65. Transition Metal Complexes with Bidentate Ligands Spanning trans-Positions. XII. [1]) The Preparation and Properties of Complexes trans-[MX₂(1)] and trans-[PtHCl(1)] (M = Ni, Pd and Pt; X = Cl and NCS; 1 = ditertiary phosphine)

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Summary

Complexes [MX₂(1)] (M = Ni, Pd and Pt; X = Cl and NCS; 1 = 2,11-bis(dialkyl-[or diaryl]phosphinomethyl)benzo[c]phenanthrene; alkyl = cyclohexyl t-butyl; aryl = m-tolyl, p-anisyl and m-CF₃ · C₆H₄) have been synthesized.

An NMR. study of the t-butyl complexes provides evidence for a "fan-like" motion of the benzo[c]phenanthrene moiety over the plane of the complex.

Introduction. – The complexing properties of the ditertiary phosphine 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene (**1a**) have been extensively studied [1][2].
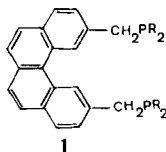
1a	R = Ph
1b	R = m-CH₃ · C₆H₄
1c	R = p-CH₃O · C₆H₄
1d	R = m-CF₃ · C₆H₄
1e	R = C₆H₁₁
1f	R = t-Bu

In order to extend these studies it became necessary to prepare ligands related to **1a** which would impart either different solubilities or different electronic and steric properties to their complexes. The synthesis of ligands **1b** to **1f** was described earlier [3] and this paper reports the preparation of a selection of their complexes together with a comparison of some physical properties.

Results and Discussion. – The complexes were prepared by standard methods and some of their physical characteristics are given in *Table 1*, while the analytical data are reproduced in *Table 2*.

It is interesting to note that while [Ni(NCS)₂(**1f**)] could be easily obtained, attempts to prepare [NiCl₂(**1f**)] were unsuccessful. As the complex [NiCl₂(**1e**)] could be obtained by standard procedures, it is presumed that the combined effect of the

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

Table 1. *Some physical properties of complexes* trans-$[MX_2(1)]$ *and* trans-$[PtHCl(1)]$

Compound	Color	P.dec.	Yield[a]	Mol. Wt.[b] Found	Calc.
3 [NiCl$_2$(1b)]	purple	320–323°	45	[c])	810.44
4 [Ni(NCS)$_2$(1b)]	orange-red	315–318°	76	872	855.70
5 [PdCl$_2$(1b)]	yellow	270–277°	42		858.13
6 [PtCl$_2$(1b)]	pale yellow	280–285°	15		946.82
7 [NiCl$_2$(1c)]	violet	208–212°	64	815	874.44
8 [Ni(NCS)$_2$(1c)]	red-brown	310–315°	62	913	919.70
9 [PdCl$_2$(1c)]	yellow	325–331°	50	926	922.13
10 [PtCl$_2$(1c)][d]	pale yellow	> 300°[e])	24		1010.82
11 [NiCl$_2$(1d)]	red-brown	273–276°	54	965	1026.32
12 [Ni(NCS)$_2$(1d)]	red-purple	283–287°	52	1042	1071.58
13 [PdCl$_2$(1d)]	yellow	265–269°	68	1068	1074.01
14 [PtCl$_2$(1d)]	pale yellow	274–277°	43	1104	1162.70
15 [NiCl$_2$(1e)]	violet	305–310°	42	770	778.51
16 [Ni(NCS)$_2$(1e)]	orange-red	310–313°	68	839	823.78
17 [PdCl$_2$(1e)]	yellow	335–337°	63	830	826.20
18 [PtCl$_2$(1e)]	pale yellow	340			
18 [PtCl$_2$(1e)]	pale yellow	340–345°	62	927	914.89
19 [PtHCl(1e)]	colorless	290–295°	74	847	880.44
20 [Ni(NCS)$_2$(1f)]	orange-red	308–316°	77	702	719.63
21 [PdCl$_2$(1f)]	orange-yellow	320–330°	80	743	722.06
22 [PtCl$_2$(1f)]	pale yellow	> 340°[c])	63	917	810.75
23 [PtHCl(1f)]	colorless	330–334°	63	757	776.30

[a]) These refer to analytically pure products. [b]) These were determined osmometrically in CH_2Cl_2. [c]) The sample decomposes during the measurement. [d]) This compound is obtained in the form of its benzene mono-solvate. [e]) Gradual decomposition above the stated temperature.

size of the *t*-butyl-substituents and the chloride ion give rise to just sufficient steric crowding to prevent the formation of the [NiCl$_2$(1f)].

All the complexes have been assigned structures of type **2** on the basis of their physical properties.

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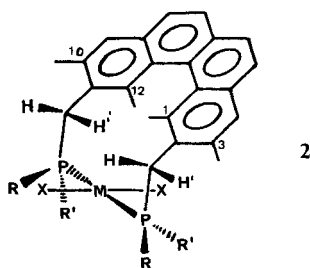
The NMR. characteristics obtained for these complexes are listed in *Table 3*. The ^{31}P-NMR. spectra of the complexes with ligands **1b** to **1f** are similar to those obtained for the corresponding complexes of ligand **1a**. Indeed, the δ (^{31}P)- and ^1J (^{195}Pt, ^{31}P)-values of complexes of substituted aryl derivatives **1b** to **1d** are almost identical with those of the corresponding complexes of the phenyl-substituted ligand **1a**. It should be noted here that the δ (^{31}P)-value for [NiCl$_2$ (**1a**)] is 6.5 ppm and not 31.4 ppm as reported earlier [4].

Table 2. *Analytical data for complexes of ligands* **1b-f**

Compound	C%		H%		Cl[b]) or N[c]) %	
	Found	Calc.	Found	Calc.	Found	Calc.
3	71.01	71.14	5.32	5.22	8.71	8.75
4	70.21	70.18	4.95	4.95	3.30	3.27
5	67.49	67.18	4.81	4.93	8.34	8.26
6	60.31	60.89	4.32	4.47	7.63	7.49
7	65.69	65.93	4.98	4.84	8.49	8.11
8	65.08	65.30	4.62	4.60	3.00	3.05
9	63.28	62.52	4.82	4.59	7.65	7.69
10	60.10	59.56	4.47	4.44	5.35	6.51
11	56.06	56.17	3.02	2.95	7.01	6.91
12	55.94	56.04	2.88	2.82	2.60	2.62
13	53.29	53.68	2.81	2.82	6.72	6.60
14	49.51	49.59	2.57	2.60	6.24	6.10
15	67.05	67.88	7.38	7.51	9.09	9.11
16	67.00	67.07	7.04	7.10	3.42	3.40
17	64.11	63.97	7.11	7.08	8.38	8.58
18	57.81	57.76	6.35	6.39	7.67	7.75
19	60.29	60.02	6.76	6.75	3.99	4.03
20	63.46	63.42	7.09	7.00	3.98	3.89
21	59.92	59.88	6.88	6.98	9.81	9.82
22[a])	49.48	49.61	5.57	5.85	15.58	15.82
23	55.83	55.70	6.54	6.62	4.59	4.57

[a]) This complex was obtained as its CH_2Cl_2-monosolvate. [b]) For metal chloride complexes. [c]) For metal isocyanate complexes.

The values of δ (^{31}P) of the complexes and those of the calculated coordination chemical shifts [5] indicate that the P-atoms in our bidentate ligand behave as if they belonged to monodentate ligands, *i. e.*, no "ring effect" [6] is observed.

The main features of the ^1H-NMR. spectra are closely related to those observed for the corresponding complexes of ligand **1a** [1]. The following additional data were obtained: *1)* the complexes of ligands **1b** and **1c** show resonances due to the presence of CH_3-groups; *2)* the complexes of ligands **1e** and **1f** show an apparently simpler spectrum in the aromatic region because of the absence of terminal phenyl-groups; *3)* the complexes of ligand **1e** show broad signals due to the CH_2-groups of the cyclohexyl substituents; *4)* the complexes of ligand **1f** show the presence of non-equivalent *t*-butyl groups at low temperatures.

While features *1* to *3* require no comment, the ^1H-NMR. spectra of complexes of ligand **1f** provide interesting information about molecular motions of the coordinated ligands in solution.

As may be seen from the formula **2**, both H and H' as well as R and R' are chemically and magnetically non-equivalent assuming the given molecular config-uration. We have previously discussed the "fan-like" type motion of the benzo[c]-phenanthrene across the top of such complexes [1]. For rapid movement of this moiety, H and H' (and R and R') will see a time averaged environment, whereas for square planar complexes of the form [MXY(**1a**)] H and H' will always be different due to the differing local anisotropic effects of X and Y [12]. For complexes

Table 3. *NMR. data for complexes* trans-$[MX_2(1)]$ *and* trans-$[PtHCl(1)]$

Compound	$\delta(H_{1,12})$ᵃ) [ppm]	$\delta(H_{CH_2})$ [ppm]	J_1ᵇ) [Hz]	$^3J(^{195}Pt, ^1H)$ [Hz]	$\delta(H_{other})$ᶜ) [ppm]	$\delta(^{31}P)$ᵈ) [ppm]	$^1J(^{195}Pt, ^{31}P)$ [Hz]
3	11.10	3.90	10.1		2.25	6.76	
4	10.66	3.75	9.8		2.30	14.92	
5	10.43	4.29	9.2		2.26	19.62	
6	10.50	4.30	9.2	29.3	2.25	16.45	2577
7	11.02	3.85	11.0		3.78	4.16	
8	10.68	3.76	10.3		3.83	13.53	
9	10.38	4.25	8.6		3.79	17.60	
10	10.43	4.25	9.2	29.0	3.78	14.66	2552
11	11.01	3.97	10.1			8.30	
12	10.70	3.85	10.1			14.36	
13	10.30	4.34	8.9			21.40	
14	10.37	4.36	8.9	30.2		18.58	2640
15	10.80	3.34	9.7		1.8–1.2	9.45	
16	10.26	3.32	9.1		1.7–1.2	27.41	
17	10.20	3.75	7.6		1.8–1.2	26.75	
18	10.28	3.79	7.9	28.1	2.05–1.23	18.93	2416
19ᵉ)	10.66	3.86	7.4	37.5	2.3–1.23	34.88	2781
20	10.32	3.82ᵍ) 2.83	n.o. 9		1.87(10.4)ᶠ) 1.39(13.5)ᶠ)	41.06	
21	10.66	5.03ʰ) 2.93	8 6		1.69(12.8)ᶠ) 1.39(13.4)ᶠ)	42.15	
22	10.73	5.10ⁱ) 2.97	9 5	n.o. 48	1.66(13.0)ᶠ) 1.40(12.5)ᶠ)	29.51	2419
23ʲ)	10.72					59.06	2836

ᵃ) Shift of protons at positions 1 and 12 on the benzo[c]phenanthrene. ᵇ) $|^2J(^{31}P, ^1H)+^4J(^{31}P, ^1H)|$ for CH_2. ᶜ) Other aliphatic protons. For compounds **3–6**: CH_3; for compounds **7–10**: OCH_3; for compounds **15–19**: C_6H_{11}; for compounds **20–23**: $C(CH_3)_3$. ᵈ) Relative to H_3PO_4; a positive value indicates a shift to lower field. ᵉ) $\delta(^1H_{hydride}) = -16.66$ ppm; $^2J(^{31}P, ^1H_{hydride}) = 25.7$ Hz; $^1J(^{195}Pt, ^1H_{hydride}) = 1282.5$ Hz. ᶠ) $|^3J(P, H)+^5J(P, H)|$. ᵍ) $^2J(H, H') = 14$ Hz; ʰ) $^2J(H, H') = 13.7$ Hz. ⁱ) $^2J(H, H') = 13.5$ Hz. ʲ) $\delta(^1H_{hydride}) = -17.89$ ppm; $^2J(^{31}P, ^1H_{hydride}) = 23.2$ Hz; $^1J(^{195}Pt, ^1H_{hydride}) = 1311.2$

of **1f**, the *t*-butyl signals provide a simple probe through which this process may be monitored. Complexes **20**, **21** and **22** all show *t*-butyl resonances at 90 MHz which are temperature-dependent and which reveal three distinct phases: *i)* a high temperature phase during which rapid organic backbone motion leads to average proton environments with signal coalescence occuring at 293 K, 323 K and > 333 K, respectively; *ii)* a period of slow benzo[c]phenanthrene motion, 258 K, 283 K and 293 K, respectively, in which the *t*-butyl resonances appear as two 1:1 triplets (see *Table* for these data), and *iii)* a new motional process in which either the R or R' resonances - but only one of these - begins to broaden as the temperature is yet further reduced. For $[PtCl_2(\mathbf{1f})]$ **(22)** we have been successful in slowing this latter process sufficiently to observe the limiting ^1H-NMR. spectrum at 213 K which consists of four *t*-butyl resonances at 1.75, 1.65, 1.38 and 1.01 in the ratio 1 : 3 : 1 : 1. Each of these signals retains the triplet structure stemming from the ^{31}P-spins $|^3J(P, H)+^5J(P, H)| = 12$, 11, 10 and 17 Hz, repectively, thereby confirming the *trans*-orientation of the P-atoms. Indeed a single frequency $^1H\{^{31}P\}$-experiment collapses all four triplets to singlets.

Returning to **2**, it is conceivable that this lower symmetry develops as a consequence of a distortion from planarity of the aromatic moiety, in keeping with the known molecular structures of these benzo[c]phenanthrene complexes [1] [2]; however, we can discard this hypothesis since the 1,12 protons are equivalent and do not change position significantly over the entire temperature range. We prefer an explanation involving relatively slow rotation about the P,C-bond of two P, t-Bu units.
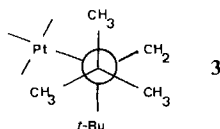
If this were true, each CH_3-resonance would see a different local environment, and as there are two such units, the ^{1}H-NMR. spectrum will contain three six-proton signals. Based on this suggestion one can assign the slow moving t-butyl groups to R in **2**, perhaps as a consequence of the nearby benzo[c]phenanthrene; however, this assignment, indeed the explanation, is rather speculative and must await further supporting evidence.

Examination of the electronic spectra of the complexes shows that, as found for the complexes of ligand **1a** [4], ligand field bands [7] are observable, only for the $NiCl_2$-complexes.

The spectra of complexes $[NiCl_2(\mathbf{1})]$ ($\mathbf{1} = \mathbf{1a} - \mathbf{e}$) are all very similar. The most interesting feature of these spectra is the change in intensity of the band at *ca.* 530 nm. While the complexes of ligands with R = Ph (**1a**), and R = m-CF$_3$ · C$_6$H$_4$ have practically identical molar extinction coefficients, *ca.* 475 and 465, respectively, the extinction coefficients of the complexes where R = m-CH$_3$ · C$_6$H$_4$ and p-CH$_3$O · C$_6$H$_4$ are much lower, *i. e.*, 230 and 115, respectively.

Even the replacement of an aryl substituent by an aliphatic group has practically no influence on the position of the low-energy absorption band. However, also in this case the change of substituent is accompanied by change of ε_{max} which, for the complex with R = C_6H_{11} is 620. As the transitions responsible for absorption in this region are "mixed-in" with charge transfer states the observed intensity changes are not unexpected [8].

In conclusion, the complexes of ligands **1a-f** give a fully analogous set of compounds with Ni(II), Pd(II) and Pt(II) metal centres. It is noteworthy that the presence of a CH$_3$-group in m-position on the terminal phenyl substituents of ligand **1** significantly increases the solubility of their complexes in hydrocarbon solvents while the presence of a CF$_3$-group, also in m-position, results in the formation of complexes which are soluble in hydroxylic solvents. This property has been exploited for the study of the kinetics of nucleophilic substitution reactions of complexes containing ligands of type **1** [9]. The results of this study will be the subject of later publication [10].

Finally, it should be noted that the postulated "fan-like" motion of the organic backbone of ligands of type **1** [12] is sufficiently slowed down by the presence of t-butyl end groups to be observable by ^{1}H-NMR. at room temperature.

Experimental Part.

Physical measurements were carried out as described elsewhere [2].

The visible and ultraviolet spectra were recorded on an *Varian Techtron* spectrophotometer, Model 635. The complexes were examined in dichloromethane solutions. The organic ligands **1b-f** were prepared by the methods of *Kapoor & Venanzi* [3]. The preparation of the complexes was carried out under N_2 up to the point where the crude complexes were obtained in the solid state. The complexes were prepared in an analytically pure state as follows.

Preparation of trans-[$NiCl_2$(**1b**)] (**3**). After dissolving $NiCl_2 \cdot 6 H_2O$ (0.10 g, 0.42 mmol) in refluxing BuOH (40 ml), **1b** (0.30 g, 0.44 mmol) was then added and the resulting purple solution refluxed for 2 h. The solvent was evaporated i.V. and the residue recrystallized from $CHCl_3/C_6H_6$.

Preparation of trans-[$Ni(NCS)_2$(**1b**)] (**4**). After adding **1b** (0.40 g, 0.59 mmol) to a refluxing solution of $Ni(SCN)_2$ (0.10 g, 0.57 mmol) in BuOH (50 ml), the orange-brown solid that separated on cooling was filtered off, washed with BuOH, dried i.V. and recrystallized from CH_2Cl_2/C_6H_6.

Preparation of trans-[$PdCl_2$(**1b**)] (**5**). After adding **1b** (0.40 g, 0.58 mmol) to a refluxing solution of $PdCl_2$ (0.10 g, 0.56 mmol) in CH_3CN (30 ml), a yellow precipitate formed immediately. The mixture was refluxed for 2 h and the precipitate, was filtered off and recrystallized from $CH_2Cl_2/MeOH$.

Preparation of trans-[$PtCl_2$(**1b**)] (**6**). To a solution of [$PtCl_2(PhCN)_2$] (0.29 g, 0.42 mmol) [13] in C_6H_6 (30 ml) was added a solution of **1b** (0.29 g, 0.43 mmol) in C_6H_6 (30 ml). The pale yellow solid which formed on stirring the solution for 4 h was filtered off. The yellow residue, obtained by evaporation of the filtrate i.V., was dissolved in $CHCl_3$ and chromatographed over silica gel, the yellow band being eluted with $CHCl_3$/hexane 3:1. This solid obtained from the eluate was recrystallized from CH_3CN.

Preparation of trans-[$NiCl_2$(**1c**)] (**7**). As described for **3**, recrystallization from CH_2Cl_2/C_6H_6/hexane.

Preparation of trans-[$Ni(NCS)_2$(**1c**)] (**8**). As described for **4**. The crude product was obtained by evaporation of the solvent and was recrystallized from CH_2Cl_2/C_6H_6.

Preparation of trans-[$PdCl_2$(**1c**)] (**9**). As described for **5**. The crude product was dissolved in C_6H_6, the solution treated with activated charcoal and evaporated to dryness. The residue was extracted with CH_3CN and the product thus obtained recrystallized from CH_3CN.

Preparation of trans-[$PtCl_2$(**1c**)] (**10**). From $PtCl_2$ and **1c** as described for **6**. The crude product was extracted with CH_3CN and the solid obtained from the extract was recrystallized from C_6H_6/CH_3CN.

Preparation and purification of trans-[$NiCl_2$(**1d**)] (**11**). As described for **3**.

Preparation of trans-[$Ni(NCS)_2$(**1d**)] (**12**). As described for **8**, recrystallization from CH_2Cl_2/hexane.

Preparation of trans-[$PdCl_2$(**1d**)] (**13**). The crude product was obtained by evaporation i.V. of the solution obtained as described for **5** and was recrystallized from $C_6H_6/EtOH$.

Preparation of trans-[$PtCl_2$(**1d**)] (**14**). As described for **10**. The crude product, obtained by evaporation of the solvent, was recrystallized from $C_6H_6/EtOH$.

Preparation of trans-[$NiCl_2$(**1e**)] (**15**). As described for **3**. The product, which precipitated out on addition of the reagents, was washed with BuOH and dried.

Preparation of trans-[$Ni(NCS)_2$(**1e**)] (**16**). From $Ni(SCN)_2$ and **1e** as described for **15**.

Preparation of trans-[$PdCl_2$(**1e**)] (**17**). As described for **5**, recrystallization from $CH_2Cl_2/C_6H_6/EtOH$.

Preparation of trans-[$PtCl_2$(**1e**)] (**18**). As described for **10**, recrystallization from $CH_2Cl_2/C_6H_6/$ EtOH.

Preparation of trans-[$PtHCl$(**1e**)] (**19**). To a solution of *trans*-[$PtHCl(Ph_3P)_2$] (0.12 g, 0.15 mmol) [14] in C_6H_6 (5 ml) was added **1e** (0.10 g, 0.16 mmol) and the solution left overnight. The solid obtained by evaporation of the solvent was extracted with ether and recrystallized from $C_6H_6/EtOH$.

obtained by evaporation of the solvent was extracted with ether and recrystallized from $C_6H_6/EtOH$.

Preparation of trans-[$Ni(NCS)_2$(**1f**)] (**20**). As described for **1b**.

Preparation of trans-[$PdCl_2$(**1f**)] (**21**). As described for **17**.

Preparation of trans-[$PtCl_2$(**1f**)] (**22**). After adding **1f** (1.1 g, 2.02 mmol) to a suspension of $AgClO_4 \cdot H_2O$ (0.72 g, 3.2 mmol), the mixture was stirred overnight, the solid residue filtered off and the solution chromatographed over silica gel. The residue obtained by evaporating the solvent, after recrystallization from CH_2Cl_2/acetone, gave pure [$Ag(ClO_4)$ (**1f**)] (0.87 g, 57%). This complex (0.15 g,

0.2 mmol) and $K_2[PtCl_4]$ (0.16 g, 0.38 mmol) were suspended in 50 ml of dry CH_2Cl_2 and the mixture was stirred at room temperature for 4 days. The solution obtained after filtration of the solid residue was reduced to a small volume and the crude product thus obtained was recrystallized from CH_2Cl_2/acetone.

Preparation of trans-$[PtHCl(1f)]$ (**23**). As described for **19**.

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