# 156. Transition-Metal Complexes with Bidentate Ligands Spanning *trans*-Positions

## Part XVII[1])

## Some Platinum(II) Complexes with Anionic Ligands such as Methoxide, Formate, Carboxylate, Hydride, and Borohydride, and the X-Ray Crystal Structure of $[PtHCl(\widehat{PP})]$ (PP = 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene)

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The complexes *trans*-[PtXY(**2**)] (X = H or Me; Y = OMe, OCHO, $CO_2H$, and $BH_4$; **2** = 2,11-bis{bis[3-(trifluoromethyl)phenyl]phosphinomethyl}benzo[*c*]phenanthrene) were prepared, and their decompositions to *trans*-[PtHX(**2**)] were studied. Some binuclear hydrido-bridged complexes, *e.g.* $[(\mathbf{2})HPt(\mu\text{-}H)PtH(\mathbf{2})]^+$, were also obtained. The preparation of complexes *trans*-$[PtHX(\mathbf{28})_2]$ (X = H or Me, **28** = bis[3-(trifluoromethyl)phenyl]benzylphosphine) is also reported. The X-ray crystal structure of *trans*-[PtHCl(**1**)] (**1** = 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene) was carried out.

**Introduction.** – Interest in Pt complexes with hydride ligands is related to a variety of factors including their potential as catalysts in processes of industrial importance [2].

A key step in many catalytic cycles is 'insertion' of an alkene into an M–H bond [3]. Mechanistic pathways for this type of reactions have been extensively studied [4], and Pt(II) complexes of the type *trans*-$[PtHCl(PR_3)_2]$ have been frequently used as model systems [5]. As in many cases, the primary product of the alkene insertion reaction has *cis*-configuration, *i.e.* *cis*-$[PtCl(R')(PR_3)_2]$, consideration was given to the possibility that a precursor of *cis*-configuration of the type *cis*-$[PtH(alkene)(PR_3)_2]^+$ is formed prior to the actual alkene insertion [6].

Recent studies of the coordination chemistry of 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene (**1**) have shown that this ligand forms preferentially complexes of the type *trans*-[PtXY(**1**)] (**3**), in which it spans *trans*-positions. Furthermore, the corresponding complexes with *cis*-configuration are formed only under special reaction conditions [7], and they easily rearrange to the corresponding *trans*-isomers. Thus, complexes

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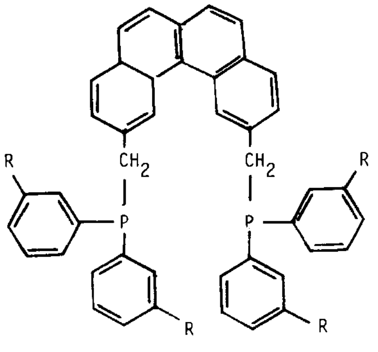
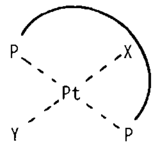
[1]) Part XVI: see [1].



**1** R = H
**2** R = $CF_3$



**3** R = H in $\widehat{\mathrm{PP}}$
**4** R = $CF_3$ in $\widehat{\mathrm{PP}}$
X = Me or H; Y = other anionic ligand

such as *trans*-[PtHX(**1**)] seemed to be well suited to test, whether alkene insertion could take place, when *trans* → *cis* isomerization was hindered in the reaction pathway. For this purpose, the complexes *trans*-[PtHX(**1**)] (X = Cl, I, $NO_3$) and *trans*-[PtHL(**1**)]$^+$ (L = acetone, $CH_3CN$, CO, and $PPh_3$) were prepared [7], and it was established that ethene does indeed insert into *trans*-[PtH(acetone)(**1**)]$^+$ leading to the formation of *trans*-[Pt(Et)(acetone)(**1**)]$^+$ [8].

Furthermore, as part of a study of the reactivity of Pt(II) hydrido complexes, some of us [9] described the kinetics of nucleophilic substitution reactions of complexes of the type *trans*-[PtY(4-PADA)(**2**)]$^+$ (Y = H; 4-PADA = pyridine-4-azo-4′-(*N*,*N*-dimethyl)aniline; **2** = 2,11-bis{bis[3-(trifluoromethyl)phenyl]phosphinomethyl}benzo[*c*]phenanthrene), and compared their reaction rates with those of the corresponding complexes where Y = Me.

Although numerous synthetic pathways can be considered for the preparation of complexes of the type *trans*-[PtHX($PR_3$)$_2$] [10], most of them are of practical value only if the starting material used, *i.e.* [Pt$X_2$($PR_3$)$_2$], has *cis*-configuration. However, as mentioned earlier, the complexes containing ligands **1** and **2** with *cis*-configuration are not generally obtainable. Thus, to prepare complexes of type **2a**, a variety of known synthetic routes was re-investigated.

The formation of Pt–H bonds from coordinated anionic ligands Y such as –OR, –OCHO, –$CO_2H$, and –$HBH_3$ is well documented [11–14]. Furthermore, there are several reports of the characterization of complexes of the type *trans*-[PtXY($PR_3$)$_2$] (X = generic anionic ligand, Y = as above) [15–20].

During the initial phase of this work, it was observed that *trans*-[PtH(Me)(**2**)] (**5**) is readily formed and quite stable, and, therefore, the hydride precursors *trans*-[PtY(Me)(**2**)] (Y = –OMe, **6**; –OCHO, **7**; –$CO_2H$, **8**, and –$HBH_3$, **9**) were prepared and their decomposition with formation of **5** investigated.

As previously reported [9], the $^1$H-NMR spectrum of the hydrido complexes of type *trans*-[PtHCl($\widehat{\mathrm{PP}}$)] ($\widehat{\mathrm{PP}}$ = **1** or **2**) show equivalent $CH_2$ protons, while in the corresponding complexes *trans*-[PtCl(Me)(**1**)] (**10**), the $CH_2$ protons are anisochronous and show geminal coupling. To establish whether the hydrido complexes of the type *trans*-[PtHCl($\widehat{\mathrm{PP}}$)] showed unusual structural features the X-ray crystal structure of *trans*-[PtHCl(**1**)] was determined.

**Results and Discussion.** – As the Pt–C and Pt–P bonds in complexes of type **2b** are rather inert in general, one only observes reactions which involve the ligand Y, *i.e.* the T-shaped arrangements of the $PtCP_2$ moiety remain unaltered during the reaction sequences carried out.

The complex *trans*-[PtCl(Me)(**2**)] (**10**) was used as the starting material for the synthesis of all the other complexes described here. Compound **10** was prepared by reacting *cis*-[PtCl(Me)(COD)] (COD = 1,5-cyclooctadiene) with ligand **2** [9].

The methanol solvento complex **11a** can be obtained *via Reaction 1:*

$$\underset{\mathbf{10}}{trans\text{-}[\mathrm{PtCl(Me)}(\mathbf{2})]} \xrightarrow{\mathrm{Ag^+/MeOH}} \underset{\mathbf{11a}}{trans\text{-}[\mathrm{Pt(Me)(MeOH)}(\mathbf{2})]^+} \tag{1}$$

It can be transformed into the corresponding methoxy species **6** *a*) by treating **11a** with an excess of NaOMe or KOH *(Reaction 2)* or *b*) by treating the hydroxy complex **12** *(vide infra)* with MeOH *(Reaction 3):*

$$\underset{\mathbf{11a}}{trans\text{-}[\mathrm{Pt(Me)(MeOH)}(\mathbf{2})]^+} \xrightarrow{\text{NaOMe or KOH}} \underset{\mathbf{6}}{trans\text{-}[\mathrm{Pt(Me)(OMe)}(\mathbf{2})]} \tag{2}$$

$$\underset{\mathbf{12}}{trans\text{-}[\mathrm{Pt(OH)(Me)}(\mathbf{2})]} \xrightarrow{\mathrm{MeOH}} \mathbf{6} \tag{3}$$

The methoxy complex obtained by *Reaction 2* is always contaminated with the corresponding hydroxy and carbonato complexes, **12** and **13**, respectively. As the hydroxy complex can also be obtained by *Reaction 4,*

$$\underset{\mathbf{6}}{trans\text{-}[\mathrm{Pt(OMe)(OMe)}(\mathbf{2})]} \xrightarrow{\mathrm{H_2O/THF}} \underset{\mathbf{12}}{trans\text{-}[\mathrm{Pt(OH)(Me)}(\mathbf{2})]} + \mathrm{MeOH} \tag{4}$$

it is presumed that traces of $H_2O$ in the solvent are responsible for the formation of **12**. Furthermore, it has been shown that the hydroxy complex can be transformed into the carbonato species *trans*-[(**2**)(Me)Pt($\mu$-$CO_3$)Pt(Me)(**2**)] (**13**) either by *Reaction 5,*

$$\underset{\mathbf{12}}{trans\text{-}[\mathrm{Pt(OH)(Me)}(\mathbf{2})]} \xrightarrow{\mathrm{Na_2CO_3\ in\ H_2O/acetone}} \underset{\mathbf{13}}{trans\text{-}[(\mathbf{2})\mathrm{(Me)Pt}(\mu\text{-}\mathrm{OCOO})\mathrm{Pt(Me)}(\mathbf{2})]} \tag{5}$$

or by exposing solutions containing **12** to air or even by storing solid **12** in air. Thus one can account for the occurrence of complex **13** through *Reactions 6* and *7.*

$$\underset{\mathbf{12}}{trans\text{-}[\mathrm{Pt(OH)(Me)}(\mathbf{2})]} \xrightarrow{\mathrm{CO_2}} \underset{\mathbf{14}}{trans\text{-}[\mathrm{Pt(OCO_2H)(Me)}(\mathbf{2})]} \tag{6}$$

$$\mathbf{12} + \mathbf{14} \rightarrow \mathbf{13} + \mathrm{H_2O} \tag{7}$$

Support for the postulation of intermediate **14** is provided by a $^{13}$C-NMR study of solutions of **13** containing coordinated $^{13}$C-enriched carbonate: these, in addition to the signals due to **13**, also show a low-intensity *triplet* centered at 159.1 ppm with a $^2J$(Pt, C) of 4 Hz which could be due to the $-O^{13}CO_2H$ moiety of **14**. A Rh complex containing this moiety was recently described [21].

Evidence for the dinuclearity of **13** is provided by *a*) a molecular-weight determination and *b*) the $^{13}C$-NMR spectrum of the coordinated $^{13}CO_3$ group which appears as the expected set of five lines of relative intensities 1:8:18:8:1 arising from the presence of the three Pt isotopomers.

The methoxy complex **6**, when heated in MeOH, decomposes with formation of **5** *(Reaction 8)*:

$$\underset{\mathbf{6}}{trans\text{-}[Pt(Me)(OMe)(\mathbf{2})]} \xrightarrow[\text{MeOH}]{\Delta} \underset{\mathbf{5}}{trans\text{-}[PtH(Me)(\mathbf{2})]} + \text{‘HCHO’} \qquad (8)$$

It is noteworthy that *Reaction 8* does not occur when carried out in benzene. This difference has been previously observed in related complexes [22].

It has also been found that the hydrido complex **5** is the main product formed, when the hydroxy or carbonato complexes, **12** or **13**, respectively, are refluxed in MeOH. As independent experiments show that **12** reacts with MeOH giving the methoxy complex **6** *(Reaction 3)*, one can presume that the formation of **5** from **12** occurs by *Reaction 3* followed by *Reaction 8*. It can also be postulated that, in refluxing MeOH, *Reactions 6* and *7* can be reversed, because of $CO_2$ evolution, regenerating the hydroxy complex which, then, reacts further as mentioned above.

Finally, mention should be made of the observation that the hydroxy complex **12** can be obtained directly from the methanol complex **11a** by reacting it with an excess of NaOH in aqueous acetone. Thus, it is apparent from the reactions described above that the species giving rise to the hydrido complex **5** is the corresponding methoxy derivative **6**, and that the solvent plays a major role in this transformation. It is also noteworthy in this context that **5** is not formed on warming **6** in the solid state, although thermal decomposition of the corresponding formato complex *(vide infra)* provides a good route to **5**.

The yields of **5** obtained using **6** or **13** as starting materials are not very good. This may be connected with the formation of a second product during these reactions. Its presence is indicated by the $^1H$-NMR spectra (in the Me region) of solutions of the crude products which, in addition to the resonances due to **5**, show a second *pseudo-triplet* at $\delta = 0.03$ ppm with a $^2J(Pt,H)$ value of 49 Hz. As it has been previously shown that *1*) the $^2J(Pt,H)$ values are diagnostic of the nature in *trans*-position to the Me group [23], and *2*) values of *ca.* 50 Hz are characteristic of complexes where the *trans*-ligand is a C-donor, one can postulate that solutions of crude **5** contain also a complex of type **4** where Y is a C-donor. It is plausible that the HCHO formed during *Reaction 8* reacts with **5** to give the hydroxymethyl complex *trans*-$[Pt(Me)(CH_2OH)(\mathbf{2})]^+$. Some hydroxymethyl complexes of Rh and Ir have been recently reported [24]. Their reactions are relevant to the chemistry described here.

As found in related compounds [16], the coordinated formate group proved to be a good precursor to **5**. The formato complex **7** is easily obtained by *Reaction 9:*

$$\underset{\mathbf{11a}}{trans\text{-}[Pt(Me)(MeOH)(\mathbf{2})]^+} \xrightarrow[< 0^\circ]{HCO_2^-/MeOH} \underset{\mathbf{7}}{trans\text{-}[Pt(OCHO)(Me)(\mathbf{2})]} \qquad (9)$$

This complex gradually decomposes, *e.g.* in refluxing MeOH, giving **5** with evolution of $CO_2$. There are three interesting features to this reaction: *a*) it is solvent-independent, *e.g.*

it takes place also in refluxing toluene, *b*) it occurs even on warming up **7** in the solid state, and *c*) when the reaction is carried out in MeOH, the formation of small amounts of *trans*-$[PtH_2(\mathbf{2})]$ (**15**) is observed.

A possible pathway for the formation of **15** could involve *1*) the reductive elimination of $HCO_2Me$ from **7**, with formation of the Pt(O) intermediate 'Pt(**2**)', *2*) the oxidative addition reaction of the latter with MeOH with formation of *trans*-[PtH(OMe)(**2**)], (**16**), and *3*) either its direct decomposition to **15** or by way of $\beta$-H abstraction from the formyl intermediate *trans*-[PtH(OCHO)(**2**)] (**17**), the latter being formed by anion exchange with **1**.

Finally, it should be noted that formyl decomposition is the method of choice for the preparation of **5**.

There are reports in the literature of the formation of Pt–H bonds from the corresponding $Pt{-}CO_2H$ species [20]. Thus, one might expect complex *trans*-$[Pt(CO_2H)(Me)(\mathbf{2})]$ (**8**) to eliminate $CO_2$ giving hydride complex **5**. This intermediate can be satisfactorily prepared by *Reactions 10* and *11*:

$$\underset{\mathbf{11a}}{trans\text{-}[Pt(Me)(MeOH)(\mathbf{2})]^+} \xrightarrow{CO} \underset{\mathbf{18}}{trans\text{-}[Pt(Me)(CO)(\mathbf{2})]^+} \qquad (10)$$

$$\mathbf{18} \xrightarrow[THF/H_2O]{NaOH} \underset{\mathbf{8}}{trans\text{-}[Pt(CO_2H)(Me)(\mathbf{2})]} \qquad (11)$$

It is noteworthy, however, that while the reaction of the hydroxy complex **12** with CO does not produce **8** cleanly, the methoxy complex **6** reacts with CO giving smoothly the methoxycarbonyl complex *trans*-$[Pt(Me)(CO_2Me)(\mathbf{2})]$ (**19**) which is analogous to several complexes described in the literature [25].

The thermal decomposition of the carboxy complex **8**, in refluxing benzene or acetone or in the solid state, failed to give the hydrido complex **5** in contrast to the behaviour of some related complexes reported by *Catellani* and *Halpern* [20a]. The carbonato complex **13** was identified as being formed when the above reaction was carried out in benzene.

One of the most commonly employed reagents to produce M–H bonds is $[BH_4]^-$ [26] and, in many cases, intermediates containing coordinated $BH_4^-$ anions have been characterized [27].

The reaction of the solvento complex *trans*-$[Pt(Me)(MeOH)(\mathbf{2})]^+$ (**11a**) with $Na[BH_4]$ in MeOH at room temperature gave mixtures of variable composition. Thus, in one case, fairly pure methanolato complex *trans*-[Pt(Me)(OMe)(**2**)] (**6**) was obtained, while in another experiment a mixture of hydrido complex **5** and another unidentified product, which showed a $^2J(Pt,H)$ value of 49 Hz for its coordinated Me groups.

The result of the first reaction indicates that initially $BH_4^-$ acts as a *Brønsted* base with the consequence that **6** may be the actual complex which interacts with $BH_4^-$ to give the product observed during the second reaction.

To avoid this difficulty the chloro complex *trans*-[PtCl(Me)(**2**)] (**10**) was reacted with $Na[BH_4]$ in THF at room temperature. This reaction, however, gave the dihydrido complex *trans*-$[PtH_2(\mathbf{2})]$ (**15**), *i.e.*, cleavage of the Pt–C bond occurred.

The desired hydride **5** was conveniently obtained by reacting **10** with $Na[BH_4]$ in MeCN containing 10% $H_2O$ *(Reaction 12)*:

$$\underset{\mathbf{10}}{trans\text{-}[PtCl(Me)(\mathbf{2})]} \xrightarrow[CH_3CN/H_2O]{Na[BH_4]} \underset{\mathbf{5}}{trans\text{-}[PtH(Me)(\mathbf{2})]} \qquad (12)$$

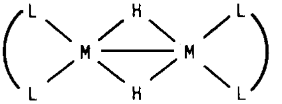
Summing up, the reactions described above clearly show that the presence of a Me group in *trans*-position to the hydride-precursor ligand induces the latter to undergo its typical reactions leading to the formation of a Pt–H bond.

The results described above indicated that analogous reactions might be used for the preparation of *trans*-[PtH$_2$(**2**)] (**15**) from *trans*-[PtHY(**2**)] (Y = OMe, **16**; Y = OCHO, **17**, and Y = Cl, **20**). Indeed, it was found that **15** could be prepared from **17** or **20**, as done for the corresponding Me compounds, although the product is considerably less stable than the corresponding Me hydrido derivative **3**.

NMR monitoring of the reaction between the chloro complex **20** and [BH$_4$]$^-$ in MeCN/H$_2$O showed that prolonged reaction times led to the formation of a second product **21** which had NMR characteristics similar to those reported for dinuclear hydrido-bridged complexes [28–31]. This compound could not be obtained in the pure state as the reaction mixture decomposed, before the transformation of **15** into **21** was complete. Its concentration appears to be related to the intensity of the red colour of the resulting solution and to gas evolution. Its formation may well be either thermally or photochemically induced.

The dinuclear nature of **21** could be established through the $^1$N-NMR spectrum in the hydride region which appears as a *quintet* with $\delta = -0.24$ ppm, $^2J(P,H) = 33$ Hz, flanked by its $^{195}$Pt satellites $^1J(Pt,H) = 610$ Hz [32].

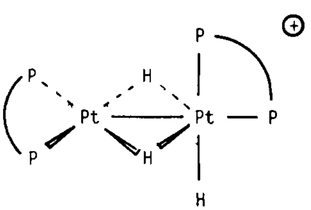
The presence of two H-atoms per dinuclear unit was established by integration *vs.* a known amount of *trans*-[PtH$_2$(**2**)] (**15**). Therefore, complex **21** is tentatively assigned the structure shown below.



**21** M = Pt; $\widehat{LL}$ = **2**
**22** M = Ni; $\widehat{LL}$ = Cy$_2$P(CH$_2$)$_3$PCy$_2$

A Ni complex, **22**, with a structure of this type, has been recently described [32].

To test whether **21** was related to complexes such as [(diphos)Pt($\mu$-H)$_2$PtH(diphos)]$^+$ (diphos = Ph$_2$PCH$_2$CH$_2$PPh$_2$; **23**) [28], an attempt was made to obtain the corresponding cation [(**2**)Pt($\mu$-H)$_2$PtH(**2**)]$^+$.



**23** $\widehat{PP}$ = Ph$_2$PCH$_2$CH$_2$PPh$_2$ = diphos

The facile formation of compounds of the type [(PR$_3$)$_2$Pt($\mu$-H)$_2$PtH(PR$_3$)$_2$]$^+$ is now well documented [29]. The formation reaction has been formally described as a 'donor-acceptor' scheme [30]. In the most commonly occurring reaction, the 'donor' is a complex with a terminal M–H bond, and the acceptor is a cationic solvento complex. An example is shown in *Reaction Sequence 13–16* [29–30]:

$$\textit{trans}\text{-}[\mathrm{PtH(MeOH)(PEt_3)_2}]^+ + \mathrm{HCO_2^-} \rightarrow \textit{trans}\text{-}[\mathrm{PtH(OCHO)(PEt_3)_2}] + \mathrm{MeOH} \tag{13}$$

$$\textit{trans}\text{-}[\mathrm{PtH(OCHO)(PEt_3)_2}] \rightarrow \textit{trans}\text{-}[\mathrm{PtH_2(PEt_3)_2}] + \mathrm{CO_2} \tag{14}$$

$$\textit{trans}\text{-}[\mathrm{PtH(MeOH)(PEt_3)_2}]^+ + \textit{trans}\text{-}[\mathrm{PtH_2(PEt_3)_2}] \rightarrow \textit{trans,trans}\text{-}[\mathrm{(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2}]^+ + \mathrm{MeOH} \tag{15}$$

$$\textit{trans,trans}\text{-}[\mathrm{(PEt_3)_2HPt(\mu\text{-}H)PtH(PEt_3)_2}]^+ \rightarrow \textit{cis,trans}\text{-}[\mathrm{(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2}]^+ \tag{16}$$

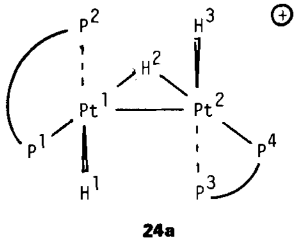
Warming up a solution of 2 equiv. of *trans*-[PtH(MeOH)(**2**)]$^+$, with 1 equiv. of HCOONa gave a complex cation which was isolated as its [BPh$_4$] salt and had the composition [Pt$_2$H$_3$(**2**)$_2$][BPh$_4$] (**24**[BPh$_4$]). Its $^1$H-NMR spectrum, in the hydride region, consisted of a *triplet of triplets* flanked by their $^{195}$Pt satellites. Integrations showed the presence of three hydride ligands. The triplet splittings originated from separate P,H couplings as confirmed by selective $^{31}$P-decoupling experiments. The following parameters were observed: $\delta(\mathrm{H}) = -5.50$ ppm, $J(\mathrm{P_{a,b}},\mathrm{H}) = 29$ Hz, $J(\mathrm{P_{c,d}},\mathrm{H}) = 49$ Hz, and $^1J(\mathrm{Pt},\mathrm{H}) = 431$ Hz. This spectrum differs significantly from that of **23** where there is only one main hydride signal at −2.8 ppm because of a fast dynamic process occurring in solution [28]. Moreover, this is in the form of a *quintet,* flanked by its $^{195}$Pt satellites, *i.e.* all four P-atoms are magnetically equivalent in solution.

The inequivalence of the phosphine donors in **24** is confirmed by the $^{31}$P{$^1$H}-NMR spectrum. This appears as a *doublet of doublets* flanked by a complex set of $^{195}$Pt satellites. The main resonances occur at 29.3 ppm ($\delta(\mathrm{P_{a,b}})$) and 9.1 ($\delta(\mathrm{P_{c,d}})$). The value of $J(\mathrm{P_{1,2}},\mathrm{P_{3,4}}) = 7$ Hz.

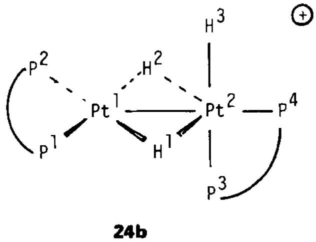
Qualitative examination of the $^{31}$P-NMR spectrum shows that the values of $^1J(\mathrm{Pt},\mathrm{P})$ and $^3J(\mathrm{Pt},\mathrm{P})$ for $\mathrm{P_{a,b}}$ are smaller than the corresponding values for $\mathrm{P_{c,d}}$, approximate values for these couplings being: $^1J(\mathrm{Pt},\mathrm{P_{1,2}}) \approx 2600$ Hz, $^3J(\mathrm{Pt},\mathrm{P_{3,4}}) \approx 55$ Hz, $^1J(\mathrm{Pt},\mathrm{P_{3,4}}) \approx 3700$ Hz, and $^3J(\mathrm{Pt},\mathrm{P_{3,4}}) \approx 350$ Hz.

The $^{195}$Pt-NMR spectrum consists of a single set of signals centered at −4825 ppm consisting of a *doublet of doublets* confirming the non-equivalence of the $^{31}$P spins.

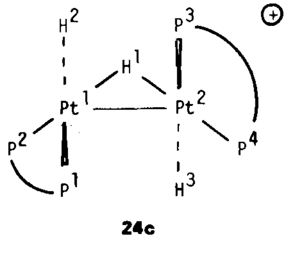
On the basis of these data, one can postulate a static structure for **24** of the type shown below (**24a**). The dynamic process, which equalizes the hydride ligands, would then



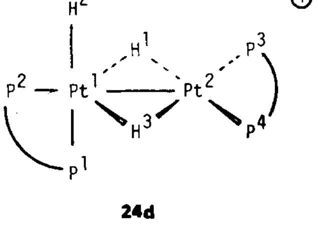
**24a**



**24b**



**24c**

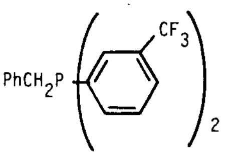


**24d**

correspond to the isomerization process **24a** $\rightleftharpoons$ **24b** $\rightleftharpoons$ **24c** $\rightleftharpoons$ **24a** $\rightleftharpoons$ *etc*. In such a process the P-atoms would not become equivalent, one of them always having a terminal hydride as a *trans*-ligand. In this respect, **24** differs from **23** in that the latter, at the dynamic limit, can be written as [(diphos)Pt($\mu$-H)$_3$Pt(diphos)]$^+$, while the former can form only a $\mu_2$-bridge. This is probably due to the optimum P–Pt–P angle which, in the case of diphos, is $< 90°$, while in the case of ligand **2** it is likely to be $> 105°$ [7].

As it is known that cation **23** reacts with CO giving [(diphos)Pt($\mu$-H)($\mu$-CO)-Pt(diphos)]$^+$ (**25**) [31], which contains platinum in the formal oxidation state Pt(I), a similar reaction was tried using hydride **24** (generated *in situ* from the solvento complex *trans*-[PtH(MeOH)(**2**)] (**26a**)) and CO. As expected, cation [(**2**)Pt($\mu$-H)($\mu$-CO)Pt(**2**)]$^+$ (**27**) was obtained.

As the kinetic data [9] for complexes of type **4** required comparison with those for complexes with monodentate ligands related to **2**, the preparation of a complex analogous to *trans*-[PtH(Me)(**2**)] (**5**) but containing the monodentate ligand PhCH$_2$P(*m*-CF$_3$C$_6$H$_4$)$_2$ (**28**), *i.e.* *trans*-[PtH(CH$_3$)(**28**)] (**29**) was investigated. As this compound proved to be less stable than **5**, milder reaction conditions and more careful workup was necessary.



**28**

However, the reaction of *trans*-[PtCl(Me)(**28**)$_2$] (**30**) with Na[BH$_4$] as well as that of *trans*-[Pt(Me)(MeOH)(**28**)$_2$]$^+$ (**31a**; obtained *in situ* by reacting **30** with Ag$^+$ ions) with formate gave **29**, albeit in relatively low yields. Also these reactions gave **29** contaminated with a second hydrido complex characterized *1*) by a $\delta(^{31}P) = 42$ ppm, a $^1J(\text{Pt, P})$ value of 4503 Hz, and *2*) a four-line spectrum in the hydride region centered at $\delta = -8.57$ ppm with a separation of 13 Hz and a $^1J(\text{Pt, H})$ value of 385 Hz. This low value of $^1J(\text{Pt, H})$ as well as integration of the $^1$H-NMR spectra suggest a binuclear structure for this complex. However, because of its low concentration in solution, the signals arising from the isotopomer with two $^{195}$Pt-nuclei could not unambiguously be recognized against signal noise, and, thus, no reliable structural assignment was possible. The hydrido complex (**29**) is best prepared by reacting *trans*-[Pt(Me)($\gamma$-picoline)(**28**)$_2$][BF$_4$] (**32**) with Na[BH$_4$] in MeCN/H$_2$O.

In conclusion, it has been shown that standard methods particularly those using formate and BH$_4^-$ can be used to produce complexes of types **4**, when the ligand in *trans*-position to the group which generates the hydride ligand is either Me or H, and that the complexes of the type *trans*-[PtHX(**2**)] show a marked tendency to form hydrido-bridged binuclear complexes despite the bulk of ligand **2** and the size of the chelate ring.

Finally, the complex *trans*-[PtHCl(**1**)] (**33**) required for an X-ray structure determination was obtained, *i.e.* by adding ligand **1** to a benzene solution of *trans*-[PtHCl(PPh$_3$)$_2$] [8].

*Description of the Crystal Structure of* trans-*[PtHCl(***1***)]* (**33**). The crystal structure consists of discrete monomeric units of [PtHCl(**1**)]. A perspective view of the molecule is shown in the *Figure*. The important bond lengths and angles are reported in *Table 1*.

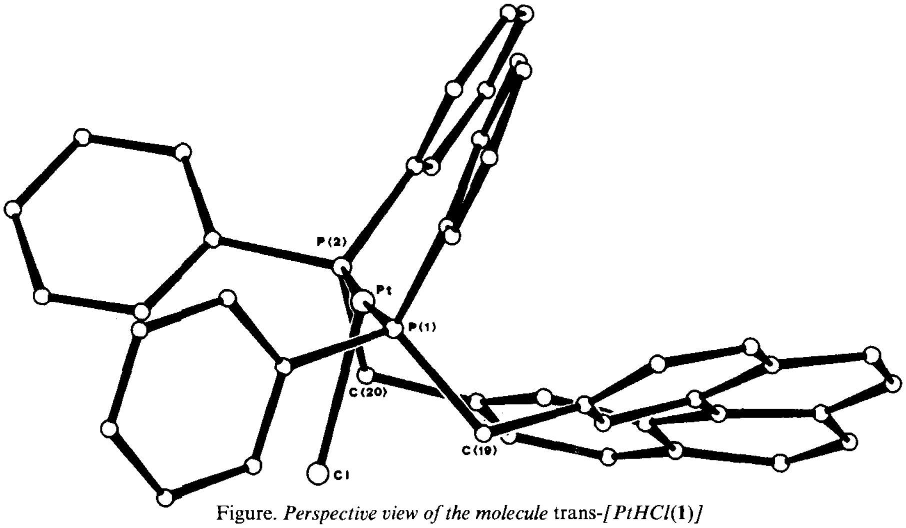


Figure. *Perspective view of the molecule* trans-*[PtHCl(***1***)]*
(**1** = 2,11-bis(diphosphinomethyl)benzo[*c*]phenanthrene)

Table 1. *Selected Interatomic Distances* [Å] *and Angles* [°] *in* trans-*[PtHCl(***1***)]*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pt–Cl | 2.397(3) | Pt–P(2) | 2.278(3) | Cl–Pt–P(2) | 93.0(1) |
| Pt–P(1) | 2.282(3) | Cl–Pt–P(1) | 89.9(1) | P(1)–Pt–P(2) | 176.2(1) |

The *trans*-P-atoms together with the Cl-atom form a T-shaped arrangement around the Pt-atom. The best plane through these four atoms is described by the equation $8.93x - 4.91y + 11.36z = 3.68$ (monoclinic coordinates), the deviations being: Pt $-0.033(1)$, Cl 0.001(3), P(1), and P(2) 0.016(3) Å.

The Pt–Cl bond (2.397(3) Å) is significantly longer than in $[PtCl_4]^-$ (2.308(2) Å) [33]. This lengthening is consistent with the high *trans*-influence of the hydride ligand [34]. The Pt–P bonds have almost the same length (average value 2.280(3) Å); they are significantly shorter than the Pd–P bonds observed in *trans*-$[PdCl_2(\mathbf{1a})]$ [35] and fall towards the low end of the range found for *trans* M–P bonds where M is a second- or third-row transition metal. Similar features were observed in the structure of the analogous hydride complex *trans*-$[PtHCl(PEtPh_2)_2]$ containing monodentate phosphines [36], to which the structure of the present compound is strictly comparable.

The shortest Pt···H contact is 2.76 Å for Pt···H·C(12). The Cl ligand is at distances ranging between 2.67 and 2.96 Å from four H-atoms. These four H-atoms are the two internal H-atoms of the two $CH_2$ groups and the two nearest Ph groups.

The geometry of the 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene ligand closely resembles that found previously for its other complexes [35]. The out-of-plane distorsion of its overcrowded tetranuclear system confers chirality at the complex which in the crystal is present in the racemic form, the two configurations being related by the centre of symmetry.

Comparison of the molecular structure of *trans*-[PtHCl(1)] with that of *trans*-$[PtCl_2(1)]$ [35] does not reveal the reason for the facile dynamic process which exchanges the positions of the 'external' H-atoms on C(19) and C(20) with the corresponding 'internal' atoms. Further analysis of this motion was not attempted.

## Experimental Part

**1. General.** – Generally, all reactions were carried out under $N_2$. IR spectra: *Beckman IR 4250* spectrometer. $^{1}$H- (if not otherwise stated), $^{13}$C{$^{1}$H}-, and $^{31}$P{$^{1}$H}-NMR spectra were measured using *Bruker HX-90* and *WH-90* NMR spectrometers. $^{195}$Pt{$^{1}$H}-NMR spectra were recorded using a *Bruker WM-250* NMR spectrometer. If not otherwise stated, the measurements were carried out at ambient temp. Chemical shifts are in ppm and relative to TMS, external $H_3PO_4$, and $Na_2[PtCl_4]$, respectively (a positive sign indicates a resonance to low field of the reference). *J* values are given in Hz. C, H, and N elemental analyses, and molecular-weight determinations were performed by the Microanalytical Laboratory and those of P and Pt by the Analytical Section of Inorganic Chemistry Laboratory of the ETH-Zürich, respectively.

**2. Preparation of the Complexes.** – The ligands *2,11-bis(diphenylphosphinophenyl)benzo[*c*]phenanthrene* (**1**) [35], *2,11-bis{bis[3-(trifluoromethyl)phenyl]phosphinomethyl}benzo[*c*]phenanthrene* (**2**), and *bis[3-(trifluoromethyl)phenyl]benzylphosphine* (**28**) [9] as well as the complexes trans-*[PtCl(Me)*(**2**)*]* (**10**), trans-*[PtHCl*(**2**)*]* (**20**), and trans-*[PtCl(Me)*(**28**)$_2$*]* (**30**) [9] were prepared as described in the literature. The complexes trans-*[Pt(Me)(MeOH)*(**2**)*][BF$_4$]* (**11a**[BF$_4$]), trans-*[PtH(MeOH)*(**2**)*][BF$_4$]* (**26a**[BF$_4$]), and trans-*[Pt(Me)(MeOH)*(**28**)$_2$*][BF$_4$]* (**31a**[BF$_4$]) were prepared by abstracting chloride with $AgBF_4$ in MeOH or MeOH/$CH_2Cl_2$. After filtering off the AgCl precipitates, the solns. were evaporated to dryness under reduced pressure.

trans-*[PtH(Me)*(**2**)*]* (**5**). *a)* trans-*[Pt(Me)(OMe)*(**2**)*]* (**6**; 220 mg, 0.19 mmol) was heated during 16 h in refluxing MeOH (5 ml). The resulting yellowish suspension was filtered off at r.t. The colorless pure product was obtained by recrystallizing the solid residue twice from benzene/MeOH. Yield: 131 mg (61 %).

*b)* trans-*[Pt(Me)(OCHO)*(**2**)*]* (**7**; 190 mg, 0.16 mmol) dissolved in toluene (3 ml) was heated during 5 h at 90°. The solvent was evaporated under vacuum and the product crystallized out on addition of MeOH to the residue. It was filtered off and dried. Yield: 150 mg (82 %).

*c)* To trans-*[PtCl(Me)*(**2**)*]* (**10**; 463 mg, 0.41 mmol) dissolved in 25 ml of MeCN, a soln. of 20 mg (0.53 mmol) of $NaBH_4$ dissolved in 5 ml of MeCN and 0.5 ml of $H_2O$ was added. After stirring for 1 h, the product was precipitated by adding 20 ml of $H_2O$. It was filtered off, washed with $H_2O$, and dried under vacuum. It was recrystallized from benzene/MeOH. Yield: 400 mg (89%). IR (nujol): 1980–2000*s* (Pt–H). $^{1}$H-NMR ($C_6D_6$): –3.31 (*tq*, not completely resolved, $^{2}J$(P,H) = 18, $^{3}J$(H,H) = 2, $^{1}J$(P,H) = 677, H–Pt); 0.39 (*dt*, $^{3}J$(P,H) = 6, $^{3}J$(H,H) = 2, $^{2}J$(Pt,H) = 49, $CH_3$–Pt); 3.92 (*t*, $^{2}J$(P,H) = $^{4}J$(P,H) = 7, $^{3}J$(Pt,H) = 43, 2 $CH_2$–P); 6.5–8.4 (24 arom. H); 9.97 (*s*, H–C(1), H–C(12)). $^{31}$P-NMR ($C_6D_6$): 30.8 (*s*, $^{1}J$(Pt,P) = 3155). Anal. calc. for $C_{49}H_{34}F_{12}P_2Pt$ (1107.8): C 53.13, H 3.09, P 5.59, Pt 17.61; found: C 53.08, H 3.00, P 5.76, Pt 17.77.

trans-*[Pt(Me)(OMe)*(**2**)*]* (**6**). To an excess of NaOMe in 15 ml of MeOH, 880 mg (0.72 mmol) of trans-*[Pt(Me)(MeOH)*(**2**)*][BF$_4$]* (**11a**[BF$_4$]) were added at r.t. After a short time, the colorless product precipitated. It was filtered off and dried: 762 mg (93 %). The product is sensitive to moisture and $CO_2$ both in soln. and in the solid state. Complex **6** could not be isolated in an anal. pure state. IR (nujol): 2770*s*, 1055*s* (MeO); 3685*w*, 1665*w* could not be assigned to complex **5**. $^{1}$H-NMR ($C_6D_6$): 0.16 (*t*, $^{3}J$(P,H) = 6, $^{2}J$(Pt,H) = 70, $CH_3$–Pt); 3.48 (*s*, $^{3}J$(Pt,H) = 24, MeO); 3.21 (*dt*, $^{2}J$(H,H) = 13, $^{2}J$(P,H) = $^{4}J$(P,H) = 7, $^{3}J$(Pt,H) = 45, $CH_2$–P); 4.81 (*dt*, $^{2}J$(H,H) = 13, $^{2}J$(P,H) = $^{4}J$(P,H) = 10, $^{3}J$(Pt,H) = 32, $CH_2$–P); 6.4–8.6 (24 arom. H); 10.66 (*s*, H–C(1), H–C(12)). $^{31}$P-NMR ($C_6D_6$): 26.66 (*s*, $^{1}J$(Pt,P) = 3340).

trans-*[Pt(Me)(OCHO)*(**2**)*]* (**7**). trans-*[Pt(Me)(MeOH)*(**2**)*][BF$_4$]* (**11a**[BF$_4$]; 490 mg, 0.40 mmol) was suspended in 2 ml of MeOH and cooled to –60°. HCOONa (51 mg, 0.75 mmol) in 3 ml of MeOH was then added. At –10°, the solid dissolved and half of the solvent was evaporated under vacuum. The *Schlenk* tube was then placed in ice-water. After a short time, the pure product crystallized out. Yield: 360 mg (78 %). IR (nujol): 1620*s* (C=O). $^{1}$H-NMR (250 MHz, $C_6D_6$): 0.34 (*t*, $^{3}J$(P,H) = 7, $^{2}J$(Pt,H) = 77, $CH_3$–Pt); 3.59 (*dt*, $^{2}J$(P,H) = $^{4}J$(P,H) = 7, $^{2}J$(H,H) = 13, $CH_2$–P); 4.05 (*dt*, $^{2}J$(P,H) = $^{4}J$(P,H) = 9, $^{2}J$(H,H) = 13, $CH_2$–P); 6.6–8.2 (24 arom. H); 8.54 (*t*, $^{4}J$(P,H) = 1.5, $^{3}J$(Pt,H) = 47, HCOO); 10.40 (*s*, H–C(1), H–C(12)). $^{31}$P-NMR ($C_6D_6$): 27.0 (*s*, $^{1}J$(Pt,P) = 3258). Anal. calc. for $C_{50}H_{34}F_{12}O_2P_2Pt$ (1151.8): C 52.14, H 2.98, P 5.38, Pt 16.94; found: C 52.10, H 2.89, P 5.50.

trans-*[Pt(Me)(CO)*(**2**)*][BF$_4$]* (**18**[BF$_4$]). Into a soln. of 500 mg (0.41 mmol) of trans-*[Pt(Me)(MeOH)*(**2**)*][BF$_4$]* (**11a**[BF$_4$]) dissolved in 20 ml of MeOH, a stream of CO was passed. The product precipitated out, it was filtered off and dried. Yield: 420 mg (84%). IR (nujol): 2130*s* (C=O). $^{1}$H-NMR (($D_6$)acetone): 1.04 (*t*, $^{3}J$(P,H) = 9, $^{2}J$(Pt,H) = 59, $CH_3$–Pt); 4.5–5.6 (2 $CH_2$–P); 7.3–8.8 (24 arom. H); 9.71 (*s*, H–C(1), H–C(12)). $^{31}$P-NMR (($D_6$)acetone): 16.9 (*s*, $^{1}J$(Pt,P) = 2647). Anal. calc. for $C_{50}H_{33}BF_{16}OP_2Pt$ (1221.6; found (in $CH_2Cl_2$): 1115): C 49.16, H 2.72; found: C 49.00, H 2.59.

trans-*[Pt(Me)(CO$_2$H)*(**2**)*]* (**8**). To a soln. of 346 mg (0.28 mmol) of trans-*[Pt(Me)(CO)*(**2**)*][BF$_4$]* (**18**[BF$_4$]) in 3 ml of acetone at –15°, 20 mg (0.36 mmol) of KOH in 0.4 ml of $H_2O$ was added. The product precipitated during warming up to r.t. It was filtered off and dried under vacuum. Yield: 223 mg (69 %). In soln., **8** slowly decomposed at r.t. IR (nujol): 3475*w* (OH); 1627*s*, 1018*s* (C=O). $^{1}$H-NMR (($D_6$)acetone): −0.33 (*t*, $^{3}J$(P,H) = 7, $^{2}J$(Pt,H) = 48, $CH_3$–Pt); 4.2–4.9 (*m*, 2 $CH_2$–P); 7.0–8.5 (24 arom. H); 10.13 (*s*, H–C(1), H–C(12)); COO*H* could not be located. $^{31}$P-NMR (($D_6$)acetone): 24.5 (*s*, $^{1}J$(Pt,P) = 3131).

trans-*[Pt(Me)(OH)*(**2**)*]* (**12**). To a soln. of 463 mg (0.37 mmol) of trans-*[Pt(Me)(acetone)*(**2**)*][BF₄]* (**11b**[$BF_4$]), prepared as described earlier, in 4 ml of acetone, 55 mg (0.98 mmol) of KOH in 0.5 ml of $H_2O$ were added. The solvent was evaporated to dryness under vacuum. The residue was extracted with benzene, the soln. dried ($MgSO_4$), filtered off, and its volume reduced to 1 ml under vacuum. The product crystallized out on addition of hexane. It was filtered off and dried under vacuum. Yield: 340 mg (82%). It is very sensitive to $CO_2$. IR ($CH_2Cl_2$): 3650*w*, 3610*w* (OH). $^{1}$H-NMR ($C_6D_6$): −1.58 (*t*, $^{3}J$(P,H) = 2, $^{2}J$(Pt,H) = 15, HO–Pt); 0.11 (*t*, $^{3}J$(P,H) = 6, $^{2}J$(Pt,H) = 71, $CH_3$–Pt); 3.22 (*dt*, $^{2}J$(H,H) = 13, $^{2}J$(P,H) = $^{4}J$(P,H) = 8, $^{3}J$(Pt,H) = 42, $CH_2$–P); 4.89 (*dt*, $^{2}J$(H,H) = 13, $^{2}J$(P,H) = $^{4}J$(P,H) = 10, $^{3}J$(Pt,H) = 34, $CH_2$–P); 6.5–8.3 (24 arom. H); 10.66 (*s*, H–C(1), H–C(12)). $^{31}$P-NMR ($C_6D_6$): 28.0 (*s*, $^{1}J$(Pt,P) = 3256).

*[Pt₂(Me)₂(μ-CO₃)*(**2**)*]* (**13**). To a soln. of 210 mg (80.17 mmol) of trans-*[Pt(Me)(acetone)*(**2**)*][BF₄]* (**11b**[$BF_4$]) in 5 ml of acetone, 70 mg (0.66 mmol) of $Na_2CO_3$ dissolved in 1 ml of $H_2O$ were added. The soln. was concentrated under vacuum until the product had precipitated. This was extracted with benzene, the latter was separated, dried ($MgSO_4$), filtered, and brought to crystallization by adding hexane. Yield: 170 mg (89%). IR (nujol): 1545*s* (C=O). $^{1}$H-NMR ($C_6D_6$): 0.03 (*t*, $^{3}J$(P,H) = 6, $^{2}J$(Pt,H) = 76, 2 $CH_3$–Pt); 2.72 (*dt*, $^{2}J$(H,H) = 14, $^{2}J$(P,H) = $^{4}J$(P,H) = 8, $^{3}J$(Pt,H) = 53, 2 $CH_2$–P); 4.96 (*dt*, $^{2}J$(H,H) = 14, $^{2}J$(P,H) = $^{4}J$(P,H) = 10, 2 $CH_2$–P); 6.0–8.5 (48 arom. H); 10.58 (*s*, 2 H–C(1), 2 H–C(12)). $^{31}$P-NMR ($C_6D_6$): 26.3 (*s*, $^{1}J$(Pt,P) = 3346). Anal. calc. for $C_{99}H_{66}F_{24}O_3P_4Pt_2$ (2273.7; found (in $CH_2Cl_2$): 2093): C 52.30, H 2.93, P 5.45, Pt 17.16; found: C 52.46, H 2.98, P 5.46, Pt 17.50.

*[Pt₂(Me)₂(μ-¹³CO₃)*(**2**)*]* (**13a**) was prepared as described above, using $K_2$ $^{13}CO_3$ instead of $Na_2CO_3$. IR (nujol): 1505*s* ($^{13}$C=O). $^{13}$C-NMR (($D_6$)acetone): 166.7 (*s*, $^{2}J$(Pt,C) = 5.5, $CO_3$–Pt); −22.6 (*t*, $^{2}J$(P,C) = 6, $^{1}J$(Pt,C) = 645, $CH_3$–Pt).

trans-*[Pt(Me)(CO₂Me)*(**2**)*]* (**19**). To 200 mg (0.18 mmol) of trans-*[Pt(Me)(OMe)*(**2**)*]* (**6**) dissolved in 5 ml of benzene, 20 ml of MeOH were added. CO was bubbled through this soln., until the colorless product precipitated. This was filtered off and dried. Yield: 152 mg (74%). IR (nujol): 1620*s*, 1028*s* (C=O). $^{1}$H-NMR ($C_6D_6$): −0.03 (*t*, $^{3}J$(P,H) = 7, $^{2}J$(Pt,H) = 48, $CH_3$–Pt); 2.72 (*s*, $^{4}J$(Pt,H) = 4, MeO); 3.6–4.3 (*m*, 2 $CH_2$–P); 6.5–8.2 (24 arom. H); 10.12 (*s*, H–C(1), H–C(12)). $^{31}$P-NMR ($C_6D_6$): 24.6 (*s*, $^{1}J$(Pt,P) = 3149). Anal. calc. for $C_{51}H_{36}F_{12}O_2P_2Pt$ (1165.9; found (in $CH_2Cl_2$): 1141.6): C 52.54, H 3.11; found: C 52.41, H 2.98.

trans-*[PtH(OCHO)*(**2**)*]* (**17**). trans-*[PtH(MeOH)*(**2**)*][BF₄]* (**26a**[$BF_4$]; 520 mg, 0.43 mmol) prepared as described in *General* was dissolved in 2 ml of MeOH. The soln. was cooled to −70°. HCOONa (31.5 mg, 0.46 mmol) dissolved in 3 ml of MeOH was added and the *Schlenk* tube placed in an ice/NaCl bath. After a short time, the product crystallized out, and it was filtered off and dried at 0°. It was recrystallized from toluene/hexane. Yield: 447 mg (92%). IR (nujol): 2810*m*, 2690*w* (HCOO); 2255*m* (Pt–H); 1610*s* (C=O). $^{1}$H-NMR ($C_6D_6$): −19.78 (*dt*, $^{4}J$(H,H) = 5, $^{2}J$(P,H) = 15, $^{1}J$(Pt,H) = 1129, H–Pt); 4.00 (*t*, $^{2}J$(P,H) = $^{4}J$(P,H) = 8, $^{3}J$(Pt,H) = 43, 2 $CH_2$–P); 6.5–8.3 (24 arom. H); 8.78 (*dt*, $^{4}J$(H,H) = 5, $^{4}J$(P,H) = 1.5, $^{3}J$(Pt,H) = 53, HCOO); 10.28 (*s*, H–C(1), H–C(12)). $^{31}$P-NMR ($C_6D_6$): 27.7 (*s*, $^{1}J$(Pt,P) = 3155).

Complex **17** decarboxylated slowly to trans-*[PtH₂*(**2**)*]* (**15**) at r.t. in soln. and in the solid state.

trans-*[PtH₂*(**2**)*]* (**15**) *a*) trans-*[PtH(OCHO)*(**2**)*]* (**17**; 296 mg, 0.26 mmol) decarboxylated during 4 days on a vacuum line at r.t. to a pale yellow solid. Yield: 284 mg (100%). The colorless product can be obtained by recrystallization from $Et_2O$.

*b*) trans-*[PtHCl*(**2**)*]* (**20**; 500 mg, 0.44 mmol) and Na[$BH_4$] (20 mg, 0.53 mmol) were suspended in 5 ml of MeCN, and 0.5 ml of $H_2O$ was added followed by 10 ml of $H_2O$ about 10 min later. The yellow suspension was filtered off, washed with $H_2O$, and dried at the vacuum. Yield: 480 mg (99%). *Freshly prepared* yellow samples of **15** did not contain by-product as indicated by the $^{1}$H- and $^{31}$P-NMR spectra. IR (nujol): 1790*s* (Pt–H; recrystallized from ether); 1750*s* (freshly prepared slightly yellow product). $^{1}$H-NMR ($C_6D_6$): −1.50 (*t*, $^{2}J$(P,H) = 19, $^{1}J$(Pt,H) = 797, 2 H–Pt); 4.05 (*t*, $^{2}J$(P,H) = $^{4}J$(P,H) = 7, $^{3}J$(Pt,H) = 48, 2 $CH_2$–P); 6.6–8.5 (24 arom. H); 10.03 (*s*, H–C(1), H–C(12)). $^{31}$P-NMR ($C_6D_6$): 34.5 (*s*, $^{1}J$(Pt,P) = 3075). Anal. calc. for $C_{48}H_{32}F_{12}P_2Pt$ (1093.8): C 52.71, H 2.95, P 5.66, Pt 17.83; found: C 52.90, H 2.94, P 5.72, Pt 17.80.

*[Pt₂H₃*(**2**)*₂][BF₄]* (**24**[$BF_4$]). trans-*[PtH(MeOH)*(**2**)*][BF₄]* (**26**[$BF_4$]; 467 mg, 0.39 mmol) and HCOONa (13 mg, 0.19 mol) were suspended in 4 ml of MeOH, which had been pre-cooled to −20°, and slowly warmed up to 50°. At ~ 20°, gas evolution was observed. After 30 min, the soln. was filtered off, and 68 mg (0.20 mmol) of Na[$BPh_4$] were added. The precipitate was filtered off and recrystallized from $CH_2Cl_2$/MeOH. Yield: 376 mg (78%), slightly yellow product. IR (nujol): 2080*m* (Pt–H). $^{1}$H-NMR (250 MHz (($D_6$)acetone): −6.41 (*tt*, $^{2}J$(P(1),H) = 30, $^{2}J$(P(3),H) = 49, $^{1}J$(Pt,H) = 431, 3 H–Pt); 1.85 (*dd*, $^{2}J$(P,H) = $^{4}J$(P,H) = 5, $^{2}J$(H,H) = 14,

$CH_2$–P); 3.08 (*dd*, $^2J$(P,H) = $^4J$(P,H) = 8, $^2J$(H,H) = 14, 2 $CH_2$–P); 4.17 (*dd*, $^2J$(P,H) = $^4J$(P,H) = $^2J$(H,H) = 14, $^3J$(Pt,H) = 108, $CH_2$–P); 4.64 (*dd*, $^2J$(P,H) = $^4J$(P,H) = $^2J$(H,H) = 14, $^3J$(Pt,H) = 41, $CH_2$–P); 6.4–8.4 (68 arom. H); 9.25, 10.04 (2*s*, 2 H–C(1), 2 H–C(12)). $^{31}$P-NMR (($D_6$)acetone): 9.1 (P(3), P(4)), 29.3 (P(1), P(2)) (1 pseudo-*d* each, $^4J$(P(1),P(2)) = 0, $^2J$(P(1),P(3)) = 7, $^4J$(P(1),P(4)) = 13, $^4J$(P(2),P(3)) = –13, $^2J$(P(2),P(4)) = 7, $^4J$(P(3),P(4)) = 30, $^3J$(Pt,P(1)) = 56, $^1J$(Pt,P(2)) = 2614, $^3J$(Pt,P(3)) = 349, $^1J$(Pt,P(4)) = 3734). $^{195}$Pt-NMR (($D_6$)acetone, 273 K): –4825 (*dddd*, $^3J$(Pt,P(1)) = 45, $^1J$(Pt,P(2)) = 2588, $^3J$(Pt,P(3)) = 351, $^1J$(Pt,P(4)) = 3758). Anal. calc. for $C_{120}H_{83}BF_{24}P_4Pt_2$ (2505.8; found (in $CH_2Cl_2$): 1639): C 57.52, H 3.34, P 4.94, Pt 15.57; found: C 57.46, H 3.29, P 5.14, Pt 15.57.

*[$Pt_2$(μ-H)(μ-CO)(**2**)][$BF_4$]* (**27**). trans-*[PtH(MeOH)(**2**)][$BF_4$]* (**26**[$BF_4$]; 140 mg, 0.12 mmol) was dissolved in 4 ml of MeOH under a CO atmosphere and heated in refluxing MeOH for 3 h. The mixture was allowed to warm up to r.t., and the soln. was filtered off. A stream of CO was blown through the soln., until the yellowish-orange product precipitated. It was filtered off and dried. Yield: 58 mg (44%). IR (nujol): 1790*b* (C=O). $^1$H-NMR (250 MHz, ($D_6$)acetone): –2.15 (*quint.*, $^2J$(P,H) = 31, $^1J$(Pt,H) = 445, H–Pt); 3.6–4.3 (4 $CH_2$–Pt); 6.9–8.0 (48 arom. H); 9.14 (*s*, 2 H–C(1), 2 H–C(12)). Anal. calc. for $C_{97}H_{61}BF_{28}OP_4Pt_2$ (2299.4; found (in $CH_2Cl_2$): 1485): C 50.67, H 2.67, P 5.39, Pt 16.97; found: C 50.68, H 2.71, P 5.41, Pt 17.33.

trans-*[PtH(Me)(**28**)$_2$]* (**29**). To 858 mg (0.71 mmol) of trans-*[Pt(Me)(γ-pic)(**28**)$_2$][$BF_4$]* (**32**) dissolved in 2 ml of dry MeCN, 29 mg (0.76 mmol) of Na[$BH_4$] were added, followed by the slow addition of 2 ml of $H_2O$. The org. layer was separated and washed twice with 3-ml portions of $H_2O$. The residue was dried under vacuum. The product crystallized out after adding 4 ml of MeOH. Yield: 300 mg (41%). IR (nujol): 1915*v* (C=O). $^1$H-NMR ($C_6D_6$): –3.94 (*tq*, not completely resolved, $^2J$(P,H) = 18, $^3J$(H,H) = 2, $^1J$(Pt,H) = 662, H–Pt); 0.22 (*dt*, $^3J$(P,H) = 6, $^3J$(H,H) = 2, $^2J$(Pt,H) = 50, $CH_3$–Pt); 3.60 (*t*, $^2J$(P,H) = $^4J$(P,H) = 7, $^3J$(Pt,H) = 40, 2 $CH_2$–P); 6.5–8.2 (26 arom. H). $^{31}$P-NMR ($C_6D_6$): 30.0 (*s*, $^1J$(Pt,P) = 3186). Anal. calc. for $C_{43}H_{34}F_{12}P_2Pt$ (1035.8): C 49.86, H 3.31, P 5.98, Pt 18.84; found: C 49.90, H 3.35, P 6.07, Pt 18.79.

trans-*[Pt(Me)(γ-pic)(**28**)$_2$][$BF_4$]* (**32**). The soln. of 178 mg (1.90 mmol) γ-picoline (γ-pic) and 2.205 g (1.87 mmol) of trans-*[Pt(Me)(MeOH)(**28**)$_2$]* (**31**) in 5 ml of $Et_2O$ was filtered. After the addition of *ca.* 5 drops of pentane, the product crystallized slowly. It was filtered off and dried. Yield: 1.735 g (76%). $^1$H-NMR ($CDCl_3$): 0.47 (*t*, $^3J$(P,H) = 7, $^2J$(Pt,H) = 70, $CH_3$–Pt); 1.98 (*s*, $CH_3$); 3.91 (*t*, $^2J$(P,H) = $^4J$(P,H) = 7, $^3J$(Pt,H) = 24, 2 $CH_2$–P); 6.5–8.2 (30 arom. H). $^{31}$P-NMR ($CDCl_3$): 23.5 (*s*, $^1J$(Pt,P) = 3053). Anal. calc. for $C_{49}H_{40}BF_{16}NP_2Pt$ (1214.7; found (in $CH_2Cl_2$): 1072): C 48.45, H 3.32, N 1.15; found: C 48.52, H 3.22, N 1.19.

trans-*[PtHCl(**1**)]* (**33**). A suspension of 1.1 g (1.45 mmol) of *trans*-[PtHCl($PPh_3$)$_2$] in 70 ml of benzene was warmed up with stirring and slight warming, until all the ligand dissolved; 1 g of solid **1** was then added. *Ca.* 10 min after the solid had dissolved, the product precipitated in micro-crystalline form. The volume of the soln. was reduced to *ca.* 20 ml by evaporation and the solid filtered off. This was washed first with acetone and then with $Et_2O$, and dried under high vacuum. Yield: 1.73 g (99%). IR (nujol): 2262*m*. $^1$H-NMR ($CDCl_3$): –16.28 (*t*, $^2J$(P,H) = 12, $^1J$(Pt,H) = 1287, H–Pt); 4.50 (*t*, $^2J$(P,H) = $^4J$(P,H) = 8.5; $^3J$(Pt,H) = 31, 2 $CH_2$–P); 10.18 (*s*, H–C(1), H–C(2)). $^{31}$P-NMR ($CDCl_3$): 26.2 (*s*, $^1J$(Pt,P) = 2990).

**3. Structure Analysis and Refinement.** – Well formed transparent colorless crystals of [PtHCl(**1a**)] were obtained by recrystallization from $CHCl_3$/toluene soln.

Lattice constants and intensity measurements were performed on a computer-controlled automatic diffractometer *Syntex P2$_1$*. A summary of the crystal data is reported in *Table 2*.

The intensities of the reflections up to $\theta = 28°$ were measured by the ω-scan technique at a scan rate automatically chosen between 2 and 29.3° $min^{-1}$ with a scan range of 0.9°. Background counts were taken, at ±0.65° from the peak position, for a time equal to the scan-time. The intensity of three standard reflections, measured every 100 reflections, remained constant through the run.

The intensity data were processed as described previously [37], with the uncertainty factor $p = 0.015$ as calculated from the variance of the standard reflections [38]. The value of $I$ of $\sigma(I)$ were corrected for *Lorentz*, polarization, and shape-anisotropy effects [39]. Of the 8963 unique data collected, 4067 independent reflections, with $I > 3\sigma(I)$, were used in the subsequent solution and refinement of the structure.

The structure was solved by the conventional *Patterson* and *Fourier* methods and refined by least-squares procedure. The isotropic refinement converged at $R = 0.065$. In the subsequent least-squares cycles, only those atoms not belonging to the Ph rings or to the benzo[*c*]phenanthrene system were refined anisotropically: convergence was reached at $R = 0.056$. At this stage, all the H-atoms except the hydride ligand were positioned geometrically[2]), and their fixed contribution was included in the subsequent two cycles. The H-atoms were then

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[2]) C–H = 1.0 Å, C–C–H = 120° ($sp^2$), H–C–H = 109.5° ($sp^3$), dihedral angle 90°; each H-atom was assigned an isotropic thermal parameter equal to that of the C-atom to which it is attached.

Table 2. *Crystal Data for [PtHCl(**1**)]*

| | |
|---|---|
| Formula | $C_{44}H_{35}ClP_2Pt$ |
| Formula wt. | 856.26 amu |
| Cell constants[a]) | $a = 18.253(9)$ Å |
| | $b = 10.583(4)$ Å |
| | $c = 18.941(7)$ Å |
| | $\beta = 103.88(3)°$ |
| | $V = 3552.0(26)$ Å$^3$ |
| Space group | $P2_1/c$, $Z = 4$ |
| Density | 1.601 (calc.), 1.61(1) (exper.)[b]) g·cm$^{-3}$ |
| Crystal dimensions | 0.20 × 0.26 × 0.28 mm |
| Radiation | Graphite monochromatized Mo*Kα* ($\lambda = 0.71069$ Å) |
| $\mu$(Mo*Kα*) | 41.85 cm$^{-1}$ |
| Diffractometer | *Syntex P2₁* |
| Scan mode | $\omega$ |
| Scan range | 0.9° |
| Bkgd | at ±0.65° from the peak |
| $2\vartheta$ limits | 3–56° |
| Total No. of refl. | 8963 |
| No. unique data | 4067 |
| Final No. of variables | 136 |
| Final $R$ | 0.054 |
| Final $R_w$ | 0.050 |

[a]) Determined by a least-squares procedure from the measured angular positions of 15 reflections.

[b]) Measured by flotation in $CdCl_2$ soln.

repositioned and included in the final structure factor calculation: $R = 0.054$ ($R_w = 0.050$). At this stage, attempts were made to locate the hydride ligand *trans* to the Cl-atom. These involved the calculations of difference *Fourier* maps, over the region of interest, successively limiting the angular range of terms included [40]. These, however, failed to locate the hydride ligand.

The refinement was carried out with a two-block approximation of the normal equations matrix, the function minimized being $\Sigma_w(|F_o| - |F_c|)^2$ with $w = 4F_o^2/\sigma^2(F_o^2)$. The 4 Ph rings of the molecule were refined as rigid groups ($D_{6h}$ symmetry, C–C = 1.392 Å).

Atomic scattering factors and anomalous dispersion terms were taken from the *International Tables for X-Ray Crystallography* [41].

The calculations were performed, using local programmes, on the *UNIVAC 1110* computer of the *University of Rome* [42] and on the *HP 21MX* minicomputer of the *CNR Research Area* [43].

The final positional parameters for the non-H-atoms are given in *Table 3.*

Table 3. *Final Positional Paramaters ( ×10$^4$) and Isotropic Displacement Parameters for the Non-H-atoms.* Standard deviations are given in parentheses.

| | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| *Non-group atoms* | | | | |
| Pt | 1967.9(3) | 625.9(5) | 2094.8(2) | 0.0353(3) |
| P(1) | 1108(2) | –914(3) | 2148(1) | 0.046(1) |
| P(2) | 2839(2) | 2178(3) | 2123(1) | 0.050(1) |
| Cl | 2427(2) | –607(4) | 1230(2) | 0.053(1) |
| C(1) | 2823(6) | –2015(11) | 3229(6) | 0.041(3) |
| C(2) | 2111(7) | –2408(11) | 3139(6) | 0.042(3) |
| C(3) | 1841(7) | –2836(11) | 3737(6) | 0.047(3) |
| C(4) | 2327(7) | –2901(12) | 4407(6) | 0.047(4) |
| C(5) | 3602(7) | –2656(11) | 5209(6) | 0.046(3) |
| C(6) | 4324(7) | –2390(11) | 5274(6) | 0.048(4) |
| C(7) | 5403(7) | –1563(12) | 4849(6) | 0.054(4) |

*Table 3* (cont.)

| | $x$ | $y$ | $z$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| C(8) | 5675(7) | -941(12) | 4352(6) | 0.059(4) |
| C(9) | 5474(7) | 400(12) | 3273(6) | 0.055(4) |
| C(10) | 5015(7) | 1028(12) | 2698(6) | 0.055(4) |
| C(11) | 4215(6) | 849(11) | 2567(5) | 0.042(3) |
| C(12) | 3935(6) | 26(11) | 2998(6) | 0.040(3) |
| C(13) | 3332(6) | -1961(11) | 3922(6) | 0.041(3) |
| C(14) | 3076(7) | -2488(11) | 4512(6) | 0.046(3) |
| C(15) | 4397(6) | -671(12) | 3574(5) | 0.038(3) |
| C(16) | 5190(6) | -405(11) | 3708(6) | 0.046(3) |
| C(17) | 4105(6) | -1499(10) | 4056(6) | 0.038(3) |
| C(18) | 4605(7) | -1840(12) | 4731(6) | 0.046(3) |
| C(19) | 1570(6) | -2473(10) | 2371(6) | 0.041(4) |
| C(20) | 3712(6) | 1588(13) | 1938(6) | 0.052(5) |
| *Rigid group atoms* | | | | |
| Ph(1) | | | | |
| C(21) | 524(5) | -755(9) | 2812(4) | 0.051(1) |
| C(22) | 680(5) | 196(10) | 3334(4) | |
| C(23) | 226(4) | 338(7) | 3825(3) | |
| C(24) | -382(5) | -472(9) | 3793(4) | |
| C(25) | -537(5) | -1423(10) | 3270(4) | |
| C(26) | -84(4) | -1564(7) | 2780(3) | |
| Ph(2) | | | | |
| C(27) | 428(4) | -1174(12) | 1287(3) | 0.053(1) |
| C(28) | -284(4) | -621(8) | 1135(3) | |
| C(29) | -771(5) | -776(15) | 453(4) | |
| C(30) | -546(4) | -1484(12) | -78(3) | |
| C(31) | 166(4) | -2037(8) | 74(3) | |
| C(32) | 654(5) | -1881(15) | 757(4) | |
| Ph(3) | | | | |
| C(33) | 2543(4) | 3310(7) | 1386(3) | 0.054(1) |
| C(34) | 2349(5) | 2829(5) | 682(4) | |
| C(35) | 2128(4) | 3645(7) | 92(3) | |
| C(36) | 2103(4) | 4942(7) | 207(3) | |
| C(37) | 2297(5) | 5422(5) | 912(4) | |
| C(38) | 2517(4) | 4607(7) | 1501(3) | |
| Ph(4) | | | | |
| C(39) | 3145(6) | 3117(11) | 2951(4) | 0.073(1) |
| C(40) | 3840(6) | 3727(14) | 3086(4) | |
| C(41) | 4079(6) | 4456(19) | 3711(5) | |
| C(42) | 3624(6) | 4574(11) | 4200(4) | |
| C(43) | 2929(6) | 3963(14) | 4065(4) | |
| C(44) | 2689(6) | 3235(19) | 3441(5) | |

| | $x$ | $y$ | $z$ | $\phi$ | $\theta$ | $\psi$ |
|---|---|---|---|---|---|---|
| *Rigid group parameters*[a]) | | | | | | |
| Ph(1) | 71(3) | -613(5) | 330(3) | 180.1(4) | 51.1(3) | -36.3(4) |
| Ph(2) | -59(3) | -1329(5) | 605(3) | 182.3(5) | -62.3(3) | 24.0(5) |
| Ph(3) | 2323(3) | 4126(5) | 797(3) | 4.6(3) | 0.8(2) | 107.2(3) |
| Ph(4) | 3384(4) | 3845(6) | 3576(3) | 183.4(7) | -64.1(7) | -22.9(7) |

[a]) The fractional coordinates $x, y$, and $z$ describe the positions of the center of the rings and the angles $\phi, \theta$, and $\psi$ (in degrees) describe rotations about an internal coordinate system [10].

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