276. Transition-Metal Complexes with Bidentate Ligands Spanning *trans*-Positions. V[1]). Crystal and Molecular Structures of Complexes [RhCl(CO)(1)] and [PdCl$_2$(1)]; 1 = 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene

by **Fiorella Bachechi** and **Luigi Zambonelli**

Laboratorio di Strutturistica Chimica «Giordano Giacomello», C.N.R., Area della Ricerca, C.P. 10, 00016 Monterotondo Stazione (Roma), Italy

and **Luigi M. Venanzi**

Laboratorium für anorganische Chemie, ETH Zürich, CH-8092 Zürich, Switzerland

(4.X.77)

Summary

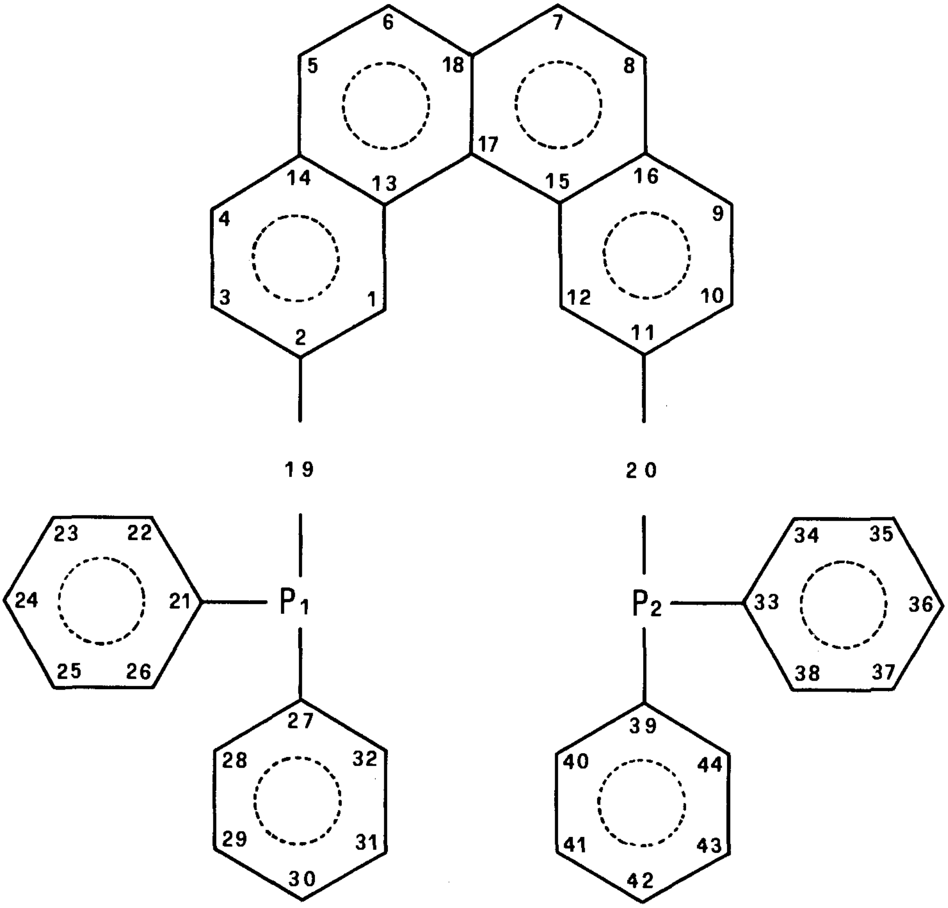
The structures of [RhCl(CO)(**1**)] and [PdCl$_2$(**1**)], where **1** is the bidentate ligand $(C_6H_5)_2P \cdot CH_2 \cdot C_{18}H_{10} \cdot CH_2 \cdot P(C_6H_5)_2$, have been determined from three-dimensional X-ray counter data collected on single crystals of the $C_6H_5 \cdot CN$ solvates. The two compounds are isomorphous and crystallize in the triclinic system, space group $P\bar{1}$, $Z=2$: $a=14.580(8)$, $b=13.029(10)$, $c=11.909(6)$ Å, $\alpha=106.33(5)$, $\beta=100.47(4)$, $\gamma=95.73(5)°$ for the rhodium complex; $a=14.361(5)$, $b=13.044(7)$, $c=11.897(4)$ Å, $\alpha=105.97(4)$, $\beta=100.27(3)$, $\gamma=94.76(4)°$, for the palladium complex. In both complexes the metal atom is four-coordinate with slightly distorted square-planar configuration. In both cases the ligand **1** spans *trans* positions with M-P bond lengths in the ranges of the literature data. Also the other bond distances fall in regular ranges. Ligand **1** has almost the same conformation in both complexes and is characterized by a strong out-of-plane deformation of the benzophenanthrene system as a consequence of severe overcrowding.

Introduction. - The bidentate ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**) easily forms mononuclear square-planar complexes [MX$_2$(**1**)] and [MX(CO)(**1**)], where M is a d^8 transition metal ion (M = Pd(II), Pt(II) [2] or Rh(I), Ir(I) [1] and X is a halide ion). These complexes show electronic and NMR. features characteristic of the square-planar complexes of these metal ions with monodentate phosphine ligands in *trans*-positions.

As these complexes are being used as models for reactions related to homogeneous catalytic processes, it was of interest to establish the detailed features of their molecular structures.

---

[1]) Part IV: see [1].



1

Furthermore, relatively few crystal structure investigations have been reported [3] [4] of mononuclear square-planar complexes containing bidentate ligands which coordinate spanning *trans*-positions. As in these compounds the two donor atoms are joined by flexible chains, structural comparisons with similar complexes containing a more rigid ligand was thought worth-while.

Discussion. - The crystal data for the complexes [RhCl(CO)(**1**)] (**2**), [PdCl$_2$(**1**)](**3**), [IrCl(CO)(**1**)] (**4**), and [PtCl$_2$(**1**)] (**5**) (see *Table 1*) show that the four compounds are strictly isomorphous and, therefore, a complete structural analysis was carried out only on complexes **2** and **3**.

The structure analyses showed that the crystals of both compounds contained one molecule of benzonitrile per molecule of complex. The two structures consist of discrete molecules of complex and benzonitrile. In each unit cell the relative positions of these two molecules are practically identical, as shown in *Figure 1*.

Table 1. *Summary of Crystal Data* (All the crystals were grown from benzonitrile solutions[a])

Compound	[RhCl(CO)(**1**)]C_6H_5CN	[IrCl(CO)(**1**)]	[$PdCl_2$(**1**)]·C_6H_5CN	[$PtCl_2$(**1**)]
Formula	$C_{52}H_{39}ClNOP_2Rh$	$C_{45}H_{34}ClIrOP_2$	$C_{51}H_{39}Cl_2NP_2Pd$	$C_{44}H_{34}Cl_2P_2Pt$
Formula-Wt.	894.19	880.4	905.1	890.70
a (Å)	14.580(8)	14.592(15)	14.361(5)	14.388(5)
b (Å)	13.029(10)	13.034(15)	13.044(7)	13.044(6)
c (Å)	11.909(6)	11.857(7)	11.897(4)	11.865(5)
α (°)	106.33(5)	106.11(8)	105.97(4)	105.91(3)
β (°)	100.47(4)	100.44(6)	100.27(3)	100.08(3)
γ (°)	95.73(5)	95.76(9)	94.76(4)	94.90(3)
V ($Å^3$)	2107.4(22)	2103.5(36)	2087.6(15)	2087.2 (15)
Dm[b]) (gcm^{-3})	1.40(1)	1.46(1)	1.35(1)	1.43(1)
Dc[b]) (gcm^{-3})	1.431	1.390	1.440	1.417
μ (Mo$K\alpha$) (cm^{-1})	5.77	35.28	6.80	37.68

[a]) A molecule of benzonitrile per molecule of complex was found during the X-ray analysis of the rhodium and palladium complexes.

[b]) Measured by flotation in $CaBr_2$ or $Cd(NO_3)_2$ solutions. Z=2 for all the crystals in the space group P$\bar{1}$ (triclinic).

Figure 2 shows the molecular structures of the two complexes. In both cases the coordination about the metal atom is distorted square-planar with the two phosphorus atoms *trans* to each other.

The distortion tends towards a tetrahedral coordination, *i.e.*, the angles P-M-P. Cl(1)-Rh-C and Cl(1)-Pd-Cl(2) are less than 180°.

The planes defined by P(1), M and Cl(1) and P(2), M and L[2]) make angles of 12.4 and 13.3° in **2** and **3** respectively. Repulsions between the Cl(1)-M-L system and benzophenanthrene part of ligand **1** may be responsible of this type of distor-

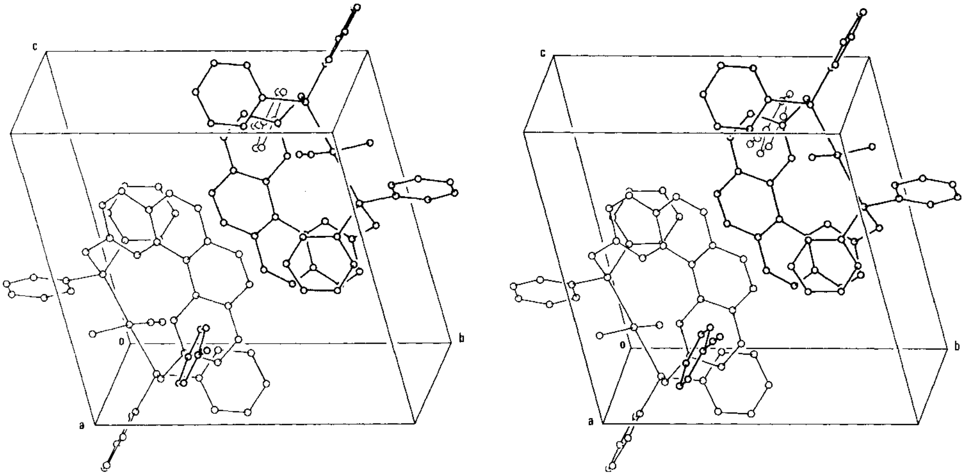


Fig. 1. *The cell contents of the benzonitrile solvates of [RhCl(CO)* (**1**)*] and [PdCl₂* (**1**)*]*

---

[2]) The symbol L represents Cl(2) in the palladium complex, and the carbon atom of the CO group in the rhodium complex.

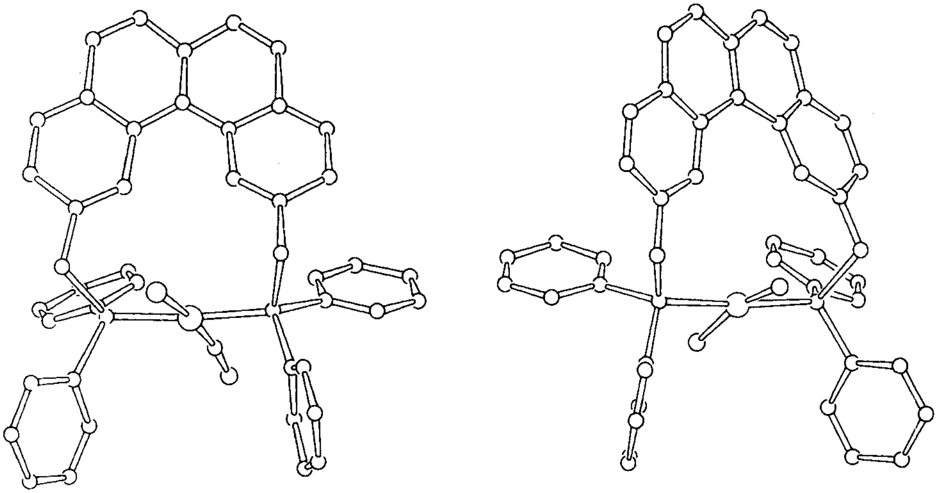


Fig. 2. *Perspective views of the molecules of [RhCl(CO)(***1***)] and [PdCl$_2$(***1***)]*

tion. In both complexes ligand **1** occurs in a conformation in which the C(19)-P(1) and C(20)-P(2) bonds point towards the same side of the approximate plane defined by the benzo[*c*]phenanthrene system (see *Figs. 2* and *3*).

The same conformation was found in the structure of the free ligand as well as in [AuCl(**1**)], while in [CuCl(**1**)] and in [AgCl(**1**)] the $-CH_2PPh_2$ groups point to opposite sides of the benzo[*c*]phenanthrene moiety [5].

In both compounds the benzophenanthrene system of the ligand is strongly deformed from planarity but this is the only distortion of the molecule that seriously breaks the molecular symmetry with respect to a mirror plane normal to the phosphorus-phosphorus axis. This mirror symmetry even extends to the phenyl rings bound to the phosphorus atoms. As can be seen in *Figure 2*, the two phenyl groups of each phosphorus atom are nearly eclipsed.

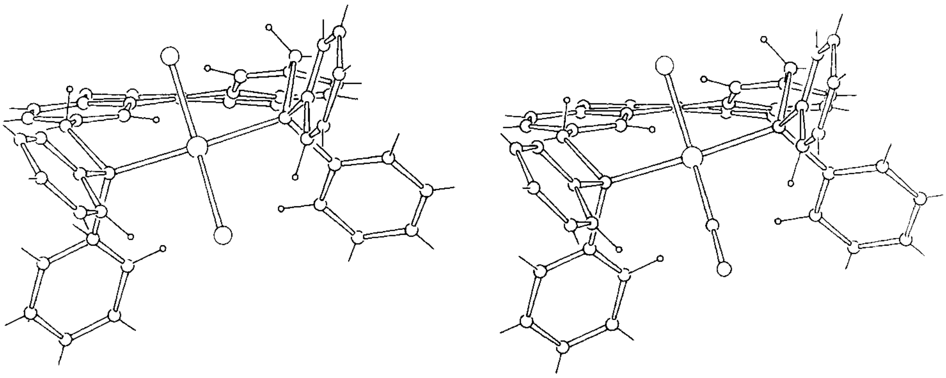


Fig. 3. *Views of the molecules of [RhCl(CO)(***1***)] and [PdCl$_2$(***1***)] projected along the direction through C(17)-C(18).* The hydrogen atoms involved in non-bonded interactions are shown, for the others only the bonds to carbon atoms are drawn

It was considered of interest to have an estimate of the magnitude of the more relevant non-bonded interactions involving hydrogen atoms. Their positions were calculated assuming sp^2-hybridization of the carbon atoms of the benzophenanthrene system of **1**. The shortest M....H contact is 2.85 Å for M–H(10) C(12) in both **2** and **3**. The short Cl....H contacts range from 2.70 to 2.90 Å, the shortest being 2.71 and 2.72 Å for Cl(1)....H(13) C(20) in **2** and **3** respectively.

The basic geometric structure of the complexes of the type [MCl(L)(**1**)] (M = Rh, Pd, Ir, Pt) is unaffected either by changing L from CO to Cl, as in the case of the rhodium and palladium complexes, or by the presence of a different metal atom, as indicated by the isomorphism of the four compounds.

Experimental Part. - *Crystal data.* Preliminary *Weissemberg* and precession photographs revealed that the crystals of the four compounds have the same diffraction pattern and belong to the same space group (triclinic, $P\bar{1}$), with practically identical cell dimensions. Cell reduction failed to detect the presence of a cell of higher symmetry. Accurate unit cell dimensions were determined from the angular positions of 15 reflections measured with a *Syntex* $P2_1$ automated diffractometer. In *Table 1* a summary of crystal data is reported.

Intensity measurement. Intensity data were collected for the rhodium and the palladium complexes by ω-scan technique on a computer controlled automatic diffractometer *Syntex* $P2_1$.

The data were processed as previously described [6]. For both compounds the ignorance factor, p, was assigned a value of 0.01 according to the variance of the standard reflections [7]. The values of I and σ(I) were corrected for *Lorentz*, polarization and shape anisotropy effects. For the latter correction the procedure described in the literature was followed [8-10]. 3861 and 4825 reflections for **2** and **3** respectively, having $Fo^2 > 3\sigma(Fo^2)$, were considered observed and used in subsequent calculations.

Structure analysis and refinement. Both structures were solved by the usual combination of *Patterson & Fourier* methods and refined by least-squares methods. The isotropic refinements converged at R = 0.090, for **2**, and R = 0.093, for **3**; anisotropic refinement led to R = 0.067 and 0.061 for the two compounds respectively. At this stage the positions of all the hydrogen atoms were estimated [11] and included in the structure factor calculations, being readjusted after each cycle of refinement. The final R indices are 0.055 (Rw = 0.046) and 0.050 (Rw = 0.045) for **2** and **3** respectively. The refinement was carried out with an eight-block approximation of the normal equations matrix. The function minimized during the refinement was $\Sigma w(|Fo| - |Fc|)^2$ with $w = 1/\sigma^2(Fo^2)$.

The scattering factors for Pd, Rh, Cl, P, O, N and C were taken from [12a] while those for H from [12b]. The anomalous terms for Pd, Rh, Cl, and P were those of *Cromer & Liberman* [12c] and were included in Fc [13].

The calculations were performed, using local programmes, on the UNIVAC 1110 computer of the University of Rome [14a] and on the HP 21MX minicomputer of the CNR. Research Area [14b].

Results. - Positional parameters for the non-hydrogen atoms are given in *Table 2*. Relevant bond lengths and angles are shown in *Table 3* and in *Figure 4*.

The Rh-P bond lengths [2.317(3) and 2.313(3) Å] are among the shortest Rh-P distances in the range (2.31-2.37) of those found in a number of Rh(I) complexes containing a *trans*-P-Rh-P unit [3] [15-19]. Rh-Cl bond of length 2.377(2) Å, Rh-CO of length 1.798(8) Å as well as C–O bond of length 1.15(1) Å compare well with the values reported for similar compounds [15, 16, 18, 20, 21].

The Pd-P bond lengths [2.326(3) and 2.322 (3) Å] are in the expected range (2.30-2.36 Å) found in Pd(II) complexes containing *trans* phosphorus ligands [22-26]. Also the mutually *trans* Pd-Cl bond lengths [2.311(2) and 2.293(2) Å] are regular [27] [28].

The benzo[*c*]phenanthrene system is strongly deformed from planarity in both compounds. This distortion is characteristic of compounds containing this aromatic system and is caused by the interaction of H(1) and H(12).

Table 2. *Positional parameters* ($\times 10^4$) *of* **2** *and* **3**. (Standard deviations are given in parentheses)

	x	*y*	*z*
Rhodium complex			
Coordination sphere			
Rh	2612(1)	616(1)	1378(1)
P(1)	3051(1)	1118(2)	-191(2)
P(2)	2315(1)	181(2)	3045(2)
Cl(1)	3886(1)	-387(2)	1420(2)
C	1509(5)	1116(7)	1148(7)
O	768(4)	1344(5)	948(6)
Benzophenanthrene system			
C(1)	4940(5)	2481(6)	2159(7)
C(2)	4750(5)	2477(7)	988(7)
C(3)	4918(5)	3468(7)	719(8)
C(4)	5324(6)	4388(7)	1617(9)
C(5)	6062(5)	5373(6)	3727(9)
C(6)	6369(5)	5348(6)	4840(9)
C(7)	6457(5)	4502(7)	6441(8)
C(8)	6184(6)	3697(7)	6871(8)
C(9)	5164(5)	2023(7)	6645(7)
C(10)	4475(5)	1177(7)	5981(7)
C(11)	4068(5)	1057(6)	4765(7)
C(12)	4391(5)	1806(6)	4257(7)
C(13)	5307(5)	3450(6)	3137(8)
C(14)	5543(5)	4404(7)	2824(8)
C(15)	5147(5)	2680(6)	4902(7)
C(16)	5495(5)	2788(6)	6112(7)
C(17)	5523(5)	3512(6)	4413(7)
C(18)	6120(5)	4432(6)	5222(8)
Methylene groups			
C(19)	4339(5)	1443(6)	-13(7)
C(20)	3344(5)	48(6)	4081(7)
Phenyl groups			
C(21)	2671(4)	2333(6)	-462(7)
C(22)	2651(5)	2532(7)	-1562(7)
C(23)	2454(5)	3501(8)	-1707(8)
C(24)	2261(6)	4305(7)	-769(10)
C(25)	2261(6)	4097(7)	287(8)
C(26)	2465(5)	3138(6)	454(7)
C(27)	2634(5)	67(6)	-1613(7)
C(28)	3229(6)	-459(7)	-2302(7)
C(29)	2845(7)	-1277(7)	-3388(8)
C(30)	1882(7)	-1559(7)	-3746(8)
C(31)	1280(6)	-1071(7)	-3097(8)
C(32)	1667(5)	-263(7)	-2028(7)
C(33)	1576(5)	-1149(5)	2610(6)
C(34)	1920(5)	-2049(7)	2826(7)
C(35)	1340(6)	-3055(6)	2443(8)
C(36)	423(6)	-3173(7)	-1816(8)
C(37)	77(5)	2275(7)	1607(8)
C(38)	659(5)	-1273(6)	1990(7)
C(39)	1695(5)	1066(6)	4019(7)
C(40)	1679(5)	2125(6)	4028(7)
C(41)	1245(6)	2800(7)	4801(8)
C(42)	815(6)	2421(7)	5593(8)
C(43)	839(6)	1375(7)	5619(7)
C(44)	1282(5)	697(6)	4837(7)
Benzonitrile molecule			
C(45)	632(6)	6269(8)	7762(11)
C(46)	1174(10)	5892(8)	7008(10)
C(47)	2085(11)	6227(12)	7305(14)
C(48)	2491(7)	6948(12)	8352(17)
C(49)	1968(10)	7386(8)	9125(11)
C(50)	1014(9)	7034(9)	8847(11)
C(51)	-339(9)	5895(12)	7371(15)
N	-1150(8)	5620(11)	7128(15)
Palladium complex			
Coordination sphere			
Pd	2611(0)	655(0)	1398(1)
P(1)	3032(1)	1162(1)	-192(2)
P(2)	2305(1)	212(1)	3071(2)
Cl(1)	3886(1)	-315(1)	1442(2)
Cl(2)	1158(1)	1254(1)	1085(2)
Benzophenanthrene system			
C(1)	4946(4)	2503(4)	2134(6)
C(2)	4738(4)	2478(5)	951(6)
C(3)	4889(4)	3428(6)	622(7)
C(4)	5305(4)	4340(6)	1536(7)
C(5)	6053(4)	5327(5)	3659(7)
C(6)	6362(4)	5316(5)	4769(7)
C(7)	6442(4)	4470(5)	6389(6)
C(8)	6181(4)	3690(6)	6840(6)
C(9)	5151(5)	2038(5)	6624(6)
C(10)	4463(5)	1193(5)	5991(6)
C(11)	4069(4)	1071(5)	4766(5)
C(12)	4396(4)	1823(5)	4258(5)
C(13)	5308(4)	3438(5)	3095(6)
C(14)	5540(4)	4385(5)	2758(7)
C(15)	5141(4)	2680(5)	4877(6)
C(16)	5492(4)	2792(5)	6101(6)
C(17)	5512(4)	3487(5)	4363(6)
C(18)	6112(4)	4407(5)	5161(6)
Methylene groups			
C(19)	4334(4)	1450(5)	-45(6)
C(20)	3359(4)	66(5)	4098(5)

Table 2 continued

	x	*y*	*z*
Phenyl groups			
C(21)	2638(4)	2382(5)	-444(5)
C(22)	2599(4)	2579(5)	-1536(6)
C(23)	2400(5)	3568(6)	-1663(7)
C(24)	2232(5)	4355(6)	-721(8)
C(25)	2260(5)	4166(5)	368(7)
C(26)	2473(4)	3187(5)	507(6)
C(27)	2606(4)	108(5)	-1590(5)
C(28)	3191(5)	-412(5)	-2296(6)
C(29)	2812(6)	-1222(6)	-3345(7)
C(30)	1838(6)	-1508(6)	-3701(6)
C(31)	1221(5)	-1009(5)	-3004(6)
C(32)	1603(5)	-216(6)	-1967(6)
C(33)	1587(4)	-1106(5)	2617(5)
C(34)	1922(4)	-1993(5)	2882(6)
C(35)	1349(5)	-2992(5)	2491(7)
C(36)	441(5)	-3094(5)	1813(7)
C(37)	98(4)	-2226(6)	1535(6)
C(38)	668(4)	-1230(5)	1919(6)
C(39)	1685(4)	1091(5)	4055(5)
C(40)	1677(4)	2149(5)	4078(6)
C(41)	1243(5)	2839(5)	4871(6)
C(42)	798(5)	2459(6)	5640(6)
C(43)	812(5)	1399(6)	5629(6)
C(44)	1248(5)	723(5)	4847(6)
Benzonitrile molecule			
C(45)	599(5)	6244(7)	7667(8)
C(46)	1279(8)	5946(6)	7047(8)
C(47)	2205(9)	6432(10)	7531(12)
C(48)	2413(6)	7172(10)	8593(13)
C(49)	1746(9)	7454(7)	9182(8)
C(50)	824(7)	7014(8)	8727(9)
C(51)	-338(8)	5705(10)	7099(13)
N	-1115(8)	5324(11)	6725(14)

[a] For the numbering scheme of the atoms of the benzophenanthrene system see *Figure 5*. Coefficients b_{ij} are defined by the expression $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$

Table 3. *Selected bond distances (Å) and angles (°) in the two complexes* **2** *and* **3**[a])

	2	**3**		**2**	**3**
M-P(1)	2.317(3)	2.326(2)	P(1)-M-P(2)	174.7(1)	175.7(1)
M-P(2)	2.313(3)	2.322(2)	P(1)-M-Cl(1)	88.6(1)	89.2(1)
M-Cl(1)	2.377(2)	2.311(2)	P(1)-M-L	92.1(4)	91.7(1)
M-L	1.798(8)	2.293(2)	P(2)-M-Cl(1)	88.4(1)	88.7(1)
C-O	1.150(10)		P(2)-M-L	91.7(4)	91.3(1)
P(1)-C(19)	1.842(7)	1.844(6)	Cl(1)-M-L	168.3(2)	167.1(1)
P(1)-C(21)	1.821(8)	1.815(6)	M-C-O	174.0(7)	
P(1)-C(27)	1.807(7)	1.808(8)	M-P(1)-C(19)	113.9(3)	113.4(2)
P(2)-C(20)	1.818(8)	1.827(7)	M-P(1)-C(21)	117.6(3)	117.4(2)
P(2)-C(33)	1.829(7)	1.817(7)	M-P(1)-C(27)	112.3(3)	111.4(2)
P(2)-C(39)	1.825(8)	1.811(6)	C(19)-P(1)-C(21)	101.0(4)	101.5(3)
C(2)-C(19)	1.507(9)	1.513(12)	C(19)-P(1)-C(27)	105.9(4)	105.8(3)
C(11)-C(20)	1.521(9)	1.519(10)	C(21)-P(1)-C(27)	104.8(4)	106.1(3)
			M-P(2)-C(20)	115.7(3)	115.1(2)
			M-P(2)-C(33)	111.0(3)	110.0(2)
			M-P(2)-C(39)	118.3(3)	118.8(2)
			C(20)-P(2)-C(33)	103.2(4)	103.5(3)
			C(20)-P(2)-C(39)	103.4(3)	102.9(3)
			C(33)-P(2)-C(39)	103.6(3)	105.1(3)
			C(2)-C(19)-P(1)	111.5(5)	110.4(4)
			C(11)-C(20)-P(2)	118.2(6)	117.5(4)

[a] L = C in **2**; L = Cl(2) in **3**.

In *Table 4* some relevant features are reported which give a measure of the deformation of the group in the two complexes. A similar deformation was found for the structure of **1** [29] and for the structure of benzo[*c*]phenanthrene [30] [31].

Table 4. *Distortion evaluation of the benzophenanthrene system*[a])

a) Atomic displacements from the best plane through C(6), C(7), C(17), C(18)

	2	3
C(1)	−0.57	−0.55
C(2)	−0.73	−0.69
C(3)	−0.53	−0.50
C(4)	−0.26	−0.24
C(5)	0.03	0.03
C(6)	0.00	0.00
C(7)	0.00	0.00
C(8)	0.09	0.08
C(9)	0.48	0.48
C(10)	0.71	0.71
C(11)	0.76	0.74
C(12)	0.55	0.54
C(13)	−0.20	−0.19
C(14)	−0.12	−0.11
C(15)	0.23	0.23
C(16)	0.25	0.25
C(17)	0.00	0.00
C(18)	−0.01	−0.01

b) Torsion angles

	2	3
C(1)-C(13)-C(17)-C(15)	− 18.8(9)	− 18.4(9)
C(13)-C(17)-C(15)-C(12)	− 12.4(12)	− 11.6(11)
C(5)-C(6)-C(18)-C(7)	−177.6(8)	−177.5(9)
C(6)-C(18)-C(7)-C(8)	174.8(8)	174.9(8)

[a]) This description of the out-of-plane deformation is arbitrary.

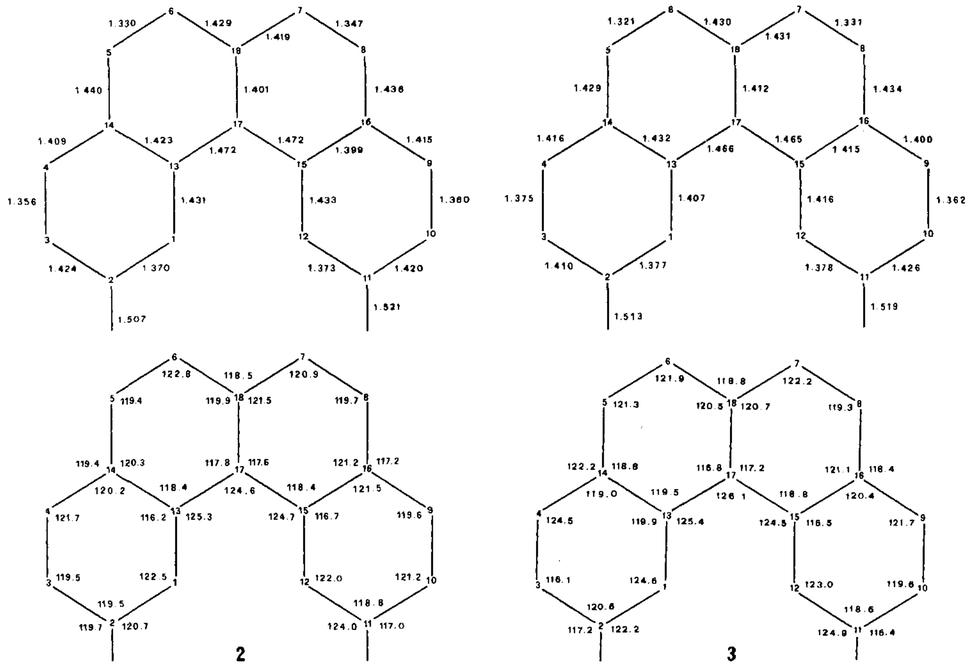


Fig. 4. *Bond lengths* (Å) *and angles* (°) *of the benzophenanthrene system in [RhCl(CO)*(**1**)*] and [PdCl$_2$*(**1**)*].* Standard deviations on bond lengths range between 0.009 and 0.014 Å; standard deviations on bond angles range between 0.5 and 0.8°.

Bond distances and angles for the aromatic tetranuclear group are reported in *Figure 4*. These data compare well with those found in the structure of benzo[*c*]-phenanthrene [30] and show trends in agreement with the theory which predicts that the bond lengths should vary over a range in different parts of a condensed aromatic hydrocarbon [32] [33]. In both complexes chirality arises from the out-of-plane distortion of the overcrowed tetranuclear system of **1**. The optically active complex, in both cases, is present in the crystal in the racemic form, the two configurations being related by the centre of symmetry.

In both compounds the benzonitrile molecule fills a crystal cavity and its heavy atoms are at distances greater than 4 Å from other heavy atoms.

REFERENCES

[1] *F. J. S. Reed & L. M. Venanzi,* Helv. *60,* 2804 (1977).
[2] *N. J. De Stefano, D. K. Johnson & L. M. Venanzi,* Helv. *59,* 2683 (1976).
[3] *F. C. March, R. Mason, K. M. Thomas & B. L. Shaw,* Chem. Commun. *1975,* 584.
[4] *N. W. Alcock, J. M. Brown & J. C. Jeffery,* Chem. Commun. *1974,* 829.
[5] *M. Barrow, H. B. Bürgi, D. K. Johnson & L. M. Venanzi,* J. Amer. chem. Soc. *98,* 2356 (1976).
[6] *F. Bachechi, L. Zambonelli & G. Marcotrigiano,* J. cryst. Mol. Structure, in press.
[7] *L. E. McCandlish, G. H. Stout & L. C. Andrews,* Acta crystallogr. *A 31,* 245 (1975).
[8] *I. C. Furnas,* Single Crystal Orienter Instruction Manual Milwakee: General Electric Company 1957.
[9] *A. C. T. North, D. C. Phillips & F. Scott Mathews,* Acta crystallogr. *A 24,* 351 (1968).
[10] *R. Spagna & L. Zambonelli,* J. chem. Soc. *(A) 1971,* 2544.
[11] C–H = 1.0 Å, C–C–H = 120°(sp^2), H–C–H = 109.5°(sp^3), dihedral angle 90°, B(H) = 3.0 Å^2.
[12] (a) *D. T. Cromer & J. T. Waber,* International Tables for X-ray Crystallography vol. IV, Kynoch Press, Birmingham, 1974, Table 2.2A; (b) *R. F. Stewart, E. R. Davidson & W. T. Simpson,* ibid., Table 2.2C; (c) *D. T. Cromer & D. Liberman,* ibid., Table 2.3.1.
[13] *J. A. Ibers & W. C. Hamilton,* Acta crystallogr. *17,* 781 (1964).
[14] (a) *J. R. Carruthers & R. Spagna,* Ital. crystallogr. Assoc. 7th Meet., Abstracts, *1975,* 65. (b) *S. Cerrini & R. Spagna,* J. Appl. Crystallogr. in the press.
[15] *J. L. De Boer, D. Rogers, A. C. Skapski & P. G. H. Troughton,* Chem. Commun. *1966,* 756.
[16] *R. Schlodder & J. A. Ibers,* Inorg. Chemistry *13,* 2870 (1974).
[17] *A. J. Gusev & Yu. T. Struchkov,* Ž. Strukt. Chim. *15,* 282 (1974).
[18] *S. J. La Placa & J. A. Ibers,* J. Amer. chem. Soc. *85,* 3501 (1963).
[19] *P. Singh, C. B. Dammaun & D. J. Hodgson,* Inorg. Chemistry *12,* 1335 (1973).
[20] *Z. G. Aliev, L. O. Atovmyan & V. J. Ponomarev,* Ž. Strukt. Chim. *14,* 748 (1973).
[21] *T. E. Nappier jr., D. W. Meek, R. M. Kirchmer & J. A. Ibers,* J. Amer. chem. Soc. *95,* 4194 (1973).
[22] *T. Debaerdemaeker, A. Kutoglu, G. Schmid & L. Weber,* Acta crystallogr. *B29,* 1283 (1973).
[23] *D. L. Weaver,* Inorg. Chemistry *9,* 2250 (1970).
[24] *S. Jacobson, Y. S. Wang, P. C. Chied & A. J. Carty,* Chem. Commun. *1974,* 520.
[25] *K. M. Chui & H. M. Powell,* J. chem. Soc. Dalton *1974,* 1879 and 2117.
[26] *P. Groth,* Acta chem. Scand. *24,* 2785 (1970).
[27] *R. H. B. Mais, P. G. Owston & A. M. Wood,* Acta crystallogr. *B28,* B93 (1972).
[28] *M. G. Miles, M. B. Hursthouse & A. G. Robinson,* J. Inorg. nuclear Chemistry *33,* 2015 (1971).
[29] *J. Murray-Rust & H. B. Bürgi,* to be published.
[30] *F. L. Hirshfeld, S. Sandler & G. M. J. Schmidt,* J. chem. Soc. *1963,* 2108.
[31] *F. L. Hirshfeld, S. Sandler & G. M. J. Schmidt,* J. chem. Soc. *1963,* 2126.
[32] *G. Ferguson & J. M. Robertson,* 'Advances in Physical Organic Chemistry' vol. 1, Ed. V. Gold, Academic Press, London 1963, p. 203.
[33] *L. Pauling,* 'The Nature of the Chemical Bond', 3rd Edition, Cornell University Press, New York 1960, p. 232.