269. Transition Metal Complexes with the Bidentate Ligand 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (1). X[1]). Preparation and Spectroscopic Properties of *cis*-[$PtCl_2$(1)] *trans*- and *cis*-[PtH(PPh_3)(1)] [BF_4] and Crystal and Molecular Structure of *cis*-[$PtCl_2$(1)] · $CHCl_3$

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Summary

It is shown that ligand **1**, designed to span *trans*-positions, under appropriate conditions also gives *cis*-mononuclear complexes of platinum(II). The structure of *cis*-[$PtCl_2$ (**1**)] (**2**) has been determined by single-crystal X-ray diffraction. The major distortion from square planar coordination is the P-Pt-P angle of 104.8°. Values of valence angles within the bidentate ligand indicate that this part of the molecule is very strained. Two phenyl groups, one on each phosphorus, lie almost parallel to each other separated by *ca.* 3.2-3.3 Å. The ^{1}H-NMR. data for this compound show that the π-phenyl interactions observed in the solid state occur also in solution. The preparation and NMR.-spectroscopic properties of *trans*- and *cis*-[PtH(PPh_3) (**1**)] [BF_4] are reported.

Introduction. - The ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene (**1**) was originally designed to cause the preferential formation of square planar complexes of the type *trans*-[MX_2(**1**)] in which the chelating phosphine ligand spans *trans*-positions [2]. A systematic study of the coordinating properties of this ligand soon revealed that it did induce some preference towards the formation of square planar complexes [3], but that it gave pseudo-tetrahedral coordination with cobalt (II) [4] and distorted trigonal coordination in complexes [MCl(**1**)] (M = Cu and Ag) [5]. Examination of molecular models indicated that while a P-M-P bond angle of 180° was optimal, smaller values of this angle were possible and a value of 131.9° was observed in [CuCl(**1**)]. The P-Co-P bond angle in [$CoCl_2$(**1**)] could not be determined as single crystals suitable for X-ray diffraction

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

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of this complex were not obtained. It also appeared that a *cis*-planar geometry in complexes of the type [MX_2(**1**)] was quite unlikely in view of the significant distortions of the organic framework that would be required to accomodate this type of coordination. The study of olefin-insertion reactions on the complex *trans*-[PtH(acetone)(**1**)] [BF_4] [6] and of the reactions of complexes [PtL(**1**)] (L = alkene or PR_3) [7] showed, however, that under suitable circumstances, complexes in which the two P-atoms of ligand **1** occupy *cis*-positions in a square planar complex could be obtained. These compounds, their structures and some of their properties are described below.

The complex *cis*-[PtCl$_2$ (*1*)]. - This was obtained from the reactions shown below:

$$1.\ [\mathrm{Pt}(1{,}5-C_8H_{12})_2]+C_2H_4+(\mathbf{1}) \rightarrow \{\mathbf{A}\} \xrightarrow{HCl_{gas}} (\mathbf{2})$$

$$2.\ trans\text{-}[\mathrm{PtHCl}(\mathbf{1})]+\mathrm{Ag}[BF_4]+CH_2{=}CH-CO_2Me \rightarrow \{\mathbf{B}\} \xrightarrow{HCl_{gas}} (\mathbf{2})$$

Intermediate **A** has been identified as [Pt(C_2H_4) (**1**)] [7] and intermediate **B** has been formulated as *cis*-[$\overline{\mathrm{Pt(CH_2CH_2CO}}$OMe) (**1**)] [$BF_4$] [6]. Full characterization of **2** was hindered by its low solubility and inconsistent microanalyses, later ascribed to the incorporation of varying amounts of solvent in the crystal lattice. The *cis*-coordination of ligand **1** in complex **2** was, however, indicated by its ^{31}P-NMR. spectrum which showed a value of ^1J(Pt, P) of 3611 Hz (see *Table 1*), *i.e.* in the range which is diagnostic for *cis*-geometry [8], and two infrared bands, at 315 and 290 cm^{-1}, characteristic for *cis*-[$PtCl_2(R_3P)_2$] [9]. To confirm the formulation of complex **2** a single-crystal X-ray diffraction study was undertaken and the solid-state structure used as a model for the interpretation of the 360-MHz-^{1}H-NMR. data of this complex.

A selection of bond lengths and angles is given in *Table 2* and a diagram of the molecular structure of the complex with the numbering scheme is given in *Figure 1.*

Table 1. *^{31}P-NMR. Chemical Shifts.* δ (ppm), *and Coupling Constants,* J*(Hz), for Complexes* cis- *and* trans-*[PtCl$_2$(1)]* (**2**) *and* (**3**), cis- *and* trans-*[PtCl$_2$(PPh$_3$)$_2$]* (**4**) *and* (**5**), cis- *and* trans-*[PtH(PPh$_3$) (1)] [BF$_4$]* (**6**) *and* (**7**), *and [PtH(PPh$_3$)$_3$] [BF$_4$]* (**8**)

Compound	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)[a])	(**7**)[a])	(**8**)[a])
Solvent	CD_2Cl_2	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	d^6-acetone	$CDCl_3$
δP_A	4.8	16.7	14.3	20.1	18.4	18.8	22.8
$^1J(Pt,P_A)$	3611	2581	3671	2637	2797	2730	2819
δP_B					26.7	18.8	22.8
$^1J(Pt,P_B)$					3000	2730	2819
δP_C					6.1	21.5	23.1
$^1J(Pt,P_C)$					2170	2174	2219
$^2J(P_A,P_B)$					338	[b])	[b])
$^2J(P_B,P_C)$					15	18	18.5
$^2J(P_A,P_C)$					18	18	18.5

[a]) The labelling of the P-atoms is as follows: P_A and P_B are mutually *trans* and therefore *cis* to the hydride ligand. In compounds **6** and **7** PPh_3 corresponds to P_B and P_C respectively.

[b]) Not determined.

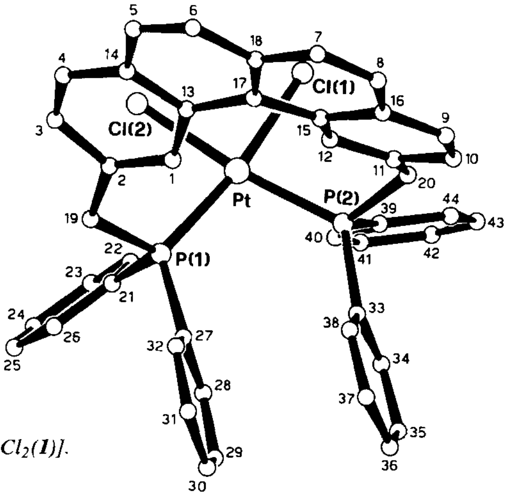

Fig. 1. *View of the molecule* cis-*[PtCl$_2$(1)].*

The crystals are built of discrete monomeric molecules of the complex and chloroform. A calculation of all intermolecular distances <4.0 Å indicates that the interactions between the molecules are of the *van der Waals* type.

The molecule of the complex adopts a *cis*-square planar configuration. The Pt-, Cl- and P-atoms are nearly coplanar and the best plane through them [$5.61(6)x - 1.37(5)y - 12.01(1)z = -0.93(1)$, triclinic coordinates] is assumed as the coordination plane. The lengths of the *trans*-related Pt–Cl and Pt–P bonds [average values: 2.353(2) and 2.255(2) Å respectively] and the size of the angle Cl-Pt-Cl [87.1°] agree with other observations [10–12].

The mutually *cis* Pt–P bonds subtend a rather large angle [104.8(1)°] at the metal; this is likely to be a result of the geometrical requirements of ligand **1**.

The present complex represents the first case in which ligand **1** spans *cis*-positions. However, besides the P-Pt-P angle, other valence angles strongly deviate from regular values, *e.g.* C(1)-C(2)-C(19) and C(12)-C(11)-C(20) which average 125.1°, the angles at C(19) and C(20) which average 119.6°, and Pt-P(1)-C(27) and Pt-P(2)-C(33) which average 124.8°. All these values, which are much larger than expected, plus the marked out-of-plane distortion of the tetranuclear aromatic system, indicate that the bidentate ligand in *cis*-[PtCl$_2$(**1**)] (**2**) is very strained.

An interesting feature of the structure is the interaction between the Ph(2) (C(27)-C(32)) and Ph(3) (C(33)-C(38)) phenyl groups. These two phenyl rings face each other (the dihedral angle between their planes is 4.3°) and give rise to numerous short distances, 3.2 ÷ 3.3 Å, of C...C and C...H types. Such non-bonded intramolecular C...H contacts between phenyl rings are regarded as important in stabilizing the conformation of many organic molecules [13] [14] and may help to stabilize the *cis*-configuration of complex **2**.

One interesting feature is the relationship between the P-M-P bond angle and the corresponding conformation of the chelate ring. For this purpose the observed structures of complexes containing **1** can be separated into those which have the P-M-P angle near to 180° and those in which this angle is much smaller (<150°).

Table 2. *Selection of bond lengths* (Å) *and angles* (°) (Standard deviations are given in parentheses)

Bond lengths		*Interbond angles*	
Pt-P(1)	2.253 (3)	P(1)-Pt-P(2)	104.8 (1)
Pt-P(2)	2.256 (2)	P(1)-Pt-Cl(1)	170.8 (1)
Pt-Cl(1)	2.358 (3)	P(1)-Pt-Cl(2)	83.7 (1)
Pt-Cl(2)	2.347 (2)	P(2)-Pt-Cl(1)	84.4 (1)
P(1)-C(19)	1.855 (8)	P(2)-Pt-Cl(2)	170.4 (1)
P(1)-C(21)	1.827 (4)	Cl(1)-Pt-Cl(2)	87.1 (1)
P(1)-C(27)	1.821 (6)	Pt-P(1)-C(19)	111.6 (4)
P(2)-C(20)	1.852 (9)	Pt-P(1)-C(21)	110.8 (4)
P(2)-C(33)	1.826 (6)	Pt-P(1)-C(27)	124.3 (2)
P(2)-C(39)	1.830 (5)	C(19)-P(1)-C(21)	102.8 (3)
C(2)-C(19)	1.505 (11)	C(19)-P(1)-C(27)	103.3 (4)
C(11)-C(20)	1.506 (10)	C(21)-P(1)-C(27)	111.0 (3)
C-Cl(3)	1.676 (13)	Pt-P(2)-C(20)	113.7 (2)
C-Cl(4)	1.703 (16)	Pt-P(2)-C(33)	125.2 (3)
Cl-Cl(5)	1.649 (12)	Pt-P(2)-C(39)	107.4 (2)
		C(20)-P(2)-C(33)	101.8 (4)
		C(20)-P(2)-C(39)	103.7 (4)
		C(33)-P(2)-C(39)	102.7 (3)
		C(2)-C(19)-P(1)	119.1 (7)
		C(11)-C(20)-P(2)	120.0 (7)
		Cl(3)-C-Cl(4)	112.1 (9)
		Cl(3)-C-Cl(5)	113.2 (8)
		Cl(4)-C-Cl(5)	116.2 (8)

Compounds in the former group are *trans*-[PdCl$_2$(**1**)], P-Pd-P = 175.7(1)° [18]; *trans*-[RhCl(CO)(**1**)], P-Rh-P = 174.7 (1)° [18]; [AuCl(**1**)], P-Au-P = 175.7(1)° [5]; [IrCl$_3$(CO) (**1**)], P-Ir-P = 170.7(1)° [19]; [RuCl(CO)(NO)(**1**)], P-Ru-P = 167.4 (1)° [16] and *trans*-[PtHCl(**1**)], P-Pt-P = 176.2 (1)° [20]. In these ligand **1** has a conformation characterized by having the two methylene-phosphorus bonds, C(19)-P(1) and C(20)-P(2), oriented in the same direction with respect to the tetranuclear part of the ligand; the torsion angles C(1)-C(2)-C(19)-P(1), C(2)-C(19)-P(1)-M, C(12)-C(11)-C(20)-P(2) and C(11)-C(20)-P(2)-M are about 85, −70, −45 and 70°, respectively.

The other group, *i.e.*, the complexes in which the P-M-P angle is less than 150°, is exemplified by [CuCl(**1**)], P-Cu-P = 131.9 (1)° [5]; [AgCl(**1**)], P-Ag-P = 140.77 (4)° [5]; and [HgCl$_2$(**1**)] P-Hg-P = 125.6 (3)° [21]. In these ligand **1** assumes conformations characterized by the two methylene-phosphorus bonds pointing in opposite directions with respect to the tetranuclear part of the ligand. The torsion angles C(1)-C(2)-C(19)-P(1), C(2)-C(19)-P(1)-M, C(12)-C(11)-C(20)-P(2) and C(11)-C(20)-P(2)-M are about 85, −60, 50 and −75°, respectively.

In both conformations the orientation of phenyl groups may differ, depending on the crowding of the other ligands. Looking at the molecule along the P(1)...P(2) direction, the phenyl groups of the first type appear almost eclipsed, the dihedral angles C(19)-P(1)...P(2)-C(20) being small, while those of the second kind appear staggered and the dihedral angles C(19)-P(1)...P(2)-C(20) are close to 70°.

The conformation assumed by **1** in the complex *cis*-[PtCl$_2$(**1**)] (**2**), P-Pt-P = 104.8 (1)°, is different from both groups previously considered. Here the two

Table 3. *^1H-NMR. Chemical shifts,* δ(ppm), *and Coupling Constants,* $J_{x,y}$*(Hz), for Compounds* cis-*[$PtCl_2(1)$]* (**2**), trans-*[$PtCl_2(1)$]* (**3**) *and* cis-*[$PtCl_2(PPh_3)_2$]* (**4**) *in CD_2Cl_2.* (The indices on the H-atoms correspond to those of the corresponding C-atoms in *Figure 1*)

	(2)	(3)	(4)
$\delta(H_{1,12})$	10.30	10.47	
$\delta(H_{3,10})$	7.28	6.98	
$\delta(H_{4,9})$	7.97	7.86	
$J(H_{3,10}, H_{4,9})$	8	8	
$\delta(H_{5,6,7,8})$	7.97, 7.92	7.92, 7.87	
$J(H_{5,8}, H_{6,7})$	8	9	
Other 'aromatic' resonances	8.09÷6.56	7.95÷6.93	7.53÷7.16
	δPh_{ortho} δPh_{meta} δPh_{para}	δPh_{ortho} δPh_{meta} δPh_{para}	δPh_{ortho} δPh_{meta} δPh_{para}
	2Ph 8.02 7.58 7.54	*4Ph* 7.61 7.37 7.46	*6Ph* 7.48 7.21 7.37
	$J_{o,P} = 11$	$J_{o,m} = 7$	$J_{o,m} = 6$
	2Ph 6.74 6.65 7.02	$J_{o,P} = 12$	$J_{o,P} = 11$
	$J_{o,m} = 7$	$J_{m,p} = 7$	$J_{m,p} = 7.5$
	$J_{o,P} = 8.5$		
	$J_{m,p} = 7.5$		
$\delta(H_{19,20})$	5.09, 3.65 $^3J(H,Pt) = 49$	4.34 $^3J(H,Pt) = 28.2$	
	$^2J(H,H) = 13$ Hz; $^2J(H,P) = 19$	$\lvert ^2J(H,P) + ^4J(H,P) \rvert = 10$	

methylene-phosphorus bonds point in opposite directions, although the dihedral angle C(19)-P(1)...P(2)-C(20) is small [11.1(6)°] and the phenyl groups are almost eclipsed. The torsion angles C(1)-C(2)-C(19)-P(1), C(2)-C(19)-P(1)-M, C(12)-C(11)-C(20)-P(2) and C(11)-C(20)-P(2)-M have values of −28.9 (13), −37.3 (7), −39.8 (13) and 59.2 (7)° respectively.

Given the steric strain present in the structure of complex **2** and its tendency to rearrange to its *trans*-isomer (**3**) [6], one must conclude that the *cis*-arrangement of phosphorus donors is the result of pathways by which **2** is formed. In view of the structural consideration on the preferential conformations of ligand **1** in complexes of different geometries, it is also likely that intermediates **A** and **B** have P-M-P bond angles less than 180° and, therefore, ring conformations in which the two methylene-phosphorus bonds point in opposite directions with respect to the tetranuclear part of the ligand. Thus, it can be supposed that, if the formation of **2** is rapid relative to the rate of rearrangement of the methylene-phosphorus bonds, the staggered configuration of these two bonds in **A** and **B** would not allow the formation of a square planar species with the two P-atoms spanning *trans*-positions. The four-coordinate product would then have *cis*-geometry.

The out-of-plane distortion of the benzo[*c*]phenanthrene nucleus confers chirality to complex **2** which, in the crystal, is present as a racemate, the two enantiomers being related by a crystallographic centre of symmetry. The asymmetry which is apparent in *Figure 1*, is not detected in the ^1H-NMR. spectrum of this complex. Thus, in solution there is no indication of magnetic inequivalence of the protons H−C(1) and H−C(12) which give a single distinctive low-field signal at 10.30 ppm. This situation is repeated for the rest of the ligand atoms such that, on the NMR. time scale, there is an effective mirror-plane through C(18), C(19) and Pt. Since this dynamic equivalence has been commented upon elsewhere [1], discussion here will be limited to just one half of the molecule and may be considered as applying equally to the mirror-related half unless otherwise stated. The ^{1}H-NMR. data for complex **2** together with those of *trans*-[PtCl$_2$(**1**)] (**3**) and *cis*-[PtCl$_2$(PPh$_3$)$_2$] (**4**) are given in *Table 3.*

The protons H–C(5) and H–C(6) (δ=7.97, 7.92) and H–C(3) and H–C(4) (δ=7.28, 7.97) of the benzo[*c*]phenanthrene moiety give rise to two distinctive *AB*-patterns (see *Fig. 2).*

In several complexes of ligand **1** we have observed that the methylene protons of C(19) are inequivalent and show both phosphorus and geminal couplings [1]. In complex **2** the chemical shift separation between these two protons is quite large and the average value of the individual chemical shifts (5.09, 3.65 ppm) is approximately equal to the chemical shift of the methylene protons of *trans*-[PtCl$_2$(**1**)] (4.34 ppm).

Homonuclear decoupling experiments were necessary to assign the remaining signals arising from the phenyl ring protons (see *Fig. 2*). These experiments showed conclusively that: (1) there are two magnetically distinct phenyl rings; (2) one phenyl ring has signals at 8.02 (*o*), 7.58 (*m*), 7.54 (*p*) ppm; values which may be considered normal for a phenyl group attached to a coordinated P-atom of a tertiary phosphine (*cf. cis*-[PtCl$_2$(PPh$_3$)$_2$] (**4**) in *Table 3*); (3) a second phenyl group has resonances occuring at 6.74 (*o*), 6.65 (*m*), 7.02 (*p*) ppm. These signals are clearly moved to high field of the region where one finds most aromatic proton resonances.

Aromatic protons resonating between 6.50 and 7.00 ppm have been observed in the helicenes and cyclophanes [22] [23]. Both represent cases where aromatic rings

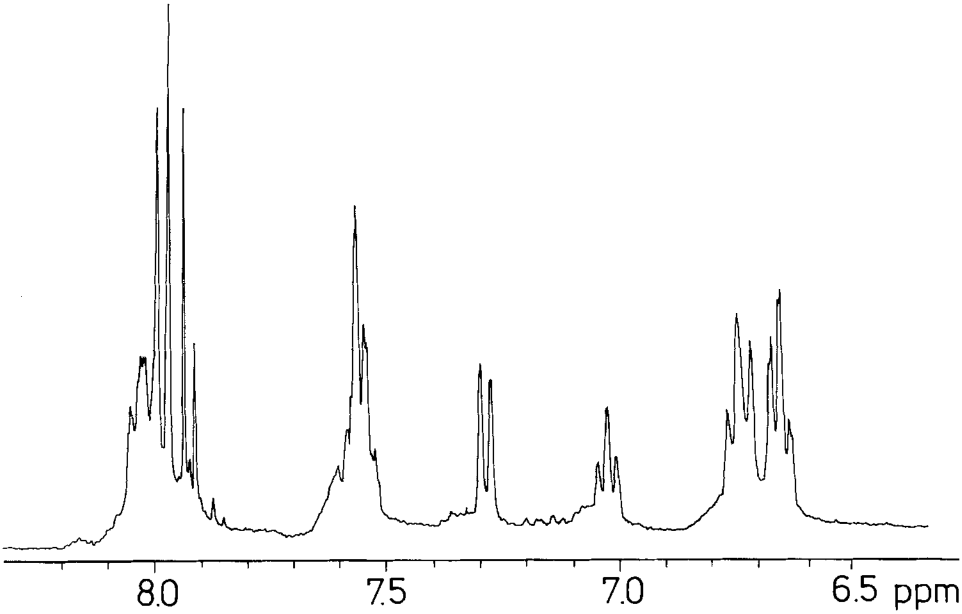

Fig. 2. *The 6.4–8.3 ppm region of the ^{1}H-NMR. Spectrum of* cis-*[PtCl$_2$(1)]* (**2**)

Table 4. *^{1}H-NMR. Chemical Shifts,* δ(ppm), *and Coupling Constants,* J_{xy}*(Hz) for Complexes* cis- *and* trans-*[$PtH(PPh_3)(1)$] [BF_4]* (**6** and **7**) *and [$PtH(PPh_3)_3$] [BF_4]* (**8**) *in $CDCl_3$* (The indices on the H-atoms correspond to those defined in Table 3)

	(6)				**(7)**				**(8)**			
$\delta(H_{1,12})$	10.70, 9.52				9.66							
$\delta(H_{3,10})$	6.78, 6.48				6.99							
$\delta(H_{4,9})$	7.73, 7.70				8.03							
$J(H_{3,10}, H_{4,9})$	8				8							
$\delta(H_{5,6,7,8})$	8.10, 8.05, 7.99, 7.88				8.02, 7.94							
$J(H_{5,8}, H_{6,7})$	8,9				8							
Other 'aromatic' resonances	8.14÷6.46				8.13÷6.91				7.50÷6.99			
		δPh_{ortho}	δPh_{meta}	δPh_{para}		δPh_{ortho}	δPh_{meta}	δPh_{para} .		δPh_{ortho}	δPh_{meta}	δPh_{para}
	3Ph	7.37	7.15	7.27	5Ph	7.46	7.27	7.40	9Ph	7.32?	7.07	7.27?
	2Ph	6.94	6.84	7.06	2Ph	7.03	6.96	7.31				
	1Ph		7.05?									
	1Ph											
$\delta(H_{19,20})$	3.80 (2H), 3.09 (1H), 1.79 (1H) $^2J(H,P) = 13$ 18 $^2J(H,H) = 8$ Hz				3.94 (4H) $\|^2J(H,P) + {}^4J(H,P)\| = 8$ $^3J(H,Pt) = 43$							

may be found to be constrained such that the skeleton of one ring is placed above another. On this evidence we conclude that the signals of the phenyl ring resonating at lower field are attributable to Ph(1) (C(21)-C(26)) and that the signals of the other phenyl arise from Ph(2) (C(27)-C(32)). In view of the mirror symmetry mentioned earlier, Ph(4) (C(39)-C(44)) and Ph(3) (C(33)-C(38)) will correspond to Ph(1) and Ph(2) respectively.

The observation of high-field phenyl group resonances indicates that complex **2** retains the parallel arrangement of Ph(2) and Ph(3) even in solution. Such interactions have been identified before in the X-ray structures of organometallic complexes [24] [25] but, to our knowledge, were not previously identified as being present in solution.

The complexes *cis*- and *trans*-[$PtH(PPh_3)$ (1)]$^+$ (*6* and *7*). - The complex *trans*-[$PtH(PPh_3)$ (**1**)] [BF_4] (**7**) was prepared by the reaction of *trans*-[PtH (acetone) (**1**)] [BF_4] with PPh_3. This complex shows ^{31}P- and ^{1}H(hydride)-NMR. parameters, which are comparable to those of [$PtH(PPh_3)_3$]$^+$ [26] (see *Tables 1* and *5*), as well as an IR. Pt-H stretching frequency at 2080 cm^{-1}. Although the aromatic region of the ^{1}H-NMR. spectrum of this complex is complicated by the presence of triphenyl phosphine, the features of *trans*-spanning **1** are evident and the methylenic protons give rise to only one signal. Molecular models of complex **7** show that the phenyl rings of PPh_3 interfere markedly with the phenyl substituents of ligand **1**.

In CH_2Cl_2 solution complex **7** was converted after several hours into its *cis*-isomer (**6**). Compound **6** has an ^{1}H-NMR. spectrum which differs from those of species containing ligand **1** coordinated in a pseudo-symmetric form, *e.g.* *cis*-[$PtCl_2$(**1**)] (**2**) and *trans*-[$PtH(PPh_3)$ (**1**)] [BF_4] (**7**). As can be seen from *Figure 3*, no motions of the C-skeleton can 'equalize' the two halves (A and B) of ligand **1** in complex **6**. Thus, all the protons of the methylene groups and of the benzo[*c*]phen-

Table 5. *Crystal data for* cis-*[PtCl$_2$(2)] · CHCl$_3$*

Formula	$C_{45}H_{35}Cl_5P_2Pt$
Formula wt	1010.08
Cell constants[a])	$a = 11.202\ (11)$ Å
	$b = 11.515\ (9)$ Å
	$c = 17.737\ (13)$ Å
	$\alpha = 73.79\ (6)°$
	$\beta = 74.40\ (7)°$
	$\gamma = 66.50\ (6)°$
	$V = 1982.1\ (23)$ Å^3
Density	1.692 (calc.), 1.67 (1) (exper.)[b]) gcm^{-3}
Crystal dimensions	$0.1 \times 0.2 \times 0.4$ mm
Radiation	Graphite-monochromatized Mo*Kα* ($\lambda = 0.71069$ Å)
μ(Mo*Kα*)	40.28 cm^{-1}

[a]) Determined by a least-squares procedure from the measured angular positions of 15 reflections. The cell is reduced according to the *Buerger* convention.

[b]) Measured by flotation in ZnI_2 solution.

anthrene system, H–C(1) to H–C(12), are inequivalent, as are the four phenyl groups of the ligand.

Characterization of **6** was achieved by conventional methods including ^{1}H-, ^{31}P-NMR. (see *Tables 1* and *4*) and IR. which showed a ν_{Pt-H} vibration at 2150 cm^{-1}. Of particular value in assigning *cis*-coordination to ligand **1** in this complex was the ^{31}P-NMR. spectrum which showed an asymmetric three-spin system for the main lines (four spins for the platinum satellites). The three magnetically inequivalent P-atoms of this complex allow the direct determination of all ^2J(P,P) coupling constants, the found values being comparable with those of related complexes [26].

The facile rearrangement of *trans*-[PtH(PPh$_3$) (**1**)]$^+$ (**7**) to the corresponding *cis*-isomer (**6**) is likely to be due to steric factors. The formation of **7** is obviously

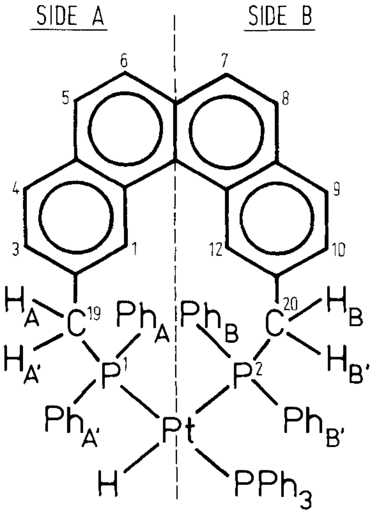

Fig. 3. *Schematic representation of the molecule* cis-*[PtH(Ph$_3$P)(1)] [BF$_4$]* (**6**)

kinetically controlled by the high *trans*-effect of the hydride ligand [27]. The resulting complex is likely to be sterically overcrowded as was found in $[PtH(PPh_3)(PCy_3)_2][PF_6]$ [28]. Thus, under these circumstances, it is not surprising that compound **7** will rearrange to its *cis*-isomeric form (**6**) taking advantage of a presumably favourable π-interaction between phenyl groups.

As shown in *Figure 3*, side A of compound **6** is in *trans*-position to a phosphine ligand while side B is in *trans*-position to a hydride ligand. As the effect of the *trans*-ligand on the NMR. parameters is much larger than that of the *cis*-ligands [29], one expects that side A of ligand **1** should give rise to a ^1H-NMR. spectrum similar to that of the same part of the molecule in *trans*-$[PtH(PPh_3)$ (**1**)] $[BF_4]$ (**7**). The other half of the spectrum of ligand **1** in compound **6** would be quite different from that of side A.

The ^1H-NMR. spectrum of compound **6** does indeed fulfil these expectations and shows the features outlined below: 1) Two 'low-field' signals at 9.52 and 10.70 ppm, each integrating as one proton, which have been assigned on the basis of the above considerations to H–C(1) and H–C(12), respectively; 2) A complex multiplet at 3.80 ppm, integrating as two protons, which is assigned to H_A and $H_{A'}$ on C(19) by analogy with the position of the methylenic protons in *trans*-$[PtH(PPh_3)$ (**1**)] $[BF_4]$ (**7**) which resonate at *ca.* 3.94 ppm; 3) A doublet of doublets at 1.79 and 3.09 ppm, each integrating as one proton, which have been attributed to H_B and $H_{B'}$ on C(20). This assignment is in agreement with the observed pattern of signals arising from the two-bond P-coupling and from geminal coupling and was confirmed by homonuclear decoupling experiments; 4) A complex set of signals in the aromatic region of the spectrum (6.46 to 8.14 ppm) most of which could not be positively identified. Dominant are the multiplets arising from PPh_3: these occur at 7.37 (*o*), 7.15 (*m*), 7.27 (*p*) ppm. Three multiplets centered at 6.84, 6.94 and 7.06 ppm, integrating as four, four and two protons, respectively, are found to high field of the PPh_3 resonances. The patterns and shifts of these signals are reminiscent of those obtained from the protons of the Ph(2) and Ph(3) phenyl groups in compound **2** and it is assumed that these multiplets arise from the Ph(A) and Ph(B) protons which are experiencing π-interactions; 5) The hydride region of the spectrum shows the basic pattern resulting from coupling to three P-atoms and to ^{195}Pt (33.8% natural abundance). This pattern is similar to that found in compound **7** but differs in that every signal is split into a doublet with a 2 Hz separation. The field-independence of this splitting led to the conclusion that it was caused by coupling to one unique proton within the molecule. Homonuclear decoupling experiments showed that this proton was located within the complex multiplet at 3.80 ppm which arises from the H_A and $H_{A'}$ protons. The value of this four-bond coupling seems larger than might be expected for a coupling pathway that goes *via* a *cis*-P-Pt-H linkage. In this context, it should be noted that examination of molecular models show a fairly close approach of one of the methylenic protons of C(19) to the hydridic proton and, thus points to the possibility of Pt-H interactions.

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Experimental Part

For generalities and physical measurements see [1]. The compounds **2**, **3**, **6** and **7** were prepared as described below. All reactions were carried out under nitrogen unless otherwise stated.

***cis*-[PtCl$_2$(*1*)] (2).** - *Method 1.* A suspension of 410 mg (1 mmol) of [Pt(1,5-C_8H_{12})$_2$] [30] in 10 ml toluene at 0° was stirred in an atmosphere of C_2H_4 to produce *in situ* [Pt(C_2H_4)$_3$] [30]. After adding 625 mg (1 mmol) **1** portionwise to the above clear yellow solution, evolution of gas occurred and the white precipitate formed was filtered off after 30 min, washed successively with 5 ml acetone and 2 ml CH_2Cl_2 and dried *i.V.* This material (650 mg) was suspended in 15 ml CH_2Cl_2 at RT. and dry HCl was passed through the mixture for 2 min. The clear yellow solution obtained, which quickly deposited a heavy white solid, was concentrated to 5 ml and the solid filtered off. The crude product was washed successively with 10 ml acetone and 15 ml $CHCl_3$ and dried *i.V.* Purification by *Soxhlet* extraction with chloroform gave 585 mg **2** as it $CHCl_3$-solvate. Recrystallization from dichloromethane gave *cis*-[PtCl$_2$(**1**)] · 0.25 CH_2Cl_2. Dec. > 300°.

$C_{44.25}H_{34.5}Cl_{2.5}P_2Pt$ Calc. C 58.28 H 3.81 Cl 9.72 P 6.79%
Found C 58.08 „ 3.85 „ 9.71 „ 6.59%

Method 2. The mixture of 0.5 ml methylacrylate and 115 mg (0.59 mmol) Ag[BF$_4$] in 5 ml CH_2Cl_2 was cooled to − 18°. After adding 504 mg (0.59 mmol) solid *trans*-[PtHCl(**1**)] [6] the mixture was stirred and then allowed to warm up to room temperature during 2 h. The AgCl was filtered off and the filtrate concentrated *i.V.* The residual oil, after washing with Et_2O, gave colourless *cis*-$\overline{\text{Pt(CH}_2\text{CH}_2\text{CO}}\text{OMe)}$ (**1**)] [BF$_4$] [6] was filtered off and dried. The pure product (350 mg) was obtained by repeated dissolution in CH_2Cl_2 and reprecipitation with Et_2O. The solution of 300 mg of the above complex in 20 ml CH_2Cl_2 was treated with dry HCl-gas for 2 min during which time **2** was precipitated. The reaction mixture was concentrated to 5 ml and the product was obtained by filtration in practically quantitative yield.

***trans*-[PtH(PPh$_3$) (*1*)] [BF$_4$] (7).** After 5 min after adding 262 mg (0.31 mmol) *trans*-[PtHCl(**1**)] to a stirred solution of 60.5 mg (0.31 mmol) of Ag[BF$_4$] in 10 ml acetone the precipitated AgCl was filtered off, 71 mg (0.31 mmol) solid PPh$_3$ was added to the stirred filtrate, which contained *trans*-[PtH(acetone) (**1**)] [BF$_4$] [6], and the solvent quickly evaporated to a colourless oil. After washing with Et_2O **7** was obtained as a white solid which was filtered off and dried *i.V.* Yield 327 mg (91%). Dec. >250°.

$C_{62}H_{50}BF_4P_3Pt$ Calc. C 63.65 H 4.31% Found C 63.15 H 4.40%

***cis*-[PtH(PPh$_3$)(*1*)] [BF$_4$] (6).** A solution of 243 mg (0.2 mmol) *trans*-[PtH(PPh$_3$) (**1**)] [BF$_4$] (**7**) in 15 ml CH_2Cl_2, containing a trace of PPh$_3$ was stirred for 24 h. After adding 15 ml EtOH the solution slowly deposited crystals of **6**. Yield 203 mg (87%). Dec. p. 220°.

Found C 63.49 H 4.36%

Crystal Data. Pale yellow crystals of *cis*-[PtCl$_2$(**1**)] were grown from a chloroform solution. They are triclinic, space group $P\bar{1}$, and contain two [PtCl$_2$(**1**)] · CHCl$_3$ units per cell. Lattice constants and intensity measurements were performed on a computercontrolled automatic diffractometer Syntex P2$_1$. Crystal data are summarized in *Table 6*.

Intensity Measurements. Reflections up to $\theta = 28°$ were measured by the ω-scan technique at a scan rate automatically chosen between 1 and 29.3° min^{-1} with a scan range of 1°. Background counts were taken, at ± 0.7° from the peak position, for half the scan time. The intensity of three standard reflections, measured every 100 reflexions, remained constant throughout the run.

The intensity data were processed as previously [31] described, using an uncertainty factor, p = 0.002, calculated from the variances of the standard reflections [32]. The values of I and σ(I) were corrected for *Lorentz*, polarization and shape-anisotropy [33] effects.

Of the 10047 unique data collected, 6116 independent reflections with $I > 3\sigma(I)$ were used in the subsequent analysis.

Structure Analysis and Refinement. - The structure was solved by *Patterson* and *Fourier* methods and refined by least-squares procedures. The isotropic refinement converged at R = 0.085. In the subsequent cycles H-atoms were included at fixed positions [34], while the heavier atoms, including C-atoms of the methylenic groups and of the solvent molecule, were allowed to vibrate anisotropically.

Table 6. *Final positional parameters* ($\times 10^4$) *for the non-hydrogen atoms* (Standard deviations are given in parentheses)

	x	y	z	
Non-group atoms				
Pt	3029 (0)	1250 (0)	2082 (0)	
Cl(1)	1975 (2)	140 (2)	1709 (1)	
Cl (2)	4216 (2)	-753 (2)	2794 (1)	
P(1)	4222 (2)	1997 (2)	2541 (1)	
P(2)	1862 (2)	2981 (2)	1269 (1)	
C(1)	1772 (8)	1840 (7)	4061 (4)	
C(2)	3042 (8)	1135 (7)	4165 (4)	
C(3)	3268 (8)	140 (8)	4848 (5)	
C(4)	2235 (8)	-6 (8)	5436 (5)	
C(5)	-164 (9)	700 (8)	6015 (5)	
C(6)	-1390 (9)	1464 (8)	5948 (5)	
C(7)	-3077 (9)	3045 (9)	5153 (5)	
C(8)	-3457 (9)	3772 (9)	4480 (5)	
C(9)	-2899 (9)	4435 (9)	3016 (5)	
C(10)	-2068 (8)	4322 (8)	2298 (5)	
C(11)	-735 (8)	3467 (7)	2289 (4)	
C(12)	-306 (8)	2823 (7)	2990 (4)	
C(13)	636 (7)	1659 (7)	4626 (4)	
C(14)	928 (8)	763 (8)	5354 (5)	
C(15)	-1152 (8)	2983 (7)	3756 (4)	
C(16)	-2509 (8)	3751 (8)	3735 (5)	
C(17)	-724 (8)	2324 (7)	4508 (4)	
C(18)	-1751 (8)	2293 (8)	5207 (5)	
C(19)	4262 (8)	1329 (8)	3618 (5)	
C(20)	70 (8)	3249 (8)	1478 (4)	
C	1922 (14)	2940 (12)	5955 (8)	solvent molecule
Cl(3)	2134 (5)	2038 (4)	6865 (2)	
Cl(4)	3335 (5)	3185 (5)	5410 (3)	
Cl(5)	564 (5)	4232 (5)	5969 (4)	

	x	y	z	
Rigid group atoms				
C(21)	5966 (4)	1407 (11)	2082 (4)	Ph(1)
C(22)	6380 (5)	754 (8)	1453 (3)	
C(23)	7719 (5)	279 (6)	1127 (3)	
C(24)	8644 (4)	458 (11)	1431 (4)	
C(25)	8230 (5)	1111 (8)	2061 (3)	
C(26)	6891 (5)	1585 (6)	2386 (3)	
C(27)	3919 (6)	3703 (4)	2454 (3)	Ph(2)
C(28)	4492 (5)	4361 (6)	1762 (3)	
C(29)	4370 (6)	5632 (5)	1713 (3)	
C(30)	3674 (6)	6244 (4)	2356 (3)	
C(31)	3101 (5)	5585 (6)	3049 (3)	
C(32)	3224 (6)	4315 (5)	3097 (3)	
C(33)	1853 (6)	4623 (4)	1108 (3)	Ph(3)
C(34)	2381 (6)	5205 (6)	365 (3)	
C(35)	2278 (6)	6491 (5)	230 (3)	
C(36)	1645 (6)	7195 (4)	837 (3)	
C(37)	1117 (6)	6613 (6)	1580 (3)	
C(38)	1220 (6)	5327 (5)	1715 (3)	
C(39)	2416 (5)	2635 (5)	260 (2)	Ph(4)
C(40)	3765 (5)	2017 (5)	16 (3)	
C(41)	4250 (4)	1814 (5)	-764 (3)	
C(42)	3388 (5)	2227 (5)	-1299 (2)	
C(43)	2039 (5)	2844 (5)	-1055 (3)	
C(44)	1553 (4)	3048 (3)	-276 (3)	

	x	y	z	φ	θ	ψ
Rigid group parameters[a]						
Ph(1)	7305 (4)	932 (3)	1757 (2)	180.0 (4)	-63.1 (2)	-5.6 (4)
Ph(2)	3797 (3)	4973 (4)	2405 (2)	180.7 (2)	-4.9 (2)	-57.3 (2)
Ph(3)	1749 (4)	5909 (4)	972 (2)	179.4 (2)	2.9 (2)	-60.5 (2)
Ph(4)	2902 (4)	2431 (3)	-520 (2)	82.6 (2)	-0.2 (2)	89.0 (2)

[a] The fractional coordinates x, y and z ($\times 10^4$) describe the positions of the centers of the rings and the angles φ, θ and ψ (in degrees) describe rotations about an internal coordinate system [38].

The H-atoms were then repositioned and included in the final structure factor calculation: $R = 0.053$ ($Rw = 0.040$). The refinement was carried out with a three-block approximation of the normal equations matrix. The function minimized was $\Sigma w(|Fo|-|Fc|)^2$ with $w = 4\ Fo^2/\sigma^2(Fo^2)$. The phenyl rings were refined as rigid groups (D_{6h} symmetry, $C-C = 1.392$ A). Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography [35]. The calculations were performed, using local programmes, on the UNIVAC 1100/20 computer of the University of Rome [36] and on the HP 21MX minicomputer of the CNR Research Area [37]. Final positional parameters for non-hydrogen atoms are given in *Table 6.*

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