

42. Transition-Metal Complexes with Bidentate Ligands Spanning *trans*-Positions. IX.¹⁾ Preparation and ¹H-NMR Studies of Complexes [MX₂(1)] and [M'Cl(CO)(1)] (M = Pd, Pt; M' = Rh, Ir; X = Cl, Br, I; 1 = 2,11-Bis-(diphenylarsinomethyl)benzo[c]phenanthrene) and Crystal and Molecular Structure of [PtCl₂(1)]

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Summary

The preparation of the bidentate ligand 2,11-bis(diphenylarsinomethyl)benzo[c]phenanthrene (**1**) is described. This ligand reacts with appropriate substrates to give mononuclear square planar complexes of type [MX₂(1)] (M = Pd, Pt; X = Cl, Br, I) and [M'Cl(CO)(1)] (M' = Rh, Ir) in which ligand **1** spans *trans*-positions. This is confirmed by the crystal structure of [PtCl₂(1)]. ¹H-NMR. spectra of the complexes are discussed and compared with those of model compounds *trans*-[MCl₂(**12**)₂] (M = Pd, Pt) and [M'Cl(CO)(**12**)₂] (M' = Rh, Ir; **12** = AsBzPh₂).

Introduction. - The general interest in square planar complexes [MXY(L)], where L is a bidentate spanning *trans*-positions and X and Y are other charged or uncharged ligands, has been outlined in the first paper of this series [2]. In complexes of this type reported until recently [3] L is normally a bidentate phosphine or, in a few cases, an amine. This state of affairs reflects the special interest in phosphine ligands [4], for which ³¹P-NMR. provides a powerful tool for detecting *cis/trans*-isomers or oligomeric species [5]. However, some complexes of the type [MX₂(L)] (M = Pd, Pt; L = Me₂As(CH₂)₃S(CH₂)₃S(CH₂)₃AsMe₂, Me₂As(CH₂)₁₂AsMe₂) [6] have been assigned square planar structure with the ligand L spanning *trans*-positions.

Since the bidentate phosphine L = 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene (**2**) readily forms mononuclear complexes *trans*-[MXY(**2**)] (M = Ni, Pd, Pt, Rh, Ir; X = Cl, Br, I; Y = Cl, Br, I, CO) [3] [7], it seemed of interest to in-

¹⁾ Part VIII: see [1].

investigate whether the arsine analogue (**1**) with increased donor atom-metal distances would form complexes of similar structures and reactivities.

We report here the first set of complexes *trans*-[MXY (**1**)].

Results and Discussion. - The synthesis of 2,11-bis(bromomethyl)benzo[*c*]-phenanthrene (**1b**) has been described in Part I [2] of this series, and ligand **1** was prepared by a reaction analogous to that of the corresponding bidentate phosphine ligand **2**. To prevent formation of oxidation products, the syntheses of the ligand and of its complexes were carried out under nitrogen. The monodentate model-ligand diphenylbenzylarsine (**12**) was prepared as described by Mann & Pragnell [8]. Physical properties for **1** and its complexes are listed in Table 1. Reasonable yields, based on pure products with analytical data as given in Table 2, were obtained. As expected from the small number of diamagnetic nickel(II)arsine complexes known [4], an attempt to prepare the complex [Ni(SCN)₂(**1**)] failed; neither anhydrous Ni(SCN)₂ in butanol nor [Ni(SCN)₂(PPh₃)₂] in benzene/dichloromethane reacted with ligand **1**. In the case of iridium (I) careful choice of starting material is needed to prevent formation of polynuclear species. Whereas for rhodium(I) dinuclear starting materials, e.g. [Rh₂Cl₂(C₈H₁₄)₄], can be split by reaction with CO before adding **1**, this is not possible for [Ir₂Cl₂(C₈H₁₄)₄], as introduction of CO leads to formation of insoluble carbonyl cluster compounds [9]. On the other hand, a dinuclear complex (**11**) is formed when [Ir₂Cl₂(C₈H₁₄)₄] is allowed to react with **1** before adding CO. Thus, a mononuclear starting material has to be used to obtain **10**.

The assignment of *trans*-configuration to complexes [MX₂(**1**)] (M = Pd, Pt; X = Cl, Br, I) is not as straightforward as for complexes [M'Cl(CO)(**1**)] (M' = Rh, Ir). Complexes [MX₂L₂] are generally assigned *cis*- or *trans*-configuration on the basis of their ν_{M-X} bands [10]. Thus, a single band at ca. 350 cm⁻¹ has been observed

Table 1. Some physical properties of ligand **1** and of the complexes prepared

Compound	Colour	M.p. ^{a)}	Yield ^{b)}	$\bar{\nu}$ (C≡O) ^{c)}
1	colourless	110–112°	50%	–
3 = <i>trans</i> -[PdCl ₂ (1)]	golden yellow	250° ^{d)}	72%	–
4 = <i>trans</i> -[PdBr ₂ (1)]	orange red	275° ^{d)}	55%	–
5 = <i>trans</i> -[PdI ₂ (1)]	brown red	220° ^{d)}	68%	–
6 = <i>trans</i> -[PtCl ₂ (1)]	yellow	> 300°	70%	–
7 = <i>trans</i> -[PtBr ₂ (1)]	orange	> 300°	37%	–
8 = <i>trans</i> -[PtI ₂ (1)]	brown orange	270° ^{d)}	64%	–
9 = <i>trans</i> -[RhCl(CO)(1)]	yellow	> 300°	51%	1963
10 = <i>trans</i> -[IrCl(CO)(1)]	yellow	> 250°	63%	1955
11 = <i>trans</i> -[IrCl(CO)(1) ₂]	yellow	> 250°	27%	1953
13 = <i>trans</i> -[PdCl ₂ (AsBzPh ₂) ₂]	golden yellow	189–191°	38%	–
14 = <i>cis</i> -[PtCl ₂ (AsBzPh ₂) ₂]	very pale yellow	222–224°	67%	–
15 = <i>trans</i> -[RhCl(CO)(AsBzPh ₂) ₂]	yellow	187–188°	84%	1963
16 = <i>trans</i> -[IrCl(CO)(AsBzPh ₂) ₂]	yellow	160° ^{d)}	61%	1949

a) Uncorrected.

b) Analytically pure products.

c) cm⁻¹.

d) Gradual decomposition occurs above the temperature stated.

Table 2. Analytical data for ligand **1** and the complexes prepared

Compound	C %		H %		X %		Mol. wt. ^{a)}	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1	74.26	74.16	4.90	4.81			b)	712
3	59.38	59.39	3.84	3.85	7.83	7.83	868	889
4	53.91	53.99	3.51	3.50	16.53	16.33	976	979
5	48.95	49.26	3.13	3.19	23.49	23.66	1135	1072
6	54.13	54.00	3.43	3.50	7.36	7.25	980	979
7	49.78	49.51	3.27	3.21	14.86	14.97	1066	1068
8	44.48	45.50	2.86	2.95	21.75	21.85	1168	1162
9	61.62	61.49	4.00	3.90	4.29	4.03	894	879
10	55.95	55.82	3.68	3.54	3.79	3.66	962	968
11	56.78	55.82	3.86	3.54	3.98	3.98	2143	1937
13	55.63	55.81	4.23	4.19	8.72	8.67		
14	50.29	50.35	3.78	3.78	7.82	7.82		
15	58.40	58.05	4.44	4.25	4.64	4.39		
16	52.45	52.27	4.00	3.82	3.92	3.96		

a) Determined osmotically in CH_2Cl_2 .

b) A mass spectrum shows the following peaks: m/z 713 (31%; M^+ (^{13}C), 712 (63%, M^+)).

in complexes $\text{trans}[\text{PdCl}_2(\text{R}_3\text{As})_2]$ while in the corresponding *cis*-complexes bands at *ca.* 316 and 300 cm^{-1} have been reported. The frequency ranges for the corresponding platinum complexes are given as *ca.* 337 cm^{-1} for the *trans*-isomers and *ca.* 310 and 290 cm^{-1} for the *cis*-isomers. As the infrared spectra of **4–8** in this region are practically identical with those of ligand **1**, no structural assignment can be made on this basis. The infrared spectrum of **3** does, however, show one additional band at 355 cm^{-1} which could correspond to the expected $\nu_{\text{Pd-Cl}}$ for a *trans*-isomeric species. The apparent absence of the appropriate M-X vibrations in the other complexes is likely to be due to their being masked by, or mixed-in with, the large number of bands from the organic ligand in this region.

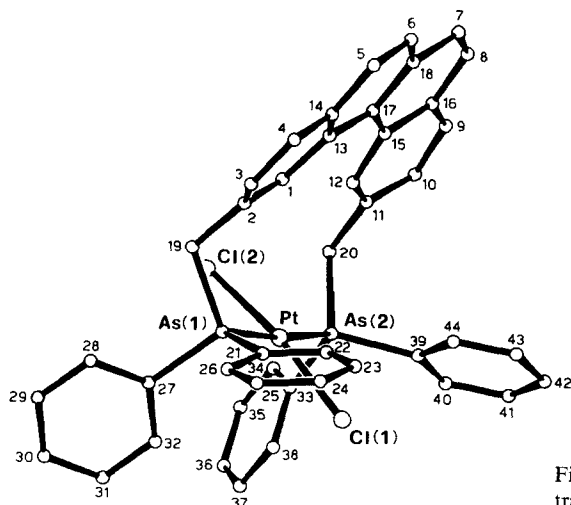


Fig. 1. View of the molecule $\text{trans}[\text{PtCl}_2(\mathbf{1})]$

Table 3. Geometrical data of complex 6

	Bond distances Å		Angles degrees ^{a)}
Pt–As(1)	2.380 (1)	As(1)–Pt–As(2)	174.1 (0)
Pt–As(2)	2.370 (1)	As(1)–Pt–Cl(1)	94.8 (1)
Pt–Cl(1)	2.304 (2)	As(1)–Pt–Cl(2)	86.4 (1)
Pt–Cl(2)	2.308 (2)	As(2)–Pt–Cl(1)	90.8 (1)
As(1)–C(19)	1.993 (6)	As(2)–Pt–Cl(2)	88.3 (1)
As(1)–C(21)	1.900 (4)	Cl(1)–Pt–Cl(2)	171.1 (1)
As(1)–C(27)	1.958 (4)	Pt–As(1)–C(19)	113.5 (2)
As(2)–C(20)	1.958 (7)	Pt–As(1)–C(21)	118.6 (1)
As(2)–C(33)	1.980 (3)	Pt–As(1)–C(27)	109.3 (1)
As(2)–C(39)	1.930 (3)	C(19)–As(1)–C(21)	101.2 (2)
C(2)–C(19)	1.527 (8)	C(19)–As(1)–C(27)	106.2 (2)
C(11)–C(20)	1.547 (8)	C(21)–As(1)–C(27)	107.2 (2)
		Pt–As(2)–C(20)	112.0 (2)
		Pt–As(2)–C(33)	109.1 (1)
		Pt–As(2)–C(39)	118.6 (1)
		C(20)–As(2)–C(33)	106.1 (2)
		C(20)–As(2)–C(39)	103.8 (3)
		C(33)–As(2)–C(39)	106.3 (2)
		C(2)–C(19)–As(1)	113.5 (4)
		C(11)–C(20)–As(2)	116.2 (4)

a) Standard deviations in parentheses.

Table 4. Some ¹H-NMR. parameters^{a)} for the ligands and complexes described

Compound	$\delta_{1,12}$	$\delta_{3,10}$	$^4J_{1,3}$	δ_{CH_2}		$^3J_{Pt,H(CH_2)}$	$^2J_{AB}$
				δ_A	δ_B		
1	8.86	b)	b)		3.59 ^{c)}	–	
3 =[PdX ₂ (1)]; X=Cl	10.12	7.01	1.7		4.27	–	
4 =[PdX ₂ (1)]; X=Br	10.09	7.00	1.4		4.49	–	
5 =[PdX ₂ (1)]; X=I	9.98	7.02	1.5		4.87	–	
6 =[PtX ₂ (1)]; X=Cl	10.20	7.05	1.5		4.24	23.5	
7 =[PtX ₂ (1)]; X=Br	10.18	7.05	1.5		4.44	24.7	
8 =[PtX ₂ (1)]; X=I	10.11	7.04	1.5		4.79	25.9	
9 =[RhCl(CO)(1)]	10.24	7.04	1.5	5.15	3.73 ^{d)}	–	12.4
10 =[IrCl(CO)(1)]	9.37	7.13	1.5	4.88	4.00	–	13.0
11 =[IrCl(CO)(1) ₂]	10.28	7.06	1.5	5.12	3.82	–	12.5
12 =AsBzPh ₂					3.37	–	
13 = <i>trans</i> -[PdCl ₂ (12) ₂]					3.92	–	
14 = <i>cis</i> -[PtCl ₂ (12) ₂] ^{e)}					3.92	15.0	
15 = <i>trans</i> -[RhCl(CO)(12) ₂]					3.99	–	
16 = <i>trans</i> -[IrCl(CO)(12) ₂]					4.04	–	

a) Measured in CD₂Cl₂; chemical shifts are relative to TMS (±0.005 ppm), coupling constants in Hz (±0.15 Hz).

b) Signal within multiplet of other aromatic protons.

c) $\delta^{13}C$ for –CH₂– = 36.1 ppm.d) $^3J_{Rh,H}$ = 1.2 Hz.e) $\delta^{195}Pt$ = –4325 ppm relative to a 0.8 M solution of Na₂[PtCl₆] in H₂O at 25°.

For complexes $[\text{MCl}(\text{CO})(\mathbf{1})]$ (**9–11**) and the corresponding model compounds **15** and **16** with the monodentate ligand AsBzPh_2 (**12**), IR.-stretching frequencies ν_{CO} (Table 1) give additional information. The values are close to those reported for analogous complexes with the phosphine ligands **2** and PBzPh_2 [7] (the structure of one of these compounds has been determined by an X-ray study [11]), and support a *trans* geometry for the complexes with both mono- and bidentate arsines, **12** and **1** respectively.

The electronic spectra of **3–8** are not informative either, as they are dominated by ligand absorption in the UV. region, with ϵ -values of more than 60.000, which also obscure the region in which the much weaker d-d-bands of the complexes are expected to occur.

To confirm the expected *trans*-configuration of the complexes $[\text{MX}_2(\mathbf{1})]$, the structure of $[\text{PtCl}_2(\mathbf{1})]$ (**6**) was determined by X-ray diffraction. The crystal consists of discrete monomeric molecules whose structure is shown in Figure 1. Important bond distances and angles are reported in Table 3.

The coordination about the metal atom is slightly distorted square-planar with the two arsenic atoms *trans*, and the Pt-As and Pt-Cl bond-lengths fall into the expected ranges [12] [13]. The bond angles at the two arsenic atoms vary between 101 and 119°. These atoms, and the attached phenyl groups, are almost symmetrical with respect to a mirror plane passing through the platinum atom. Indeed,

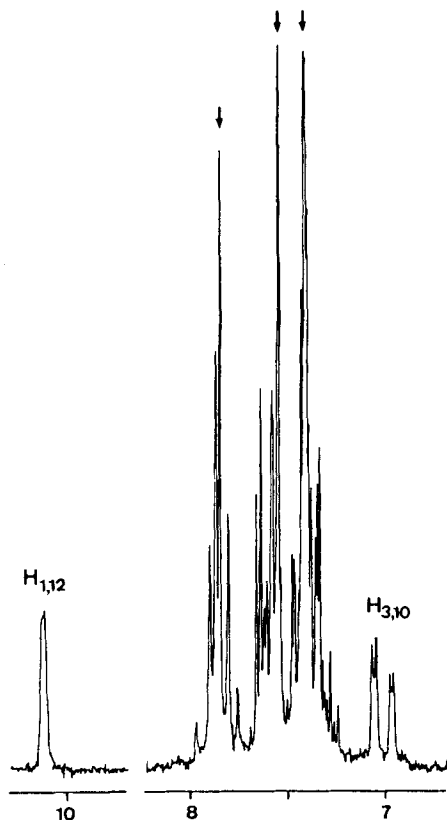


Fig. 2. Aromatic region of the ^1H -NMR. spectrum of *trans*- $[\text{PdCl}_2(\mathbf{1})]$

the only feature that seriously breaks the molecular mirror symmetry is the expected out-of-plane distortion of the overcrowded ligand **1**. The molecular structure is comparable with that of $[\text{PdCl}_2(\mathbf{2})]$, which is isostructural with $[\text{PtCl}_2(\mathbf{2})]$ [11]. The space group $P1$ ensures that the crystal is racemic. ^1H -NMR. spectra of **3-8** are similar and show the following features (see Table 4): a broad signal at low field (between 9.9 and 10.3 ppm) due to the inner ring protons at positions 1 and 12; 2) a sextet at 7.9 ppm with an integrated intensity corresponding to eight protons; 3) two (sometimes overlapping) multiplets between 7.25 and 7.75 ppm; 4) a doublet of doublets at 7 ppm with an integral corresponding to two protons; 5) a rather broad signal in the aliphatic region between 4.2 and 4.9 ppm arising from the 4 methylene protons (in the platinum complexes accompanied by their ^{195}Pt satellites).

A typical example of the aromatic region is given in Figure 2. As the free ligand does not give a well-separated signal to high field of the aromatic multiplet (nor do the corresponding complexes of the phosphorus analogue (**2**) [3]) a detailed

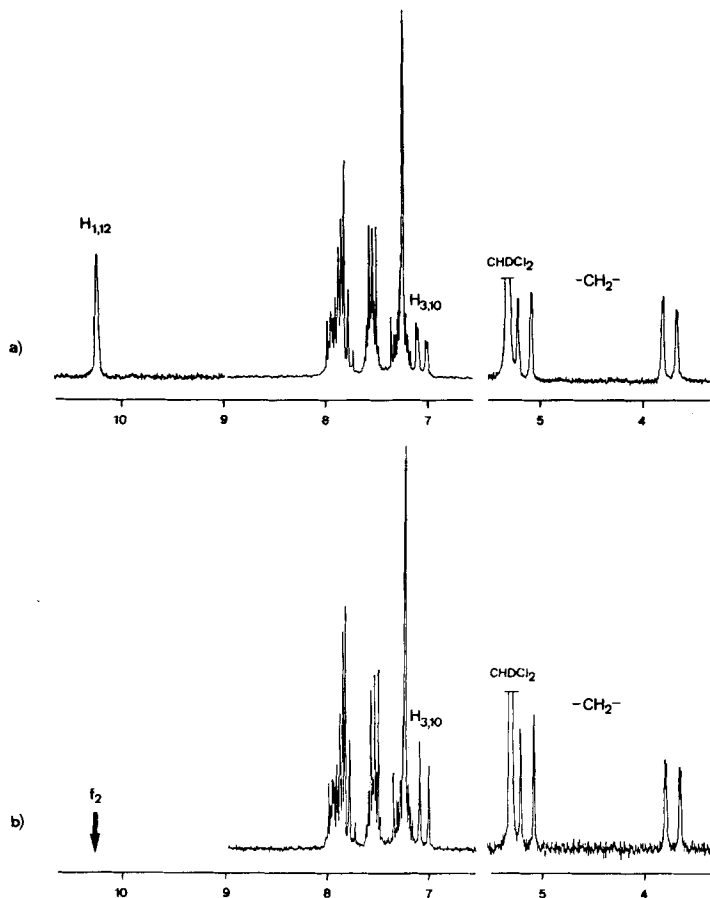


Fig. 3. ^1H -NMR. spectrum of $\text{trans-}[\text{RhCl}(\text{CO})(\mathbf{1})]$: a) normal spectrum, b) with irradiation at the frequency of $\text{H-C}(1)$ and $\text{H-C}(12)$.

Table 5. $^1\text{H-NMR}$ parameters for precursors **1a** and **1b** of ligand **1** (**1a** = 2,11-dimethylbenzo[c]phenanthrene; **1b** = 2,11-bis(bromomethyl)benzo[c]phenanthrene)

A. Chemical shifts ^{a)}						
Compound	$\delta_{1,12}$	$\delta_{3,10}$	$\delta_{4,9}$	$\delta_{5,8}$	$\delta_{6,7}$	$\delta_{19,20}$
1a ^{b)}	9.05	7.54	7.99	7.91	7.81	2.74
1b ^{c)}	9.07	7.65	7.99	7.88	7.82	4.80

B. Coupling constants ^{d)}						
Compound	$^4J_{1,19}$	$^4J_{3,19}$	$^4J_{1,3}$	$^5J_{1,4}$	$^3J_{3,4}$	$^3J_{5,6}$
1a ^{b)}	0.9	0.5	1.5	0.8	8.2	< 0.3
1b ^{c)}	< 0.5	< 0.5	1.6	< 0.5	8.5	< 0.3

^{a)} Relative to TMS (± 0.005 ppm).^{b)} Measured in CD_2Cl_2 .^{c)} Measured in CDCl_3 .^{d)} In Hz (± 0.15 Hz).Table 6. Crystal data for $[\text{PtCl}_2(\text{1})]$ (**6**)

Formula	$\text{C}_{44}\text{H}_{34}\text{As}_2\text{Cl}_2\text{Pt}$		
Formula-Wt.	978.0		
Cell constants ^{a)}	$a = 15.683$ (3) Å		$\alpha = 77.34$ (1)°
	$b = 12.313$ (3)		$\beta = 88.34$ (2)
	$c = 9.948$ (2)		$\gamma = 75.05$ (2)
	$V = 1810.2$ (6) Å ³		
Space group	$\text{P}\bar{1}$ (triclinic; $Z = 2$)		
Density (gcm^{-3})	1.795 (calc.), 1.78 (1) (found) ^{b)}		
$\mu(\text{MoK}\alpha)$ (cm^{-1})	59.06		

^{a)} Determined by least squares from the measured angular positions of 15 reflections.^{b)} Measured by flotation in ZnI_2 solution.Table 7. Coordinates ($\times 10^4$) for non-hydrogen atoms (standard deviations in parentheses)

	x	y	z
<i>Non-group atoms</i>			
Pt	2666 (0)	1541 (0)	4578 (0)
As(1)	2925 (0)	3173 (0)	5270 (1)
As(2)	2265 (0)	— 42 (0)	3986 (1)
Cl(1)	3844 (1)	1380 (1)	3139 (2)
Cl(2)	1627 (1)	1490 (1)	6268 (2)
C(1)	747 (4)	4288 (5)	3879 (6)
C(2)	1243 (4)	4826 (5)	4472 (6)
C(3)	1182 (5)	6001 (6)	3962 (8)
C(4)	578 (5)	6592 (6)	2903 (8)
C(5)	— 577 (5)	6738 (6)	1242 (7)
C(6)	— 1080 (5)	6262 (6)	647 (7)
C(7)	— 1521 (5)	4629 (6)	186 (7)
C(8)	— 1427 (5)	3502 (7)	333 (8)

Table 7 (continued)

	x	y	z			
<i>Non-group atoms</i>						
C(9)	− 715 (6)	1504 (7)	1354 (9)			
C(10)	− 108 (5)	657 (7)	2232 (8)			
C(11)	402 (4)	990 (5)	3114 (6)			
C(12)	332 (4)	2141 (5)	3056 (6)			
C(13)	158 (4)	4838 (5)	2741 (6)			
C(14)	63 (4)	6046 (6)	2309 (7)			
C(15)	− 268 (4)	3044 (5)	2148 (6)			
C(16)	− 805 (5)	2689 (6)	1288 (7)			
C(17)	− 354 (4)	4290 (5)	2015 (6)			
C(18)	− 979 (4)	5032 (6)	985 (7)			
C(19)	1836 (4)	4207 (5)	5725 (6)			
C(20)	1007 (4)	36 (5)	4166 (7)			
<i>Rigid group atoms</i>						
C(21)	3443 (3)	4217 (3)	3999 (4)			
C(22)	3392 (3)	4270 (3)	2591 (4)			
C(23)	3749 (3)	5062 (4)	1663 (3)	Ph(1)		
C(24)	4159 (3)	5801 (3)	2144 (4)			
C(25)	4210 (3)	5747 (3)	3553 (4)			
C(26)	3852 (3)	4956 (4)	4480 (3)			
C(27)	3660 (3)	2676 (3)	6947 (4)			
C(28)	3452 (2)	3165 (3)	8085 (4)			
C(29)	3956 (3)	2733 (4)	9292 (3)	Ph (2)		
C(30)	4668 (3)	1812 (3)	9362 (4)			
C(31)	4875 (2)	1324 (3)	8225 (4)			
C(32)	4371 (3)	1756 (4)	7017 (3)			
C(33)	2854 (3)	−1458 (3)	5283 (4)			
C(34)	2396 (2)	−2261 (4)	5951 (4)			
C(35)	2822 (3)	−3209 (3)	6924 (4)	Ph(3)		
C(36)	3707 (3)	−3353 (3)	7229 (4)			
C(37)	4165 (2)	−2550 (4)	6561 (4)			
C(38)	3739 (3)	−1603 (3)	5588 (4)			
C(39)	2509 (3)	− 306 (4)	2157 (3)			
C(40)	2700 (3)	−1396 (3)	1883 (4)			
C(41)	2836 (3)	−1531 (3)	535 (4)	Ph(4)		
C(42)	2780 (3)	− 578 (4)	− 540 (3)			
C(43)	2589 (3)	511 (3)	− 266 (4)			
C(44)	2454 (3)	647 (3)	1082 (4)			
	x	y	z	ϕ	θ	ψ
<i>Rigid group parameters^{a)}</i>						
Ph(1)	3801 (2)	5009 (2)	3072 (3)	− 29.0 (2)	− 1.1 (1)	93.8 (2)
Ph(2)	4164 (2)	2244 (2)	8155 (3)	53.1 (2)	− 1.7 (1)	99.9 (2)
Ph(3)	3281 (2)	−2406 (2)	6256 (3)	179.9 (1)	29.0 (2)	13.9 (2)
Ph(4)	2645 (2)	− 442 (3)	809 (3)	9.8 (2)	− 0.8 (1)	82.3 (2)

^{a)} The coordinates x, y, z give the ring centers, and the angles ϕ , θ , ψ (in degrees) describe rotations about an internal coordinate system [27].

analysis of the ^1H -NMR. spectra of the two precursors 2,11-dimethylbenzo[*c*]phenanthrene (**1a**) and 2,11-bis(bromomethyl)benzo[*c*]phenanthrene (**1b**) was undertaken using double resonance techniques (see Fig. 3).

The results (Table 5) are in good agreement with parameters reported for benzo[*c*]phenanthrene [14]. The doublet of doublets can be assigned to the two ring protons at positions 3 and 10. This assignment holds for the complexes where irradiation at the low field signal not only sharpens the signal of the methylene protons but also suppresses the small coupling of the doublet at 7 ppm. Thus, the protons which experience the largest (and opposite) shifts on coordination of ligand **1** are those next to positions 2 and 11.

The three multiplets between 7.25 and 7.75 ppm represent an $AA'BB'C$ -spin system of the terminal phenyl groups and two AB -systems of the aromatic bridge. Whereas the central multiplet moves to higher field on substituting Cl^- for Br^- and I^- , the shifts of the high field multiplet and the low field sextet are independent of the metal centre and the halide X ; the sextet therefore is most likely to arise from the eight protons in *meta*-position on the phenyl rings. As the spectrum of the aromatic region remains of higher order even when run at 360 MHz, an unambiguous assignment could not be made.

The appearance of one signal due to the four methylene protons in complexes **3-8** requires some comment. If the solution structure of **6**, in the static limit, were that of the crystal, $\text{H}-\text{C}(1)$ and $\text{H}-\text{C}(12)$ should be inequivalent (see Fig. 4I). The same would be true of the methylene protons pointing inward, H_i and H_i' , and of those pointing outwards, H_o and H_o' . Recent calculations give an energy difference between the planar and helical configurations of benzo[*c*]phenanthrene of 38.9 kJ/mol [15] but older estimates and measurements suggest even lower energies (25–30 kJ/mol) [16] [17]. Thus, the inversion of configuration of the helicene moiety is likely to be fast on the NMR. time-scale at room temperature and, as a consequence, H_i and H_i' will appear as equivalent and the same will apply to H_o and H_o' . If, however, only this process occurred, the two types of methylene protons would not interconvert and should give rise to two signals as well as to geminal coupling. As only one signal is observed, it is proposed that the equalisation of H_i and H_o is due to rapid inversion of conformation of the chelate ring as shown in Figure 4. This is supported by the spectra at -50° , where all signals, most of all the

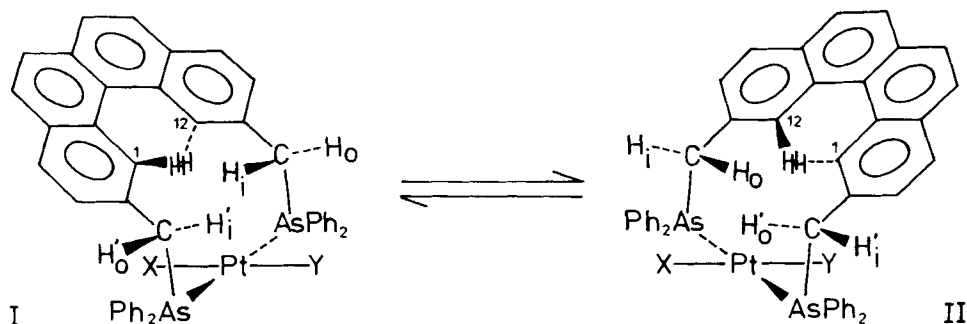


Fig. 4. Schematic representation of conformational inversion of the chelate ring in $[\text{PtXY}(\mathbf{1})]$

aliphatic ones, are considerably broadened, whereas the reference and solvent peaks remain sharp.

Processes of this type have been observed in complexes of $[MXY(L)]$ (L = phosphorus analogue of ligand (1)) [3] [7]. More recently the use of related phosphorus ligands, having terminal *t*-butyl groups, has allowed the 'freezing' in solution of the 'static' structures at low temperatures, clearly showing the inequivalent methylene protons and their geminal couplings [18].

The most unexpected ^1H -NMR. parameters are the $^3J_{\text{Pt,H}(\text{CH}_2)}$ of compounds 5-7 (see Table 4). It has been observed [19] that the $^3J_{\text{Pt,H}}$ for complexes $[\text{PtCl}_2\text{L}_2]$ (L = monodentate arsine) are larger for the *cis*- than for the *trans*-isomers, e.g., 23.5 and 17.1; 22.4 and 17.8; 17.5 and 14.0 Hz for $L = \text{AsMe}_3$, AsMePh_2 and AsEt_3 respectively. The coupling constants observed for 6-8 are equal or larger than those of the *cis*-complexes mentioned above and much larger than those for the corresponding *trans*-complexes. This suggests that an assignment of *cis*- or *trans*-configuration, based on $^3J_{\text{Pt,H}}$ -values, can only be reliably made when these values are known for both geometries.

The ^1H -NMR. spectra of 9-11 are similar to those of 3-8 in the aromatic region, but two signals in the aliphatic region are split by a geminal coupling. This is because the chemical shift of H_i (and therefore H_o as well) now depends on whether the $\text{H}_i\text{-C}(19)$ bond is pointing to the Cl^- or CO ligand. Furthermore, the high field doublet of 9 shows a further splitting of 1.2 Hz (Fig. 3a). The origin of this splitting was established as follows: irradiation at the frequency of the low-field $\text{H-C}(1)$ and $\text{H-C}(12)$ not only collapses the signal at 7.04 ppm to a single doublet, but also sharpens the signals of the methylene protons both at 5.15 and 3.73 ppm, thereby revealing the small splitting even more clearly (Fig. 3b). A coupling $^4J_{1,19}$ or $^4J_{3,19}$ can therefore be excluded. A further possibility is slow interconversion between structures I and II in Figure 4 by a process of type a) as described above, thus giving rise to two detectable species (and therefore four doublets with different chemical shift). This should result in an increased separation when going to a higher field. As a 360-MHz- ^1H -NMR. spectrum still shows a splitting of 1.2 Hz, this can be assigned to a $^3J_{\text{Rh,H}}$ coupling, and provides additional support for the rapid interconversion between structures I and II with inversion of configuration at C(19) and C(20). A similar $^3J_{\text{Rh,H}}$ coupling has not been observed for any of the complexes with the phosphine 2 [7].

It has been shown [19] that ^{195}Pt -NMR. chemical shifts for *cis*- and *trans*-isomers of $[\text{PtCl}_2\text{L}_2]$ (L = arsine) complexes differ by 500-650 ppm, the *cis*-isomers appearing at higher field than the *trans*-isomers which resonate between -3600 and -3800 ppm (for ^{195}Pt -NMR. data see [5]). Complex 14 was assigned *cis*-configuration using this criterion. As ^{195}Pt -linewidths for such complexes are rather broad (40-140 Hz and 80-400 Hz for the *trans*- and *cis*-isomers respectively) due to residual coupling of the Pt-atom to the rapidly relaxing As-nucleus [19], reasonable signal-to-noise ratios can be obtained only for fairly concentrated solutions, a condition which was not fulfilled by 6-8.

In summary, all available evidence indicates that ligand 1, like its phosphorus analogue, easily forms square planar complexes with the ligand spanning *trans*-

positions and that the basic geometric structure of such complexes is unaffected by the donor atom of the bidentate ligand L.

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Experimental Part. – Melting points were determined using a *Büchi* SMP 20 melting point apparatus and are uncorrected. Elemental analyses and molecular weight determinations were performed by the Microanalytical Laboratory, mass spectra by the Laboratory for Organic Chemistry, both at ETH Zürich. IR. spectra were recorded on a *Beckman* IR 4250, UV./VIS. spectra on a *Varian-Techtron* 635 spectrophotometer. ^1H -, ^{13}C - and ^{195}Pt -NMR. spectra were recorded on a *Bruker* HX 90 FT spectrometer operating at 90, 22.63 and 19.34 MHz respectively, the deuterium resonance of the deuterated solvent being used for an internal frequency lock. Standard double resonance techniques were used to assign ^1H - and ^{13}C -NMR. spectra. ^1H -NMR. spectra were also recorded on the *Bruker* HXS 360 FT spectrometer of the Institute for Molecular Biology at ETH Zürich. Preparations of ligands and complexes were carried out under a nitrogen atmosphere in dried and deoxygenated solvents, whereas purification of the complexes was carried out in normal atmosphere except for the complexes of Rh and Ir.

The Pd(II) and Pt(II) starting materials not commercially available were prepared using methods cited by *Hartley* [20]. The Rh and Ir dimers $[\text{M}_2\text{Cl}_2(\text{C}_8\text{H}_{14})_4]$ were synthesized as described by *van der Ent* [21], $[\text{IrCl}(\text{CO})_2(p\text{-toluidine})]$ by a standard procedure [22].

Yellow crystals of $[\text{PtCl}_2(\mathbf{1})]$ for X-ray analysis were grown from a $\text{CH}_2\text{Cl}_2/\text{EtOH}$ solution; the dimension of the crystal chosen for analysis being $0.10 \times 0.16 \times 0.32$ mm. Details of X-ray measurement, data processing and structure analysis were similar to those described in [1].

A summary of crystal data is given in Table 6. Of the 9060 unique data collected, 6786 independent reflections, having $I > 3\sigma(I)$, were used in the analysis.

Isotropic refinement converged at $R=0.057$. In the subsequent least-squares cycles the heavier atoms and the carbon atoms of the two methylenic groups were allowed to vibrate anisotropically: convergence at $R=0.048$. At this stage H-atoms were positioned geometrically [23] and after two cycles repositioned: final $R=0.040$ ($RW=0.044$). A two-block approximation of the normal equations matrix was used, and the function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w=4 F_o^2/\sigma^2(F_o)^2$. Phenyl rings were refined as rigid groups (D_{6h} symmetry, $\text{C}-\text{C}=1.392$ Å). Atomic scattering factors and anomalous dispersion terms were taken from International Tables for X-ray Crystallography [24]. The calculations were performed, using local programmes, on the UNIVAC 1100/20 computer of the University of Rome [25] and on the HP 21MX minicomputer of the CNR Research Area [26].

Final positional parameters for non-hydrogen atoms are given in Table 7.

2,11-Bis(diphenylarsinomethyl)benzo[c]phenanthrene (1). A solution of lithiumdiphenylarsenide was prepared by the addition of 20.2 ml of a 2.1M solution (42.24 mmol) of butyllithium in hexane to a stirred solution of 9.72 g (7.5 ml) diphenylarsine (42.24 mmol) in 50 ml of THF at 0°. The orange solution was allowed to warm up to RT. and added dropwise to a stirred solution of 7.23 g (17.5 mmol) of 2,11-bis(bromomethyl)benzo[c]phenanthrene (**1b**) in 60 ml of THF at 0° until addition of one drop caused the reaction mixture to retain an orange coloration. The cooling was then removed and the solution stirred another 15 min before taking it to dryness i.V. The sticky residue was redissolved in 60 ml dichloromethane, washed four times with 50 ml of water to remove the lithium bromide formed during the reaction and then evaporated to dryness again. The solid residue was dissolved in benzene/ethanol and slowly reprecipitated by gradually concentrating the solution. The colourless powder was filtered off, stirred in light petroleum for 1 h, filtered off again and dried i.V. Yield: 6.23 g (50%).

trans-[PdCl₂(1)] (3). A solution of 600 mg (0.84 mmol) **1** in acetone was added to a stirred solution of 323 mg (0.84 mmol) $[\text{PdCl}_2(\text{PhCN})_2]$ in the same solvent. A dark yellow solid started to precipitate immediately, and after 12 h the solution was taken to dryness and the residue recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ and dried i.V. Yield: 537 mg (72%).

trans-[PdBr₂(1)] (4). A solution of 500 mg (0.7 mmol) **1** in acetone was added to a stirred solution of 331 mg (0.7 mmol) $\text{Na}_2[\text{PdBr}_4]$ in 20 ml of acetone. After stirring the suspension for 12 h, light petroleum was added to completely precipitate the product, which was then filtered off, recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ and dried i.V. Yield: 377 mg (55%).

trans-[PdI₂(1)] (5). A solution of 600 mg (0.84 mmol) **1** in acetone was added to a stirred solution of 508 mg (0.42 mmol) (NEt₃Me)₂[Pd₂I₆] in 50 ml acetone. After stirring for 12 h, charcoal was added, the mixture filtered, taken to dryness and the residue recrystallized from CH₂Cl₂/EtOH and dried i.V. Yield: 611 mg (68%).

trans-[PtCl₂(1)] (6). It was prepared and purified as described for **3**. 600 mg (0.84 mmol) **1** and 398 mg (0.84 mmol) [PtCl₂(PhCN)₂] were used. Yield: 574 mg (70%).

trans-[PtBr₂(1)] (7). It was prepared by placing 300 mg (0.84 mmol) PtBr₂ in the thimble of a Soxhlet extractor and extracting them with acetone containing 600 mg (0.84 mmol) **1**. After 24 h the suspension in the reservoir was taken to dryness, the residue recrystallized from CH₂Cl₂/EtOH and dried i.V. Yield: 332 mg (37%).

trans-[PtI₂(1)] (8). The same procedure as described for **4** was adopted, using 600 mg (0.84 mmol) **1** and 583 mg (0.42 mmol) (NEt₃Me)₂[Pt₂I₆]. Yield: 623 mg (64%).

trans-[RhCl(CO)(1)] (9). CO-gas was passed through a solution of 330 mg (0.459 mmol) [Rh₂Cl₂(C₈H₁₄)₄] in 20 ml benzene until the colour turned from deep orange to deep yellow. After adding 654 mg (0.917 mmol) **1** in 5 ml benzene, the solution was stirred for 1 h and then taken to dryness under reduced pressure. The yellow residue was washed three times with 10 ml of acetone and dried i.V. Yield: 407 mg (50%).

trans-[IrCl(CO)(1)] (10). A solution of 55 mg (0.22 mmol) **1** in 5 ml benzene was added to a stirred solution of 80 mg (0.2 mmol) [IrCl(CO)₂(*p*-toluidine)], whereupon the colour changed from deep green to a bright yellow. After adding some carefully dried charcoal, stirring for a further 15 min and filtration, the solution was taken to dryness. The yellow residue was then stirred up in ether to redissolve the *p*-toluidine liberated during the reaction, filtered off, washed with some ether and dried i.V. Yield: 126 mg (63%).

trans-[IrCl(CO)(1)]₂ (11). A solution of 239 mg (0.335 mmol) **1** in benzene was added to a stirred solution of 150 mg (0.169 mmol) [Ir₂Cl₂(C₈H₁₄)₄] in 40 ml benzene. After stirring for a further 15 min, CO gas was passed through the solution until the coloration had changed to a bright yellow. The solution was then taken to dryness. The yellow residue was stirred in a few ml of acetone, and after adding a few drops of light petroleum, the product was filtered off and dried i.V. Yield: 88 mg (27%).

trans-[PdCl₂(AsBzPh₂)₂] (13). The suspension of 97 mg (0.547 mmol) PdCl₂ and 350 mg (1.094 mmol) AsBzPh₂ (**8**) in 50 ml acetone were stirred for 24 h at RT. The solution was then boiled with some charcoal, filtered, taken to dryness and the residue recrystallized from CH₂Cl₂/EtOH and dried i.V. Yield: 170 mg (38%).

cis-[PtCl₂(AsBzPh₂)₂] (14). The solution of 211 mg (0.11 mmol) Na₂[PtCl₄] in water and of 353 mg AsBzPh₂ (**8**) in ethanol were mixed and stirred for 12 h at RT. The resulting precipitate was then filtered off, recrystallized from CH₂Cl₂/EtOH and dried i.V. Yield: 336 mg (67%).

trans-[RhCl(CO)(AsBzPh₂)₂] (15). This complex was prepared as described for **9**. The yellow residue was then stirred with a few ml of acetone and, after adding a few drops of light petroleum, the product was filtered off and dried i.V. The yield from 135 mg (0.189 mmol) [Rh₂Cl₂(C₈H₁₄)₄] and 242 mg (0.753 mmol) AsBzPh₂ (**12**) was 256 mg (84%).

trans-[IrCl(CO)(AsBzPh₂)₂] (16). This complex was prepared and purified as described for **11**. Using 176 mg (0.197 mmol) [Ir₂Cl₂(C₈H₁₄)₄] and 252 mg (0.787 mmol) AsBzPh₂ (**12**), the yield was 215 mg of product (61%).

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