles for the three complexes is reported in Table 2. A molecular and crystallographic twofold axis passes through the metal atom, C(17) and C(18). Among the numerous complexes of the ligands of type (1) so far studied, having distorted C_2 or C_s symmetry, the three complexes are the only ones with exact C_2 symmetry.

The square-planar coordination geometry is only slightly distorted, when compared to distortions gen-

* Lists of structure factors, anisotropic thermal parameters, bond distances and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54723 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and isotropic thermal parameters (\AA^2) for the non-H atoms with e.s.d.'s in parentheses

Ni, Pd, Pt, P, Cl, C(19) and ethyl C atoms refined anisotropically;
 $U_{eq} = (1/6\pi^2) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$.

	x	y	z	U_{eq}/U_{iso}
Ni complex				
Ni	0.00000	0.18118 (8)	0.25000	0.042 (1)
P	-0.10396 (15)	0.17685 (17)	0.10189 (22)	0.047 (1)
Cl	0.09029 (15)	0.18317 (17)	0.08500 (21)	0.064 (1)
C(1)	-0.08724 (45)	0.37146 (41)	0.18403 (71)	0.039 (3)
C(2)	-0.14793 (51)	0.33878 (42)	0.10350 (78)	0.044 (3)
C(3)	-0.18399 (50)	0.38346 (50)	-0.00493 (84)	0.057 (3)
C(4)	-0.16393 (50)	0.45971 (48)	-0.02049 (84)	0.057 (3)
C(5)	-0.09556 (52)	0.58264 (48)	0.06063 (84)	0.054 (3)
C(6)	-0.04881 (50)	0.61856 (46)	0.15173 (86)	0.061 (3)
C(13)	-0.06178 (47)	0.45318 (42)	0.16460 (78)	0.046 (3)
C(14)	-0.10762 (48)	0.49749 (52)	0.06428 (88)	0.052 (3)
C(17)	0.00000	0.49365 (60)	0.25000	0.046 (3)
C(18)	0.00000	0.57814 (62)	0.25000	0.056 (3)
C(19)	-0.17891 (48)	0.25625 (45)	0.13026 (81)	0.050 (3)
C(21)	-0.16623 (51)	0.08730 (48)	0.12603 (87)	0.062 (4)
C(22)	-0.11702 (62)	0.01140 (51)	0.10490 (120)	0.11 (1)
C(23)	-0.08039 (55)	0.18017 (53)	-0.08175 (76)	0.061 (3)
C(24)	-0.15176 (65)	0.17716 (66)	-0.17995 (92)	0.11 (1)
Pd complex				
Pd	0.00000	0.18028 (8)	0.25000	0.0388 (2)
P	-0.10878 (17)	0.17718 (19)	0.09966 (37)	0.049 (2)
Cl	0.09539 (19)	0.18302 (19)	0.07664 (36)	0.063 (2)
C(1)	-0.08824 (65)	0.37614 (67)	0.18105 (110)	0.042 (3)
C(2)	-0.14766 (74)	0.34170 (68)	0.09880 (120)	0.047 (4)
C(3)	-0.17976 (70)	0.38626 (78)	-0.00716 (125)	0.053 (4)
C(4)	-0.16025 (74)	0.46044 (75)	-0.02139 (13)	0.058 (4)
C(5)	-0.09126 (75)	0.58531 (81)	0.06696 (129)	0.056 (4)
C(6)	-0.04708 (73)	0.62101 (72)	0.15374 (134)	0.057 (4)
C(13)	-0.06333 (67)	0.45592 (68)	0.16269 (121)	0.047 (3)
C(14)	-0.10727 (71)	0.50033 (86)	0.05996 (126)	0.052 (4)
C(17)	0.00000	0.49715 (94)	0.25000	0.052 (4)
C(18)	0.00000	0.58041 (94)	0.25000	0.058 (4)
C(19)	-0.18003 (66)	0.25886 (76)	0.12779 (13)	0.05 (1)
C(21)	-0.17042 (75)	0.08765 (8)	0.12460 (138)	0.07 (1)
C(22)	-0.12126 (100)	0.01166 (87)	0.10583 (181)	0.10 (1)
C(23)	-0.08326 (73)	0.18113 (92)	-0.08517 (107)	0.059 (5)
C(24)	-0.15067 (89)	0.17819 (113)	-0.18144 (138)	0.11 (1)
Pt complex				
Pt	0.00000	0.17961 (5)	0.25000	0.0399 (2)
P	-0.10814 (33)	0.17621 (37)	0.10054 (66)	0.049 (2)
Cl	0.09506 (35)	0.18296 (36)	0.07632 (56)	0.061 (2)
C(1)	-0.08819 (106)	0.37366 (103)	0.18340 (185)	0.046 (4)
C(2)	-0.14607 (116)	0.34144 (111)	0.10212 (203)	0.053 (5)
C(3)	-0.18045 (128)	0.38347 (132)	-0.00556 (221)	0.06 (1)
C(4)	-0.16003 (122)	0.46146 (132)	-0.02296 (203)	0.062 (5)
C(5)	-0.09094 (126)	0.58609 (132)	0.06386 (212)	0.061 (5)
C(6)	-0.04638 (131)	0.61997 (129)	0.15106 (220)	0.06 (1)
C(13)	-0.06207 (98)	0.45443 (108)	0.16276 (170)	0.046 (4)
C(14)	-0.10435 (103)	0.50030 (128)	0.06499 (197)	0.05 (1)
C(17)	0.00000	0.49523 (149)	0.25000	0.05 (1)
C(18)	0.00000	0.57922 (163)	0.25000	0.07 (1)
C(19)	-0.18115 (109)	0.25832 (126)	0.13079 (232)	0.06 (1)
C(21)	-0.17130 (119)	0.08931 (131)	0.12222 (265)	0.07 (1)
C(22)	-0.12439 (180)	0.01319 (157)	0.10533 (442)	0.13 (2)
C(23)	-0.08183 (153)	0.18132 (141)	-0.08088 (183)	0.07 (1)
C(24)	-0.15198 (179)	0.17896 (194)	-0.17801 (273)	0.10 (1)

Table 2. Selected bond distances (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

	Ni	Pd	Pt
M—P	2.214 (2)	2.307 (3)	2.293 (6)
M—Cl	2.167 (2)	2.306 (3)	2.304 (6)
P—C(19)	1.829 (8)	1.82 (1)	1.85 (2)
P—C(21)	1.833 (9)	1.83 (1)	1.80 (2)
P—C(23)	1.821 (8)	1.87 (1)	1.84 (2)
C(2)—C(19)	1.50 (1)	1.52 (2)	1.54 (3)
Angles			
P—M—Cl	92.0 (1)	92.4 (1)	92.4 (2)
P—M—Cl'	88.0 (1)	87.7 (1)	87.6 (2)
P—M—P'	176.2 (1)	177.4 (1)	177.1 (3)
Cl—M—Cl'	178.2 (1)	177.7 (1)	177.2 (3)
M—P—C(19)	112.5 (3)	111.9 (4)	111.8 (7)
M—P—C(21)	111.3 (3)	110.7 (5)	112.5 (8)
M—P—C(23)	118.2 (3)	117.0 (4)	116.2 (8)
C(19)—P—C(21)	102.7 (4)	104.8 (6)	102.9 (9)
C(19)—P—C(23)	105.3 (4)	106.4 (6)	106 (1)
C(21)—P—C(23)	105.4 (4)	106.4 (6)	107 (1)
C(2)—C(19)—P	115.6 (6)	116.5 (8)	114 (1)

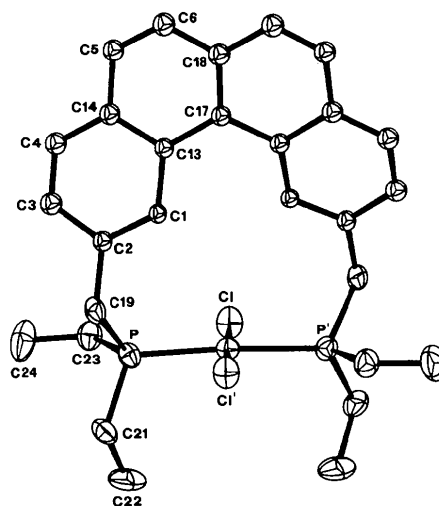


Fig. 1. Perspective view of the complex $trans\text{-}[\text{NiCl}_2(1c)]$. The ellipsoids represent 30% probability.

plexes, $trans\text{-}[\text{PtCl}_2(1c)]$ and $trans\text{-}[\text{PtClH}(1a)]$ (Bracher, Kellemerger, Venanzi, Bachechi & Zambonelli, 1988), the P—Pt—P angle is closer to 180° in the (1c) complex [$177.1(2)^\circ$] than in the (1a) complex [$176.2(1)^\circ$]. The same trend is observed in Ag complexes of the type $[\text{AgX}(1)]$, X = Cl, Br, I, NO_3 , ClO_4 . The (1c) ligand gives larger P—Ag—P angles [$164.8(1)$ and $167.6(1)^\circ$] (Camalli, Caruso, Chaloupka & Venanzi, 1988) than the (1a) ligand [$151.5(1)^\circ$] (Barrow *et al.*, 1983).

The M—P bond lengths fall on the short side of the normal range for $trans$ alkylphosphine ligands (Alcock, O'Sullivan & Parkins, 1980; Ferguson, McCrindle, McAlees & Parvez, 1982; Huffman, Laurent & Kochi, 1977; Krogsrud & Ibers, 1975) and are comparable with the shortest observed in the square-planar complexes of the ligand (1a) (Table 3). The M—Cl bond lengths fall in the range generally found for Cl $trans$ to Cl in complexes of the three

erally observed in the analogous complexes of (1a) and (1b) (Table 3). Their strong distortions were regarded as caused by the rigidity and steric bulk of this type of ligand. This different degree of distortion is particularly evident when the two analogous complexes, $trans\text{-}[\text{PdCl}_2(1c)]$ and $trans\text{-}[\text{PdCl}_2(1a)]$ (Bachechi, Zambonelli & Venanzi, 1977), are considered. In the first, the P—Pd—P and Cl—Pd—Cl angles are both very close to 180° [$177.4(1)$ and $177.7(1)^\circ$], while in the second they are $175.7(1)$ and $167.1(1)^\circ$. Considering the two strictly related com-

Table 3. Bond distances (Å) and angles (°) in the metal core of related complexes of the ligands of type (1)

	P—M—P	Cl—M—Cl	Cl—M—X	M—P	M—Cl _{trans} Cl	M—Cl	Reference
PdCl ₂ (1c)	177.4 (1)	177.7 (1)		2.307 (3)		2.306 (3)	(i)
PtCl ₂ (1c)	177.1 (2)	177.2 (2)		2.293 (6)		2.304 (6)	(i)
NiCl ₂ (1c)	176.2 (1)	178.2 (1)		2.214 (2)		2.167 (2)	(i)
PtClH(1a) ¹	176.2 (1)			2.283 (3)		2.397 (3)	(ii)
				2.278 (3)			
PdCl ₂ (1a)	175.7 (1)	167.1 (1)		2.326 (2)	2.311 (2)		(iii)
				2.322(2)	2.293 (2)		
RhCl(CO)(1a)	174.7 (1)		168.3 (2)	2.317 (3)		2.372 (1)	(iii)
				2.313 (3)			
PtCl ₂ (1a') ²	174.1 (1) ³	171.1 (1)		2.380 (1) ⁴	2.304 (2)		(iv)
				2.370 (1)	2.308 (2)		
IrCl(CO)(1a)	173.9 (2)		168.9 (2)	2.310 (4)		2.355 (4)	(v)
				2.310 (4)			
RhCl(CO)(1b)	173.0 (1)		168.5 (1)	2.366 (3)		2.399 (3)	(vi)
				2.387 (3)			
IrCl ₂ (CO)(1a) ⁵	170.7 (1)	168.9 (1)	172.0 (3)	2.403 (3)	2.357 (3)	2.371 (3)	(v)
				2.419 (3)	2.366 (3)		
RuCl ₂ (NO)(1a) ⁵	170.1 (1)	168.2 (1)	172.0 (3)	2.465 (4)	2.378 (3)	2.331 (4)	(vii)
				2.461 (4)	2.387 (4)		
RuCl(CO)(NO)(1a) ⁶	167.4 (1)			2.410 (2)			(viii)
				2.391 (2)			

Notes: (1) hydride ligand not localized; (2) (1a') = 2,11-bis(diphenylarsinomethyl)benzo[*c*]phenanthrene; (3) in this case As—M—As; (4) in this case M—As; (5) octahedral coordination; (6) trigonal bipyramidal coordination.

References: (i) This work; (ii) Bracher, Kelleberger, Venanzi, Bachechi & Zambonelli (1988); (iii) Bachechi, Zambonelli & Venanzi (1977); (iv) Balimann, Venanzi, Bachechi & Zambonelli; (v) Baumgartner, Reed, Venanzi, Bachechi, Mura & Zambonelli (1984); (vi) Bachechi, Camalli, Caruso, Mura, Ughetto, Zambonelli & Venanzi (1979); (vii) Bachechi, Mura, Zambonelli, Holderegger & Venanzi (1981); (viii) Holderegger, Venanzi, Bachechi, Mura & Zambonelli (1979).

Table 4. Geometrical parameters characterizing the conformation of ligand (1c)

	<i>trans</i> -[MCl ₂ (1c)] ¹			[Ag(ClO ₃)(1c)] ²		Conformations	
	Ni	Pd	Pt	Molecule 1	Molecule 2	<i>P</i> -type	<i>A</i> -type
ω_1 (°)	66 (1)	70 (1)	70 (2)	81	84	85	80
ω_2 (°)	-66 (1)	-66 (1)	-66 (2)	-56	-65	-70	-60
ω_3 (°)	66 (1)	70 (1)	70 (1)	-59	-49	-50	50
ω_4 (°)	-66 (1)	-66 (1)	-66 (1)	73	75	70	-75
P—M—P (°)	176.2 (1)	177.4 (1)	177.1 (2)	164.8 (1)	167.6 (1)	140–180	125–160
P...P (Å)	4.426 (3)	4.612 (4)	4.59 (1)	4.71	4.75	4.61–4.81	4.08–4.72
β (°)	31	32	32	22	18	17–27	28–36
M—P (Å)	2.214 (2)	2.307 (3)	2.292 (6)	2.377 (4)	2.389 (3)		
				2.378 (3)	2.393 (3)		

Notes: (1) $\omega_1 = \omega_3$ and $\omega_2 = \omega_4$ for *C*₂ symmetry; (2) two independent molecules in the asymmetric unit.

metals (Ferguson *et al.*, 1982). Both the M—P and the M—Cl bond lengths increase significantly on going from the 3*d* to the 4*d* derivative, but not from 4*d* to 5*d* complexes.

The benzo[*c*]phenanthrene system shows significant distortions in the three compounds, as in the parent hydrocarbon (Hirshfeld, Sandler & Schmidt, 1963), in the free ligands (1*a*) and (1*b*) (Bürgi, Murray-Rust, Camalli, Caruso & Venanzi, 1989) and in all the complexes of ligand (1). The short H...H contact in the bay region of the tetracycle can be relieved through an opening of the angles as far as 126°, and an out-of-plane distortion of the tetracycle moiety. The deviation from planarity can be measured by the angle (β) between the best planes through the C atoms of the two outer rings. On coordination in this type of bidentate ligand can assume two conformations (Bracher, Grove, Venanzi, Bachechi, Mura & Zambonelli, 1980; Burgi *et al.*, 1989), as the two CH₂—P bonds of the 12-membered ring can point to the same side of the

mean plane of the benzo[*c*]phenanthrene (*P*-type conformation) or to opposite sides (*A*-type conformation). In the *A* conformation the overcrowding in the bay region is mainly relieved by a strong deviation from planarity ($\beta = 28$ –36°). In the *P* conformation the in-plane distortion can reach the maximum values, but less deviation from planarity is allowed ($\beta = 17$ –27°). The title compounds show the *A*-type conformation, with β values of 31° in the Ni and 32° in the Pd and Pt complexes.

Other features, characteristic of each conformation and related to the prevalent type of distortion adopted, are the values of the internal torsion angles around the C—CH₂ and the CH₂—P bonds* (Table 4) and the P—M—P angle. When the P—M—P angle is greater than 160° (Table 4) the *P* conformation is assumed, when smaller than 140° the *A*

* Torsion angles are defined as $\omega_1 = [C(1)–C(2)–C(19)–P(1)]$, $\omega_2 = [C(2)–C(19)–P(1)–M]$, $\omega_3 = [C(12)–C(11)–C(20)–P(2)]$, $\omega_4 = [C(11)–C(20)–P(2)–M]$, and refer to the left-handed helix conformation of the benzo[*c*]phenanthrene backbone.

conformation is adopted (Barrow *et al.*, 1983; Barrow, Bürgi, Johnson & Venanzi, 1976; Camalli, Caruso, Chaloupka, Kapoor, Pregosin & Venanzi, 1984; Kunz, Pregosin, Camalli, Caruso & Zambonelli, 1983). Between 160–140° both conformations can be found (Barrow *et al.*, 1983; Kunz *et al.*, 1983).

In this respect the three isomorphous complexes are exceptional, since they present P—M—P angles close to 180° but assume the *A* conformation. In Table 4, torsion angles are compared with average values for *A* and *P* conformations and with the values found in the only other complex of ligand (1c) so far studied [Ag(ClO₄)(1c)] (Camalli *et al.*, 1988; *P* conformation).

The main structural difference of the three complexes from the corresponding (1a) complexes is that they have P—M—P angles closer to 180°. This feature, which seems to be favoured by the (1c) ligand, could perhaps account for the difference in conformation. Some support for this view came from calculations performed with the Tripos Force Field method (SYBYL; Tripos Associates, Inc., 1989). The crystal structure of *trans*-[PdCl₂(1c)] was examined for the *A*-type conformation. Since the transformation from *A* to *P* was not possible with minor changes of bond distances and angles, for the *P*-type conformation the similar crystal structure of *trans*-[PtClH(1a)] was chosen. The total energy of each structure was minimized constraining the P—M—P angle and the M—P distances to the values found in the X-ray study. The energy of the Pd complex, which showed strains in the bay region, was easily minimized by an increase of the β angle. In contrast, the energy of the Pt complex could be minimized only when the constraint on the P—M—P angle was relaxed. The structure was strained in the bay region and at the M—P—CH₂ angles and could be optimized by distortions not only of the hydrocarbon backbone, but also of the P—M—P angle, which tended to decrease. These results suggest that the closer the P—M—P angle is to 180°, the more the flexible *A*-type conformation is favoured, and that the P—M—P angle observed in the structure of *trans*-[PtClH(1a)] could represent the upper limit for the *P*-type conformation.

The ethyl groups are in a staggered conformation around the P—C bonds. The plane defined by P, C(21) and C(22) is nearly normal to the plane through P, C(23) and C(24) which is almost coincident with the Pt coordination plane. A similar arrangement is observed also in monodentate triethylphosphine ligands, and considered favourable for minimization of steric repulsions (Caldwell, Manojlovic-Muir & Muir, 1977; Russell, Mazis & Tucker, 1980).

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