288. Transition-Metal Complexes with Bidentate Ligands Spanning *trans*-Positions. II[1]). Preparation and Properties of Complexes *trans*-$[MX_2(\mathbf{1})]$ (M = Ni, Pd and Pt; X = Cl, Br and I; 1 = 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene)

by **N. J. DeStefano, D. K. Johnson** and **L. M. Venanzi**[2])

Department of Chemistry, University of Delaware, Newark, Del., USA, and
Laboratorium für Anorganische Chemie, ETH Zürich, Switzerland

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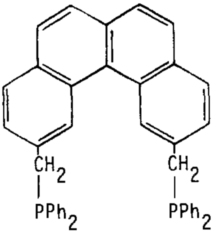
Summary. It is shown that the ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**) reacts with nickel(II), palladium(II) and platinum(II) substrates giving either exclusively, or predominantly, mononuclear complexes of the type *trans*-$[MX_2(\mathbf{1})]$ in which the organic ligand spans *trans*-positions. It is further shown that the spectroscopic properties which are mainly associated with metal and donor atoms in complexes of this type are closely related to those of the corresponding square planar complexes of the type *trans*-$[MX_2(Ph_2PCH_2Ph)_2]$.

1. Introduction. – In Part I of this series [1] we reported the preparation of 2,11-bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene (**1**), a bidentate ligand designed to span *trans*-positions in square planar complexes of the type *trans*-[MQZ(**1**)] (**2**), where M is the metal atom or ion while Q and Z are the other two ligands which may be charged or uncharged (ionic charges have been omitted to simplify this general formulation).



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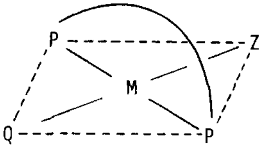

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At the time this project was started the only well-characterized complex containing a bidentate ligand spanning *trans*-positions was *trans*-$[NiBr_2\{cy_2P(CH_2)_5Pcy_2\}]$ (cy = *cyclo*hexyl) described by *Issleib & Hohlfeld* [2]. More recently several sets of square planar complexes containing ligands which are either bidentate or acting as bidentate and coordinate spanning *trans*-positions have been reported: (i) *trans*-

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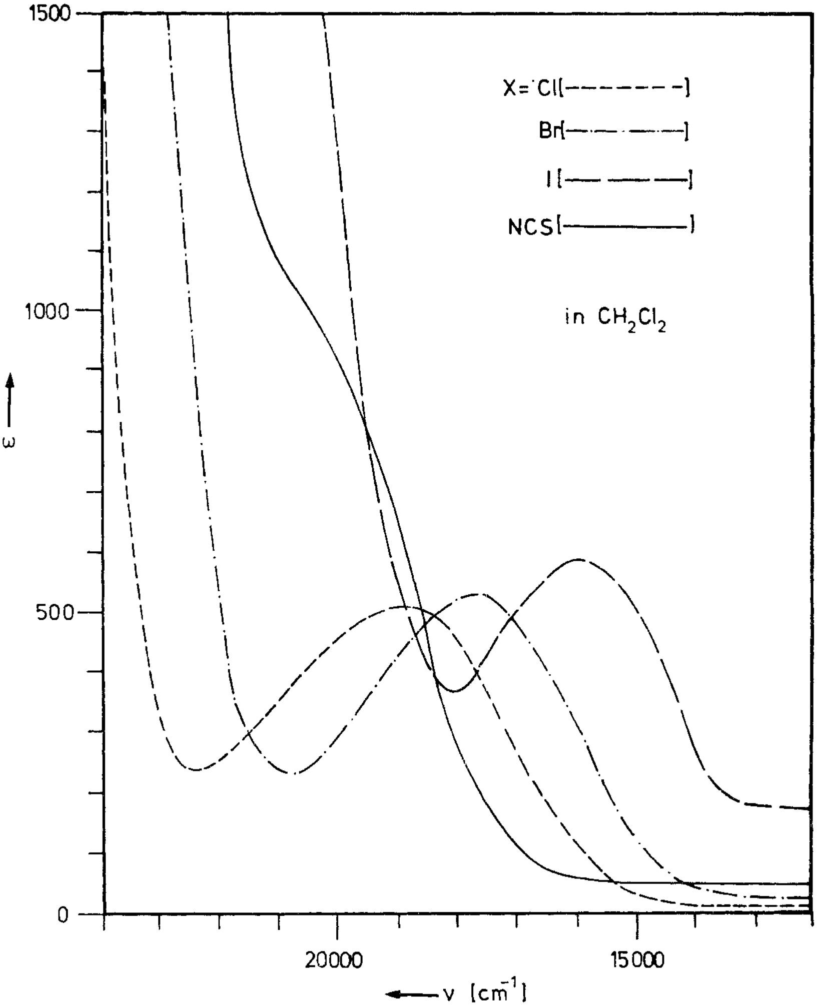
[1]) Part I: preceding paper [1].

[2]) Present address: Laboratorium für anorganische Chemie, ETH-Zentrum, CH-8092 Zürich, Switzerland.



Electronic spectra of complexes trans-[*Ni*X_2(**1**)]

[MCl_2(*ligand*)] and *trans*-[IrCl(CO)(*ligand*)] (M = Pd and Pt; *ligand* = (t-Bu)$_2$-P(CH_2)$_n$P(t-Bu)$_2$, n = 8, 9, 10 and 12) [3]; (ii) *trans*-[MX_2(**1**)] (M = Ni, Pd and Pt; X = anionic ligand) [4]; (iii) *trans*-[$PtCl_2$(*ligand*)] (*ligand* = CH_2=CH(CH_2)$_x$(CH)$_3${2-[4,6-$Me_2C_5H_2N$]}, x = 1, 2, 4 and 8) [5]; *trans*-[RhCl(CO)(*ligand*)] (*ligand* = Ph_2P-(CH_2CH_2O)$_x$$CH_2CH_2PPh_2$, x = 1, 2 and 3) [6] and (iv) *trans*-[Pt(NH_3)$_2$(*ligand*)]Cl_2 (*ligand* = RNH($CH_2CH_2NH_2$)$_2^+$$Cl^-$) [7]. In all these ligands, with the exception of **1**, the two donor atoms are joined by flexible chains and the compounds are most easily obtained if the chelate rings consist of at least eight atoms. Furthermore, the mononuclear complexes are normally accompanied by substantial amounts of oligomeric species.

The expected geometrical features of ligand **1** have been discussed in Part I [1]. These predictions are now being tested by studying the coordinating properties of this ligand with a variety of metal centres. We report here the first set of such tests designed to compare the properties of square planar complexes *trans*-[MX_2(**1**)] (M = Ni, Pd and Pt) with those of the corresponding species *trans*-[$MX_2(Ph_2PCH_2Ph)_2$].

2. Results and discussion. – The complexes prepared and some of their physical properties are listed in Table 1 and the related analytical data are given in Table 2. As can be seen, these species can be isolated in reasonable yields. Their mononuclear nature was established by molecular weight determinations.

Tests for the presence of species [M_xCl_{2x}(**1**)$_x$], where $x > 1$, were carried out as follows: the appropriate substrate and ligand **1** were reacted together and the resulting mixture examined by ^{31}P-NMR. It was found that the reaction of $Na_2[PtCl_4]$ and **1** in aqueous acetone gave *ca.* 92% of the mononuclear species and *ca.* 8% of another species with very similar NMR. characteristics ($\delta_{^{31}P} = 15.4$ ppm, $|^1J_{^{195}Pt-^{31}P}| = 2560$ Hz) which is presumed to be an oligomer with the phosphorus atoms occupying mutually *trans*-positions. On the other hand, the reaction of ligand **1** with $[Pt_2Cl_4(C_2H_4)_2]$ in $CDCl_3$ gave *ca.* 65% monomer and the remainder in the form of at least two other species ($\delta_{^{31}P} = 15.6$ ppm, $|^1J_{^{195}Pt-^{31}P}| = 2594$ Hz and $\delta_{^{31}P} = 15.5$ ppm, $|^1J_{^{195}Pt-^{31}P}| = 2597$ Hz respectively) which were not identified further. The reaction of $[PdCl_2(PhCN)_2]$ and **1** in acetone gave over 98% of the mononuclear species. This is to be contrasted with the results of *Pryde et al.* [3] who have shown that ligands $(t\text{-}Bu)_2P(CH_2)_nP(t\text{-}Bu)_2$ ($n = 9$, 10 and 12) react with substrates $[MCl_2(PhCN)_2]$ (M = Pd and Pt) giving mixtures of species [M_xCl_{2x}(ligand)$_x$] ($x = 1$, 2 and 3) and that yields of mononuclear species range from 20 to 30%.

Table 1. *Some physical properties of complexes* trans-[*MX*$_2$(**1**)]

Compound	M	X	Colour	Dec. p. a)	Yield (%) b)	Mol.-Wt. c)
(I)	Ni	Cl	purple	300°	47	d) (754)
(II)		Br	v. dark brown	280°	48	d) (843)
(III)		I	dark green	260°	63	950 (937)
(IV)		NCS	orange red	285°	49	814 (799)
(V)	Pd	Cl	deep yellow	260°	58	818 (802)
(VI)		Br	orange	265°	67	811 (891)
(VII)		I	red brown	285°	60	974 (985)
(VIII)	Pt	Cl	yellow	300°	71	891 (936)
(IX)		Br	bright yellow	300°	27	e) (980)
(X)		I	orange	300°	43	e) (1047)

a) Gradual decomposition occurs above the temperature stated.

b) These refer to analytically pure products. For a semi-quantitative estimate of the species actually obtained during the reactions see text.

c) These were determined osmometrically in CH_2Cl_2. The calculated values are given in parentheses.

d) Not sufficiently soluble for this measurement.

e) The sample decomposes during the measurement.

Table 2. *Analytical data for complexes* trans-[*MX*$_2$(**1**)]

Compound	C %		H %		P %		X %	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
(I)	69.88	70.04	4.51	4.54	8.14	8.21	9.35	9.40
(II)	62.28	62.36	3.83	4.03	7.50	7.36	18.78	18.98
(III)	56.02	56.22	3.69	3.62	6.61	6.60	27.46	27.26
(IV)	68.88	69.08	4.34	4.26	7.56	7.76	[a]	[b]
(V)	65.76	65.90	4.44	4.27	7.92	7.72	9.00	8.84
(VI)	59.58	59.32	4.00	3.85	7.11	6.95	17.59	17.94
(VII)	53.45	53.66	3.43	3.48	6.18	6.29	25.92	25.77
(VIII)	59.09	59.33	3.90	3.85	6.68	6.95	8.09	7.96
(IX)	54.04	53.95	3.66	3.50	6.18	6.32	16.23	16.31
(X)	49.29	49.23	3.13	3.19	5.88	5.77	23.73	23.64

[a] N %, 3.52; S %, 7.90.
[b] N %, 3.50; S %, 8.01.

The *trans*-configuration of complexes [MX$_2$(**1**)] was deduced from their NMR. spectra. The proton spectra of all the complexes are very similar and show the following features (see Table 3):

1) a resonance between 9 and 11 ppm due to the protons at positions 1 and 12 of the benzo[*c*]phenanthrene ring [1];

2) a complex multiplet of resonances between 6.8 and 8 ppm originating from the aromatic protons and

3) a pseudo-triplet, in the region 3.5–5 ppm, arising from the –CH$_2$– protons (in the platinum complexes this triplet is accompanied by its ^{195}Pt-satellites)[3]) which is generally indicative of *trans*-configuration [8].

The ^{31}P-NMR. spectra (see Table 3) consist of a single resonance for each of the nickel(II) and palladium(II) complexes and of one resonance, accompanied by the appropriate satellites, for each of the platinum(II) complexes. The values of $|^1J_{^{195}Pt-^{31}P}|$ (see Table 3) are also consistent with a *trans*-configuration [8]. Finally, it is interesting to note that the NMR. parameters for complexes of ligand **1** are almost identical to those of the corresponding complexes *trans*-[MX$_2$(Ph$_2$PCH$_2$Ph)$_2$] and significantly different from those of complexes *cis*-[MX$_2$(Ph$_2$PCH$_2$Ph)$_2$] (see Table 3).

The IR. spectra of complexes *trans*-[MX$_2$(**1**)] were also examined. They are very similar to those of the free organic ligand. Features worth noting are:

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[3]) A detailed study of the ^{1}H-NMR. spectra of these and related complexes will be reported at a later date.

Table 3. *NMR. parameters for complexes* trans-[MX_2(**1**)] *and related species*

Compound	$\delta_{1,12}$[a] (ppm)	δ_{-CH_2-} (ppm)	J_1[b] (Hz)	J_2[c] (Hz)	δ_{31P} (ppm)	J_3[d] (Hz)
1[e]	8.91	3.65	<1	–	–8.7	–
(I)	11.10	3.93	7.3	–	31.4	–
(II)	10.99	4.22	10.3	–	12.1	–
(III)[f]	10.76	4.70	8.8	–	26.4	–
(IV[g])	10.70	3.80	9.1	–	14.9	–
(V)	10.40	4.30	9.1	–	19.7	–
(VI)	10.39	4.56	8.1	–	16.0	–
(VII)	10.32	5.00	7.8	–	5.7	–
(VIII)	10.46	4.32	9.6	28.2	16.8	2602
(IX)	10.47	4.57	8.9	34.1	12.6	2492
(X)	10.43	4.98	8.8	31.3	4.1	2429
(XI)[h]	–	3.53	3.1	–	14.1	–
(XII)[i]	–	3.95	8.3	–	20.1	–
(XIII)[j]	–	4.11	11.6	–	30.3	–
(XIV)[k]	–	3.98	8.5	23.0	15.6	2585
(XV)[l]	–	4.04	12.2	25.0	9.7	3733

[a] Shift of protons at positions 1 and 12 on the benzo[*c*]phenanthrene ring.

[b] $|^2J_{P-H}+^4J_{P-H}|$ for —CH_2—.

[c] $|^3J_{Pt-H}|$ for —CH_2—.

[d] $|^1J_{^{195}Pt-^{31}P}|$.

[e] For —CH_2— $\delta_{^{13}C}$ = 36.7 ppm and $|^1J_{^{31}P-^{13}C}|$ = 15.9 Hz.

[f] For —CH_2— $\delta_{^{13}C}$ = 41.8 ppm and $|^1J_{^{31}P-^{13}C}+^3J_{^{31}P-^{13}C}|$ = 29.3 Hz.

[g] For —CH_2— $\delta_{^{13}C}$ = 33.4 ppm and $|^1J_{^{31}P-^{13}C}+^3J_{^{31}P-^{13}C}|$ = 29.3 Hz.

[h] $[Ni(NCS)_2(Ph_2PCH_2Ph)_2]$.

[i] *trans*-$[PdCl_2(Ph_2PCH_2Ph)_2]$.

[j] *cis*-$[PdCl_2(Ph_2PCH_2Ph)_2]$.

[k] *trans*-$[PtCl_2(Ph_2PCH_2Ph)_2]$.

[l] *cis*-$[PtCl_2(Ph_2PCH_2Ph)_2]$.

1) the complexes show one medium-to-strong band at *ca.* 1100 cm^{-1} whereas the free ligand shows only a weak band in this region; the presence of this band appears to be characteristic of all complexes of ligand **1** and thus may be used as an empirical criterion for the presence of coordinated **1**;

2) the spectrum of *trans*-[$Ni(NCS)_2$(**1**)] shows only one ν(CN) band at 2086 cm^{-1} which is taken as indicating the presence of N-bonded thiocyanate in this complex [9];

3) the spectra of the complexes in the region 650–200 cm^{-1} show one additional band which is likely to be associated with an M-X vibration; however, in view of the very large number of ligand bands in this region and of low symmetry of the complexes further studies will be required in order to make reliable assignments.

Complexes *trans*-[MX_2(**1**)] give rather uninformative electronic spectra. These are dominated by ligand absorptions and only in species *trans*-[NiX_2(**1**)] the typical absorption pattern of square-planar diamagnetic [$NiX_2(R_3P)_2$] complexes [10] can be clearly observed (see Figure).

Browning et al. [11] have shown that complexes [$NiX_2(Ph_2PCH_2Ph)_2$] (X = Cl, Br and I) can be obtained in both tetrahedral (paramagnetic) and square-planar (diamagnetic) forms and that both forms occur in solution. As the complexes of ligand **1** with the nickel(II) halides give only square-planar diamagnetic forms, it is concluded that while the ligand field effects of ligand **1** and of two molecules of Ph_2PCH_2Ph are very similar, the steric requirements of the former ligand are responsible for the preferential formation of square-planar species.

In summary, all available evidence indicates that ligand **1** easily forms normal square-planar complexes with electronic and NMR. characteristics which are very similar to those of the corresponding square-planar complexes *trans*-[$MX_2(Ph_2PCH_2Ph)_2$].

Experimental Part. – For generalities see [1]. The VIS. and UV. spectra were recorded on a *Cary* 14 spectrophotometer. The conductivities were measured as described elsewhere [12]. All solvents were dried and purified by standard methods [13]. Ligand **1** was prepared as described in Part I [1]. Diphenylbenzylphosphine [14] was conveniently prepared as follows: 20.5 ml of 2.2M *n*-BuLi in hexane (*Eastman-Kodak*) was added to 7.8 ml Ph_2PH (*Strem Chemicals*) in 30 ml THF at 0°. The Ph_2PLi solution thus prepared was added dropwise to a stirred solution of 7.2 g (5 mmol) $PhCH_2Br$ in 25 ml THF at 0°. Addition of the phosphide was stopped when one drop of it gave an orange colour to the solution. Stirring was continued for 1 h and then the solvent was evaporated under reduced pressure. The yellow residue was dissolved in 25 ml CH_2Cl_2 and the solution washed 4 times with 50 ml water. The organic layer was dried over $MgSO_4$ and evaporation of the solvent left a white residue which was recrystallized from ethanol. Yield 75%. M.p. 75–77° (lit. 74° [14]).

The preparation of the complexes was carried out in an atmosphere of nitrogen up to the point where the crude complexes were obtained in the solid state. Further treatment was carried out in air unless otherwise stated. The complexes were prepared in an analytically pure state as follows:

trans-[*$NiCl_2$*(**1**)]. 0.62 g (1.0 mmol) **1**, in 60 ml acetone, was added dropwise over 1 h to a stirred solution of 0.24 g (1.0 mmol) $NiCl_2 \cdot 6H_2O$ in 40 ml water/acetone 12:88. The purple-red precipitate was filtered off, washed twice with 15 ml acetone and dried i.V. *Soxhlet*-extraction (in N_2-atmosphere) of the crude complex with 200 ml CH_2Cl_2 for 3 days gave a deep red extract which, on concentration to *ca.* 25 ml over 4 days in a stream of N_2, gave crystals of the pure complex. These were filtered off, washed twice with 10 ml CH_2Cl_2 and dried for 7 days at *ca.* 70°/1×10^{-6} Torr.

trans-[*$NiBr_2$*(**1**)]. This complex was prepared as above using $NiBr_2$. The crude product was recrystallized by dissolving it in *ca.* 400 ml CH_2Cl_2, filtering off the solution, reducing the volume to *ca.* 20 ml in a slow stream of nitrogen, filtering off the precipitate, washing it twice with 5 ml CH_2Cl_2 and drying it for 5 days at *ca.* 25°/1×10^{-5} Torr.

trans-[*NiI_2*(**1**)]. A solution of NiI_2 was freshly prepared by refluxing 0.58 g (2 mmol) $Ni(NO_3)_2 \cdot 6H_2O$ and 1 g (6 mmol) KI in 30 ml *n*-BuOH for 2 h. The resulting mixture was cooled and filtered. The filtrate was concentrated to *ca.* 10 ml under reduced pressure and diluted with 60 ml acetone. 0.94 g (1.5 mmol) **1** were added dropwise over 2 h to the above solution. Precipitation of the crude product was complete after *ca.* 2 h. The solid was filtered off, washed 3 times with 15 ml acetone and dried. The crude product was dissolved in *ca.* 100 ml CH_2Cl_2, the solution filtered off and the solvent allowed to evaporate slowly in a stream of N_2. The pure complex was filtered off, washed twice with 5 ml CH_2Cl_2 and dried for 5 days at *ca.* 90°/1×10^{-5} Torr.

trans-[*Ni*(*NCS*)$_2$(**1**)]. 10 ml of a solution of $Ni(SCN)_2$ was freshly prepared as described above from 0.58 g (2 mmol) $Ni(NO_3)_2 \cdot 6H_2O$, 0.58 g (6 mmol) KSCN and 30 ml *n*-BuOH. The complex was prepared and purified as its iodo-analogue.

trans-[*PdCl*$_2$(**1**)]. 0.61 g (0.97 mmol) **1** in 80 ml acetone was added dropwise to a stirred solution of 0.38 g (1 mmol) $[PdCl_2(PhCN)_2]$ [15] in 15 ml acetone. The precipitate was filtered off after 15 h, washed with acetone and dried i.V. It was recrystallized by dissolving it in a large volume of CH_2Cl_2, filtering off the solution, slowly evaporating most of the solvent in a stream of N_2 and filtering off the crystalline product which was then dried i.V. ($110°/6 \times 10^{-7}$ Torr) for 5 days.

trans-[*PdBr*$_2$(**1**)]. It was prepared and purified analogously to the chloro-complex.

trans-[*PtI*$_2$(**1**)]. 0.51 g (3.38 mmol) NaI in 10 ml acetone, were added dropwise to a stirred suspension of 0.30 g (0.37 mmol) [$PdCl_2$(**1**)] in 20 ml acetone. Stirring was continued for *ca.* 18 h and then the mixture evaporated to dryness. The residue was extracted with *ca.* 90 ml CH_2Cl_2, the solution filtered off and evaporated slowly to a small volume over a stream of N_2. The crystalline product was filtered off, washed and dried as described above.

trans-[*PtCl*$_2$(**1**)]. 1 g (1.6 mmol) **1** in 60 ml acetone, was added dropwise to a filtered solution of $Na_2[PtCl_4] \cdot 4H_2O$, in 20 ml ethanol. Stirring was continued for 1 h, the precipitate was filtered off, washed with a small amount of water, then acetone and dried. The crude product was purified as described for the corresponding palladium complex.

trans-[*PtBr*$_2$(**1**)]. 0.36 g (1 mmol) $PtBr_2$ was placed in the thimble of a *Soxhlet* extractor and 0.75 g **1** in 170 ml acetone were placed in the reservoir. Extraction was carried out, in a nitrogen atmosphere, for 13 h. The solution, on cooling, gave the pure product which was filtered off, washed with acetone and dried i.V.

trans-[*PtI*$_2$(**1**)]. 1 g (2.41 mmol) $K_2[PtCl_4]$ and 3.20 g (19.3 mmol) KI, in 20 ml water, were stirred for *ca.* 18 h. The mixture was filtered off and the solution treated with 1.55 g (1.01 mmol) $[(n\text{-Bu})_4N]Br$. The resulting oil was extracted with CH_2Cl_2 and the iodo-complex re-precipitated by addition of petroleum ether. The solid was filtered off and dried. Yield 1.72 g. This solid was presumed to be $[(n\text{-Bu})_4N]_2[Pt_2I_6]$ [16]. 0.50 g (0.80 mmol) **1** in 60 ml acetone, were added to 0.66 g (0.40 mmol) of the above iodo-complex, in 20 ml acetone. The mixture was stirred for *ca.* 18 h, the solid filtered off, washed with acetone and then with ether and dried i.V. The crude product (0.62 g) was dissolved in *ca.* 75 ml of CH_2Cl_2, the solution filtered and the filtrate evaporated to a small volume in a slow stream of N_2. The pure product was filtered off, washed with CH_2Cl_2 and dried i.V.

trans-[*Ni*(*NCS*)$_2$(*Ph*$_2$*PCH*$_2$*Ph*)$_2$]. It was prepared as described elsewhere [11].

cis- *and* trans-[*PdCl*$_2$(*Ph*$_2$*PCH*$_2$*Ph*)$_2$]. 0.5 g (1.81 mmol) Ph_2PCH_2Ph in 15 ml de-oxygenated acetone were added to a stirred solution of 0.36 g (0.92 mmol) $[PdCl_2(PhCN)_2]$ [15] in 10 ml deoxygenated acetone. The yellow suspension which formed within 10 min was taken to dryness under reduced pressure and the residue recrystallized from boiling ethanol. Yield 0.60 g (88%), m.p. 205–210°.

$C_{38}H_{34}Cl_2P_2Pd$	Calc.	C 62.53	H 4.69	P 8.48%	Mol.-wt. 729.96
	Found	,, 62.41	,, 4.68	,, 8.31%	,, 751

Integration of the ^{31}P-NMR. spectrum of a $CDCl_3$ solution of this sample indicates that it is a mixture containing 62% of the *trans-* and 38% of the *cis*-isomer.

cis-[*PtCl*$_2$(*Ph*$_2$*PCH*$_2$*Ph*)$_2$]. 1.0 g (3.62 mmol) Ph_2PCH_2Ph in 50 ml ethanol was added to a stirred solution of 1.02 g (2.25 mmol) $Na_2[PtCl_4] \cdot 4H_2O$ in 25 ml ethanol. A suspension was formed over several hours. This was taken to dryness under reduced pressure and the residue extracted with CH_2Cl_2. The extract was treated with active charcoal and the product precipitated with ethanol, filtered off and dried i.V. Yield 0.90 g (50%).

$C_{38}H_{34}Cl_2P_2Pt$	Calc.	C 55.75	H 4.19	Cl 8.66	P 7.57%
(818.62)	Found	,, 55.74	,, 4.30	,, 8.64	,, 7.31%

trans-$[\mathit{PtCl_2(Ph_2PCH_2Ph)_2}]$. 0.5 g (0.61 mmol) *cis*-$[PtCl_2(Ph_2PCH_2Ph)_2]$ and 0.011 g (0.04 mmol) Ph_2PCH_2Ph, in 75 ml benzene, were refluxed for 1 h. 0.012 g (0.02 mmol) $[Pt_2Cl_4(C_2H_4)_2]$ [17] were added and the pale yellow reaction mixture cooled to RT. The insoluble *cis*-isomer was filtered off and treated again as above. 0.25 g *cis*-isomer were recovered after the second isomerization. The benzene solutions were united, taken to dryness under reduced pressure and gave 0.38 g of crude product. This was dissolved in 10 ml of benzene, a small amount of insoluble *cis*-complex was filtered off and the solvent evaporated slowly in a stream of N_2. The precipitated yellow product was filtered off and dried i.V. Yield 0.16 g (64%).

$C_{38}H_{34}Cl_2P_2Pt$	Calc.	C 55.75	H 4.19	Cl 8.66	P 7.57%
(818.62)	Found	,, 55.48	,, 4.47	,, 8.41	,, 7.36%

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