Journal of Organometallic Chemistry, 275 (1984) 303–313
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE PREPARATION OF *cis*- AND *trans*-[PtH(C_6Cl_5)(PEt_3)$_2$] AND A STUDY OF THE "HYDRIDE-DONOR CAPACITY" OF THE COMPLEXES *trans*-[PtH(C_6X_5)(PEt_3)$_2$] (X = F and Cl)

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(Received May 24th, 1984)

Summary

The preparations of *cis*- and *trans*-[PtH(C_6Cl_5)(PEt_3)$_2$] by thermal decomposition of *cis*- and *trans*-[Pt(OCHO)(C_6Cl_5)(PEt_3)$_2$], respectively, are reported. Also described are *cis*- and *trans*-[Pt($SnCl_3$)(C_6Cl_5)(PEt_3)$_2$], obtained by treating $SnCl_2$ with *cis*- and *trans*-[PtCl(C_6Cl_5)(PEt_3)$_2$], respectively. It is shown that while *trans*-[PtH(C_6Cl_5)(PEt_3)$_2$] does not form hydrido-bridged complexes in the presence of *trans*-[PtH(MeOH)(PEt_3)$_2$]$^+$, the corresponding complex *trans*-[PtH(C_6F_5)(PEt_3)$_2$] reacts with the same solvento complex, in methanol, giving labile [(PEt_3)$_2$HPt(μ-H)Pt(C_6F_5)(PEt_3)$_2$]$^+$.

During the study of bimetallic hydrido-bridged compounds [1] it was observed [2,3] that the relatively unstable [4] mononuclear platinum(II) hydride **1a** reacted readily with the solvento-complex **2f** to form the stable, hydrido-bridged cationic species **3a/f** [2].

As several stable complexes of the type *trans*-[PtHR'(PR_3)$_2$] have been prepared [5,6], it was of interest to establish whether they would also form binuclear species of type **3**.

Since the X-ray structure determination of the cation **3a/f** [2] shows that the presence of bulky phosphines might hinder hydrido-bridge formation, only complexes containing PEt_3, i.e., *trans*-[PtH(CH_2SiMe_3)(PEt_3)$_2$], **1b**, [6] and *trans*-[PtH(C_6F_5)(PEt_3)$_2$], **1c**, [7,8] were considered. However, as compound **1b** is reported to be an oil [6] compounds **1c** and *trans*-[PtH(C_6Cl_5)(PEt_3)$_2$], **1d**, were prepared and their reactions with some cations of type **2** studied.

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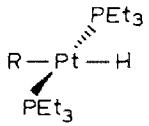
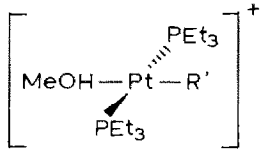
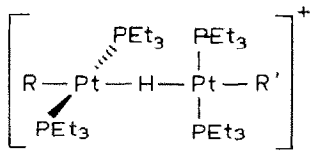


(**1a**, R = Ph,
1b, R = CH_2SiMe_3,
1c, R = C_6F_5,
1d, R = C_6Cl_5,
1e, R = 2,4,6-$Me_3C_6H_2$,
1f, R = H)



(**2a**, R' = Ph;
2c, R' = C_6F_5,
2d, R' = C_6Cl_5,
2f, R' = H)



(**3a/f**, R = Ph; R' = H,
3c/f, R = C_6F_5, R' = H,
3a/a, R = R' = Ph,
3a/e, R = Ph; R' = mesityl,
3f/e, R = H; R' = mesityl,
3f/f, R = R' = H)

Results and discussion

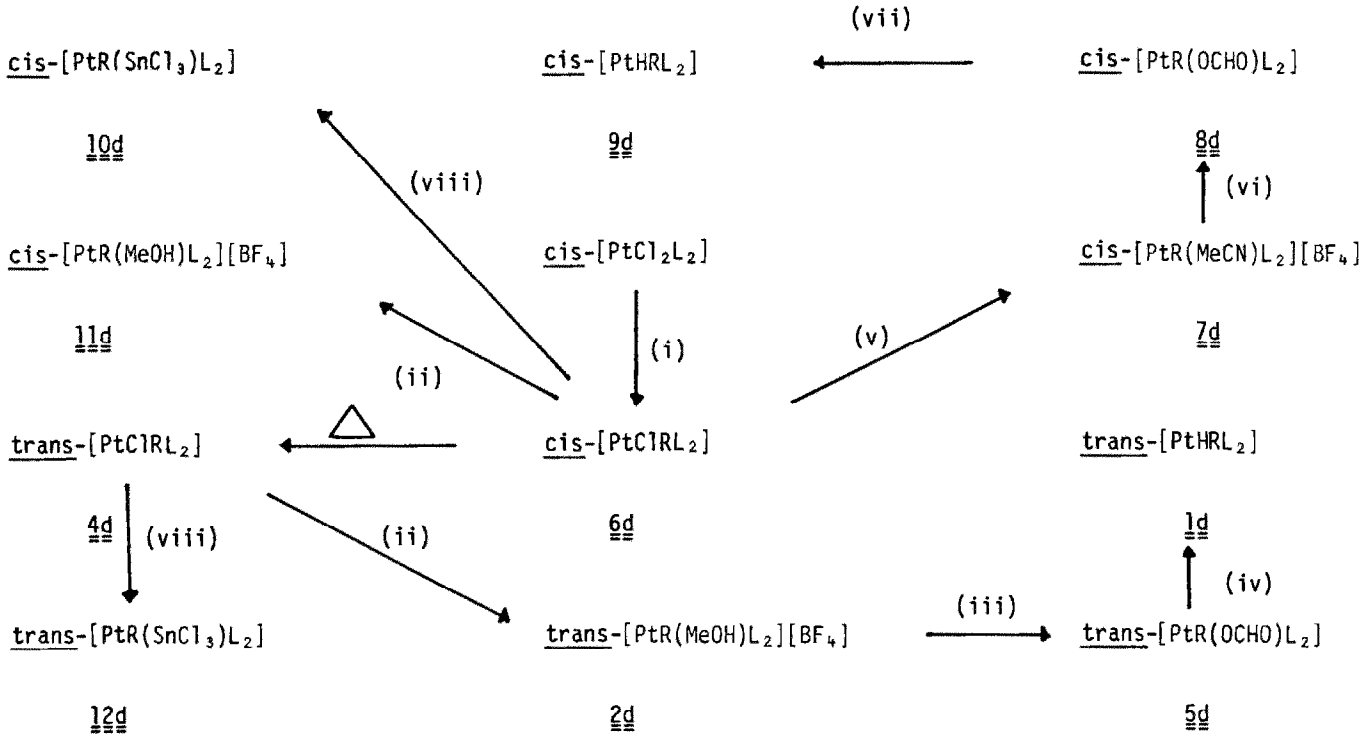
The reactions of the mononuclear complexes containing the C_6Cl_5-ligand are summarized in Scheme 1.

Treatment of *trans*-[$PtCl(C_6Cl_5)(PEt_3)_2$], **4d**, [9] with $AgBF_4$ in methanol gave the solvento-complex *trans*-[$Pt(C_6Cl_5)(MeOH)(PEt_3)_2$][$BF_4$], **2d**. During the halogen-abstraction reaction **2d** and a related complex were simultaneously formed. The latter complex rearranged to **2d** during the recrystallization of the crude product mixture. The halogen abstraction reaction on *cis*-[$PtCl(C_6Cl_5)(PEt_3)_2$], **6d**, when carried out in methanol also produced a mixture of two cationic species. One of them has been identified spectroscopically as *cis*-[$Pt(C_6Cl_5)(MeOH)(PEt_3)_2$]$^+$, **11d**. The NMR parameters of the other indicate that it is closely related to **11d**. Both species slowly isomerize to **2d** (see Experimental Section). However, the reaction of *cis*-[$PtCl(C_6Cl_5)(PEt_3)_2$], **6d**, with $AgBF_4$ in acetonitrile gave *cis*-[$Pt(C_6Cl_5)$-$(CH_3CN)(PEt_3)_2$][BF_4], **7d**, i.e. the chloride replacement occurs with retention of geometry.

Replacement of a halide by an oxygen donor has previously been used to isomerize *cis*-[$PtCl(Ar)(PEt_3)_2$] into the corresponding *trans*-species [10]. Thus, our results indicate that the use of nitrile as a solvent favours the retention of *cis*-geometry during this solvolytic reaction.

Addition of HCOONa to a methanolic solution of **2d** resulted in the rapid formation of *trans*-[$Pt(C_6Cl_5)(OCHO)(PEt_3)_2$], **5d**, which, when refluxed in methanol, gave *trans*-[$PtH(C_6Cl_5)(PEt_3)_2$], **1d**, in practically quantitative yield.

A solution of the formate *cis*-[$Pt(C_6Cl_5)(OCHO)(PEt_3)_2$], **8d**, obtained from **7d**, decomposed at room temperature over 2 hours to give *cis*-[$PtH(C_6Cl_5)(PEt_3)_2$], **9d**. Its formation was accompanied by deposition of small amounts of metallic platinum.



SCHEME 1. R = C_6Cl_5; L = PEt_3; (i) C_6Cl_5MgCl; (ii) $AgBF_4$, MeOH (a second product is also formed during this reaction, see Exptl. Section); (iii) NaOCHO; (iv) reflux in MeOH; (v) $AgBF_4$, CH_3CN; (vi) NaOCHO; (vii) stirring at room temp. in soln.; (viii) $SnCl_2$.

It is noteworthy that the CO_2-elimination from the *cis*-complex, **8d**, requires milder conditions than in the corresponding *trans*-species, **5d**.

The preparation of hydrido complexes of platinum(II) by CO_2 elimination from formate complexes occurs remarkably smoothly and cleanly [11] and, in our experience, this route is often preferable to the use of BH_4^- on solvento-complexes of type **2**.

The high stability of *trans*-[$PtH(C_6Cl_5)(PEt_3)_2$], **1c**, is not unexpected in view of properties of known compounds of similar type [6]. More interesting is the relative stability of *cis*-[$PtH(C_6Cl_5)(PEt_3)_2$], **9**. Although several stable complexes of the type *cis*-[PtHR'(LL)] (LL = chelating diphosphine) have been reported [4,12], usually compounds of the type *cis*-[$PtHR'(PR_3)_2$] have very low thermal stabilities and could only be characterized in solution [13].

Attempts to produce binuclear hydrido-bridged cationic complexes of type **3**, i.e.,

TABLE 1

NMR DATA FOR COMPLEXES [$PtY(C_6X_5)(PEt_3)_2$] AND [$Pt(C_6X_5)$(solvent)$(PEt_3)_2$][BF_4]

Compound [a]	X	Y or solvent	Phosphine geometry	$\delta(^{31}P)$ (ppm)	$^1J(^{195}Pt-^{31}P)$ (Hz)	$^2J(^{31}P-^{31}P)$ (Hz)	$\delta(^1H)$ (ppm)
1c	F	H	*trans*	17.6	2682		−7.88 [b]
1d	Cl	H	*trans*	15.9	2772		−9.80 [c]
2c	F	MeOH	*trans*	19.5	2464		
2d	Cl	MeOH	*trans*	14.4	2616		[d]
4c	F	Br	*trans*	12.2	2448		
4d	Cl	Cl	*trans*	9.8	2609		
5d	Cl	HCOO	*trans*	11.1	2738		8.47 [e]
6d [f]	Cl	Cl	*cis*	7.3 [g]	2036	19.5	
				−0.75 [h]	3934		
7d [f]	Cl	CH_3CN	*cis*	6.4 [g]	2015	21.1	2.44 [i]
				−4.1 [h]	4003		
8d	Cl	HCOO	*cis*	12.8 [g]	2123	19.1	8.21 [j]
				−5.4 [h]	3854		
9d	Cl	H	*cis*	8.6 [g]	2359	16.2	−5.50 [k]
				6.7 [h]	1976		
10d [l,f]	Cl	$SnCl_3$	*cis*	0.0 [g]	2164	20 6	
				5.0 [h]	3322		
11d	Cl	MeOH	*cis*	12.6 [g]	2083	19.1	[d]
				−1.9 [h]	4310		
12d [m,f]	Cl	$SnCl_3$	*trans*	2.8	2290		

[a] The spectra were measured in acetone-d_6 unless otherwise stated. [b] Hydride resonance; ^1J(Pt,H) 787 Hz; ^2J(P,H) 16.9 Hz; $^4J(F_{ortho},H)$ 14.7 Hz; $^5J(F_{meta},H)$ 5.9 Hz. [c] ^1J(Pt,H) 729 Hz; ^2J(P,H) 17.1 Hz. Ethyl group resonances (measured in $CDCl_3$): δ (CH_2) 1.68; $\delta(CH_3)$ 1.02 ppm. [d] See Experimental section. [e] Formate resonance; ^3J(Pt,H) 49.4 Hz; ^4J(P,H) 2.4 Hz. [f] Measured in $CDCl_3$. [g] Resonance of the P-atom in *trans*-position to C_6Cl_5, P_b. [h] Resonance of the P-atom in *trans*-position to Y, P_a. [i] Acetonitrile resonance (at 90 MHz in $CDCl_3$): $\delta(CH_3)$ 2.44 ppm; ^4J(Pt,H) 3.7 Hz. Ethyl group resonances: $\delta(CH_2)$ 1.79 and 2.02; $\delta(CH_3)$ 1.08 and 1.27 ppm; ^3J(H,H) 7.5 Hz; ^2J(P,H) 7.5 Hz; ^3J(P,H) 17.2 Hz. [j] Formate resonance; ^3J(Pt,H) 66.3 Hz; $^4J(P_a,H)$ 5.0 Hz; $^4J(P_b,H)$ 0.5 Hz. [k] Hydride resonance in $CDCl_3$; ^1J(Pt,H) 1016 Hz; $^2J(P_a,H)$ 171 Hz; $^2J(P_b,H)$ 24 Hz. Ethyl group resonances: $\delta(CH_2)$ 1.61 and 1.87, $\delta(CH_3)$ 1.05 and 1.16 ppm; ^3J(H,H) 7.0 Hz. [l] $\delta(^{119}Sn)$ −5.8 ppm (relative to $SnMe_4$ a negative sign denotes a resonance at high field of the reference; measured in $CH_2Cl_2/CDCl_3$); $^1J(Pt,^{119}Sn)$ 17200 Hz; $^2J(^{119}Sn,P_a)$ 340 Hz; $^2J(^{119}Sn,P_b)$ 262 Hz. [m] $\delta(^{119}Sn)$ −7.3 ppm; $^1J(Pt,^{119}Sn)$ 11895 Hz.

$[(PEt_3)_2(C_6Cl_5)Pt(\mu\text{-}H)Pt(R')(PEt_3)_2]^+$ where $R' = C_6Cl_5$, Ph or H, from *trans*-$[PtH(C_6Cl_5)(PEt_3)_2]$, **1d**, and *trans*-$[Pt(R')(MeOH)(PEt_3)_2]^+$ ($R' = Ph$, C_6Cl_5 and H; **2a**, **2d** and **2f** respectively), in methanol solution, led to the recovery of the starting material. This is to be contrasted with the following observations: (a) $[(PEt_3)_2(Ph)Pt(\mu\text{-}H)Pt(Ph)(PEt_3)_2]^+$, **3a/a**, is quantitatively obtained from **1a** and **2a** [2] and (b) $[(PEt_3)_2(H)Pt(\mu\text{-}H)Pt(C_6F_5)(PEt_3)_2]^+$, **3c/f**, can be obtained in solution.

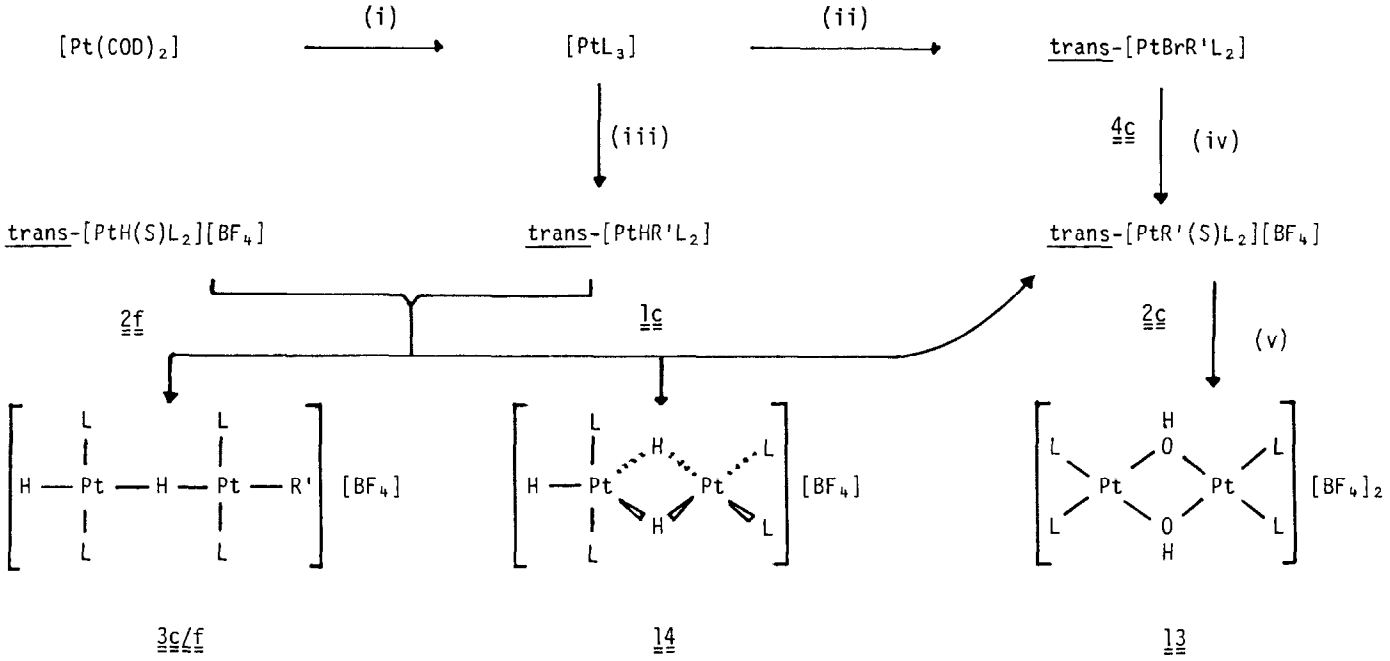
Finally both *cis*- and *trans*-$[PtCl(C_6Cl_5)(PEt_3)_2]$, **6d** and **4d**, respectively, react smoothly with $SnCl_2$, in CH_2Cl_2, to give the corresponding trichlorostannate complexes, *cis*- and *trans*-$[Pt(SnCl_3)(C_6Cl_5)(PEt_3)_2]$, **10d** and **12d**, respectively.

The reactions carried out on complexes containing the C_6F_5 group are summarized in Scheme 2. Compound **1c** was prepared as described by Forniés et al. [7], i.e. by the oxidative-addition reaction between $[Pt(PEt_3)_3]$ and C_6F_5H, while treatment of the same platinum(0) complex with C_6F_5Br gave the expected product, **4c**. The bromide abstraction reaction with silver fluoroborate occurs normally when carried out in methanol. When acetone is used as a solvent the AgBr precipitation occurs very slowly and is accompanied by decomposition of the acetone complex to the binuclear hydroxo-bridged species $[(PEt_3)_2Pt(\mu\text{-}OH)_2Pt(PEt_3)_2]^{2+}$, **13**, [14].

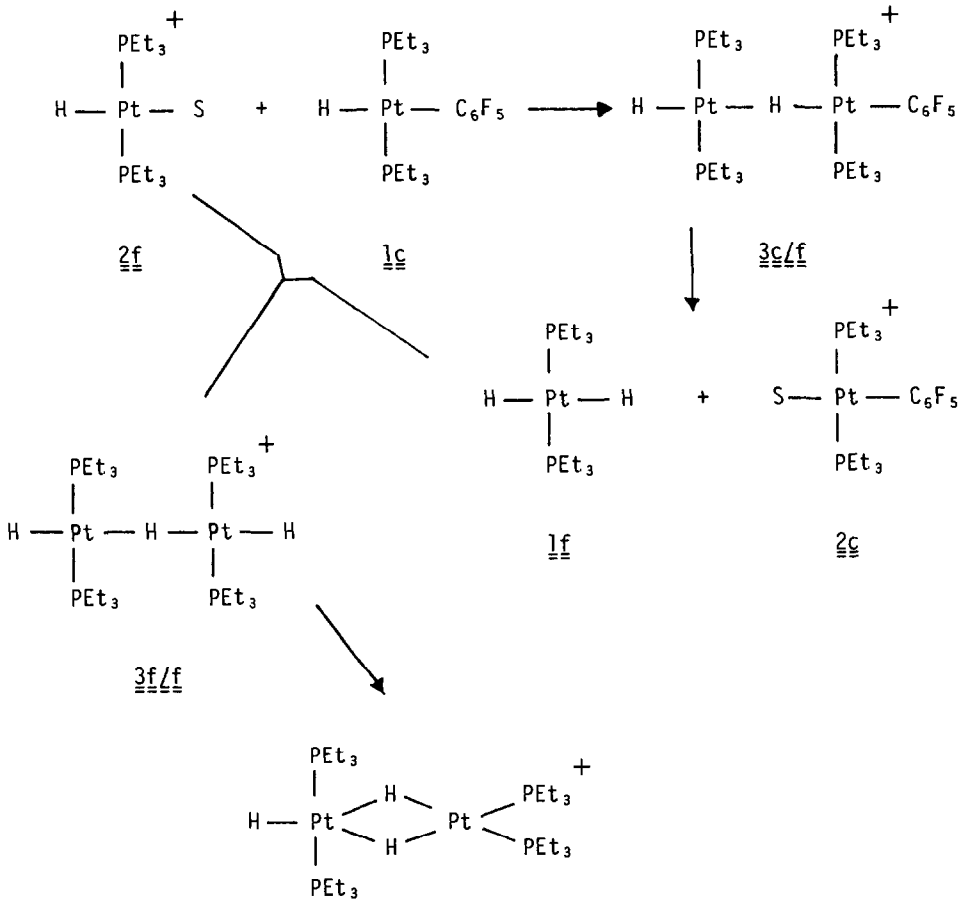
Addition of the mononuclear hydride *trans*-$[PtH(C_6F_5)(PEt_3)_2]$, **1c**, to a methanol solution of the C_6F_5-containing cation *trans*-$[Pt(C_6F_5)(MeOH)(PEt_3)_2]^+$, **2c**, does not give the expected binuclear complex $[(PEt_3)_2(C_6F_5)Pt(\mu\text{-}H)Pt(C_6F_5)(PEt_3)_2]^+$. Also the cation *trans*-$[PtPh(MeOH)(PEt_3)_2]^+$, **2a**, fails to give a hydrido-bridged complex with **1c** in the same solvent. Only the cation *trans*-$[PtH(MeOH)(PEt_3)_2]^+$, **2f**, reacts with **1c** giving the corresponding binuclear species $[(PEt_3)_2(C_6F_5)Pt(\mu\text{-}H)PtH(PEt_3)_2]^+$, **3c/f**. This reaction begins to occur at $-20\,^\circ C$ and after ca. 3 h at the same temperature one observes approximately equimolecular amounts of starting materials and of product, **3c/f**. If the reaction is carried out at room temperature one observes the formation of **3c/f** which slowly decomposes to give the C_6F_5-mononuclear species **1c** and **2c** as well as dihydrido-bridged species $[(PEt_3)_2Pt(\mu\text{-}H)_2PtH(PEt_3)_2]^+$, **14**, which has been described elsewhere [15]. One can presume that the Pt–H–Pt bridge can split either by giving the starting materials **1c** and **2f** or with formation of **2c** and *trans*-$[PtH_2(PEt_3)_2]$, **1f** [16,17]. The latter could then react with *trans*-$[PtH(solvent)(PEt_3)_2]^+$, **2f**, to give the binuclear, dihydrido-bridged compound **3f/f**, which is known to rearrange to the final reaction product **14** (see Scheme 3) [11,15,17]. Attempts to isolate the binuclear hydrido-bridged cationic complex $[(PEt_3)_2(H)Pt(\mu\text{-}H)Pt(C_6F_5)(PEt_3)_2]^+$, **3c/f**, from the reaction mixtures, obtained either at low or at room temperatures as described above, led to decomposition.

These results indicate that the tendency towards formation of Pt–H–Pt bridges, in complexes of type **3**, decreases in the order: $R' = Ph > C_6F_5 > C_6Cl_5$. It was previously shown [20] that complexes *trans*-$[PtH(C_6X_5)(PEt_3)_2]$ (X = F and Cl, **1c** and **1d** respectively) form stable hydrido-bridged complexes of the type $[(PR_3)Au(\mu\text{-}H)Pt(C_6X_5)(PEt_3)_2]^+$ (R = Et and Ph; X = F and Cl). Thus, it can be presumed that **1c** and **1d** retain a significant "hydrido-donor" capacity even when the electron-attracting C_6X_5-group is bonded to the platinum atom.

While it is conceivable that the "$(PR_3)Au$"-moiety is a better "hydride-acceptor" than the "$PtY(PEt_3)_2$"-fragment (Y = H or aryl group), it is obvious that, on steric grounds, hydride-bridge formation by *trans*-$[PtH(C_6H_5)(PEt_3)_2]$ is more favourable



SCHEME 2. COD = cycloocta-1,5-diene; L = PEt_3, R' = C_6F_5; S = MeOH or acetone; (i) PEt_3; (ii) C_6F_5Br; (iii) C_6F_5H; (iv) $AgBF_4$, MeOH or acetone, (v) for S = acetone.



SCHEME 3

with the gold than with the platinum "Lewis acid". Furthermore, steric interactions have been shown to be significant in mono-hydrido-bridged diplatinum complexes [18], i.e., the binuclear species $[(PEt_3)_2(mesityl)Pt(\mu\text{-}H)Pt(mesityl)(PEt_3)_2]^+$ is not formed and the related compounds $[(PEt_3)_2(Ph)Pt(\mu\text{-}H)Pt(mesityl)(PEt_3)_2]^+$, **3a/f** [18] and $[(PEt_3)_2(H)Pt(\mu\text{-}H)Pt(mesityl)(PEt_3)_2]^+$, **3e/f** [19] are unstable despite the electron-donating properties of the mesityl group.

One can then deduce that the lability of the hydrido-bridged diplatinum complex containing C_6F_5, **3c/e**, and the failure to observe the formation of a complex containing C_6Cl_5 bonded to platinum are caused by a combination of electronic effects (decrease of electron-donating capacity at the hydride ligand in the mononuclear species of type **1**) and by steric effects which are particularly severe in the C_6Cl_5 compounds [21].

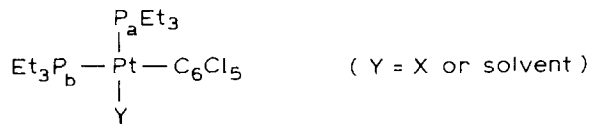
The NMR data for the complexes obtained are given in Table 1. The data for the C_6F_5 derivatives require some comment. The ^1H NMR spectrum of compound

trans-[PtH(C_6F_5)(PEt_3)$_2$] in the hydride region has been described [7] as "^{1}H, τ 17.68 (t, PtH, J(PH) 16.4 Hz)". The hydride spectrum, however, is a symmetrical multiplet of at least 21 lines (flanked by the corresponding platinum satellites) arising from couplings to the phosphorus and the *o*- and *m*-fluorine atoms. First-order analysis of the spectrum gives the following parameters: ^2J(P,H) 16.9 Hz; $^4J(F_{ortho},H)$ 14.7 Hz and $^5J(F_{meta},H)$ 5.9 Hz and these data reproduce the experimental results when used as input for a calculated spectrum.

The ^{195}Pt NMR spectrum of *trans*-[PtBr(C_6F_5)(PEt_3)$_2$] is particularly interesting as it clearly shows couplings to all five fluorine atoms as well as to the phosphorus atoms. A picture of this spectrum and the relevant parameters have appeared elsewhere [22].

The presence of the binuclear species [(PEt_3)$_2$(H)Pt(μ-H)Pt(C_6F_5)(PEt_3)$_2$]$^+$, **3c/e**, has been deduced mainly by examination of the ^{31}P NMR spectrum of the reaction mixture. No attempt has been made to assign its ^{1}H NMR spectrum because of (a) the presence of several other hydrido complexes, mainly **13** and **2c**, and (b) its complexity compared with that of the mononuclear species, **1c**.

Comparison of the NMR parameters obtained shows the following trends:
(1) The replacement of C_6H_5 ligand by a C_6Cl_5 moiety in complexes *cis*- and *trans*-[PtCl(R)(PEt_3)$_2$] causes a high field shift of the phosphorus resonance(s). This shift is twice as large for the phosphorus atom in *cis*-position, P_a, than for that in *trans*-position, P_b.



(2) The changes of $^1J(^{195}Pt,^{31}P)$ coupling constants with changes of aryl groups are less marked for Pt–P bonds in *cis*-position to the group R than for the corresponding *trans*-bonds. Thus the change $C_6H_5 \rightarrow C_6Cl_5$ causes a decrease of ca. 250 Hz in $^1J(^{195}Pt,^{31}P_{cis})$ but an increase of ca. 550 Hz in $^1J(^{195}Pt,^{31}P_{trans})$.
(3) If one estimates the relative *trans*-influences [23] of the R groups, as measured by the changes in $^1J(^{195}Pt,^1H)$ coupling constants for complexes of the type *trans*-[PtHR(PEt_3)$_2$] one obtains the following relative order Ph[2] > CH_2SiMe_3[6] > C_6Cl_5 > C_6F_5. Not unexpectedly [24], there is no apparent correlation between the changes in $\delta(^1H_{hydr})$ and those in $^1J(^{195}Pt,^1H)$ values as the ligand R is varied (see Table 1).

If one considers the formation of bimetallic complexes containing the unit "M(μ-H)M" as arising from the reaction:

$$L_nM + HML_n \rightarrow L_nM(\mu\text{-H})ML_n$$

and one tried to correlate empirically the "donor capacity" of the HML_n to the chemical shift of the hydride ligand one would deduce that hydride-bridge formation towards the unit *trans*-[PtH(vacant site)(PEt_3)$_2$]$^+$ is possible if the $\delta(^1H)$ of the "donor" is lower than ca. -8 ppm. This relatively low-field chemical shift is typical of a hydride bound to platinum *trans* to a ligand of strong *trans*-influence [24]. It should be noted here that, although *trans*-[PtH(CN)(PEt_3)$_2$] has a $\delta(^1H)$ value of -7.6 ppm, it forms the compound [(PEt_3)$_2$HPt(μ-CN)Pt(H)(PEt_3)$_2$]$^+$ [25] and not the isomer with the Pt(μ-H) bridge, presumably because cyanide is a better bridging ligand than hydride.

Experimental

The infrared spectra were recorded on samples in KBr discs, on a Beckman, Model 4250 spectrophotometer. The ^{31}P NMR spectra were measured using a Bruker HX 90 spectrometer. A positive sign denotes a resonance at low field of the reference (H_3PO_4). The ^{1}H and ^{13}C NMR spectra were obtained using a Bruker WM 250 spectrometer. Elemental analyses for C, H and Cl were carried out by the Microanalytical Laboratory of the ETH Zürich. The compounds containing the coordinated C_6Cl_5 group show characteristic infrared bands in the regions 1335–1330(s), 1305–1295(s), 840–825(m), 675–665(s) and 625–615(m) cm^{-1} [9]. The complexes also show the characteristic infrared bands due to the presence of PEt_3 [25] while the complexes containing $[BF_4]^-$ as counter-ion, **2c**, **2d**, **7d** and **11d** show the strong characteristic band for this anion [26] centered at around 1050 cm^{-1}.

trans-[PtH(C_6F_5)(PEt_3)$_2$], **1c**, was prepared as described by Forniés et al., [7].

cis- and *trans*-[PtCl(C_6Cl_5)(PEt_3)$_2$], **6d** and **1d** respectively, were prepared as described by Coronas et al. [9]. The other complexes were prepared as described below. An oxygen-free, dry nitrogen atmosphere was used.

*trans-[Pt(C_6Cl_5)(MeOH)(PEt_3)$_2$][BF_4], **2d.*** A chloroform solution of 201.3 mg (10.28 mmol) of *trans*-[PtCl(C_6Cl_5)(PEt_3)$_2$], **4d**, was added to a methanol solution of 57.0 (0.29 mmol) $AgBF_4$. A white precipitate began to form after a few minutes. The suspension was stirred at room temperature for 3 days and then filtered through Celite. The colourless filtrate was evaporated to dryness and the residue recrytallized from $CHCl_3$/hexane (b.p. 30–60 °C). ^{31}P NMR examination of the reaction mixture after filtration through Celite during chloride-abstraction shows the simultaneous formation of comparable amounts of **2d** and of a second complex A, with ^{31}P NMR parameters $\delta(^{31}P)$ 13.7 ppm and $^{1}J(^{195}Pt,^{31}P)$ 2625 Hz, which are very similar to those of **2d**, i.e., $\delta(^{31}P)$ 14.4 ppm and $^{1}J(^{195}Pt,^{31}P)$ 2616 Hz. Only **2d** is observed after recrystallization. Yield: 160 mg (71%). decomp. pt. 210 °C. Found: C, 28.25; H, 4.52; Cl, 22.01. $C_{19}H_{34}BCl_5F_4OP_2Pt$ calcd.: C, 28.54; H, 4.28; Cl, 22.17%.

*trans-[Pt(OCHO)(C_6Cl_5)(PEt_3)$_2$], **5d.*** A solution of **2d**, obtained from 514.0 mg **4d**, prepared as described above, was treated with a methanol solution of 152.3 mg sodium formate. A precipitate formed immediately. The suspension was stirred for 1 h and the solvent evaporated under reduced pressure. The residue was extracted with $CHCl_3$ (3 × 10 ml) and the extracts were evaporated to a small volume. Addition of methanol gave 417 mg of pure product (80% yield). decomp. pt. 125 °C. Found: C, 31.72; H, 4.54; Cl, 24.23. $C_{19}H_{31}Cl_5O_2P_2Pt$ calcd.: C, 31.44; H, 4.30; Cl, 24.42%. ν(C=O) 1625 cm^{-1} (vs); ν(C–O) 1270 cm^{-1} (s).

*trans-[PtH(C_6Cl_5)(PEt_3)$_2$], **1d.*** A suspension of **5d** in methanol was refluxed for 2 1/2 h. The solid was filtered off, washed with methanol and dried (yield > 95%). M. pt. 107 °C. Found: C, 31.81; H, 4.51; Cl, 25.81. $C_{18}H_{31}Cl_5P_2Pt$ calcd.: C, 31.71; H, 4.58; Cl, 26.00%. ν(Pt–H) 2000 cm^{-1} (vs).

*trans-[Pt($SnCl_3$)(C_6Cl_5)(PEt_3)$_2$], **12d.*** A suspension of 99.4 mg (0.52 mmol) of $SnCl_2$ in 5 ml of CH_2Cl_2 was added to a solution of 375.6 mg (0.52 mmol) of **4d** in 5 ml of CH_2Cl_2. A colourless solution was obtained after stirring at room temperature for 20 min. Stirring was continued overnight and the solution was evaporated to a small volume under reduced pressure. Addition of EtOH to the residual oil which contained a 75/25 mixture of product and starting material, gave a solid which was purified by recrystallization from CH_2Cl_2/acetone (yield ca. 50%), decomp. pt.

180 °C. Found: C, 23.78; H, 3.63; Cl, 31.51. $C_{18}H_{30}Cl_8P_2PtSn$ calcd.: C, 23.87; H, 3.33; Cl, 31.31%. ν(Sn–Cl): 300(s), 315(s) and 340(s) [26].

cis-[Pt(C_6Cl_5)(MeCN)(PEt_3)$_2$][BF_4], **7d**. A solution of 411.4 mg (0.57 mmol) **6d** in MeCN was added to a solution of 113.9 mg (0.58 mmol) $AgBF_4$ in MeCN. The resulting suspension was stirred at room temperature for $2\frac{1}{2}$ h, filtered through Celite and the filtrate evaporated to dryness under reduced pressure. The white residue was recrystallized from MeCN/Et_2O and pure **7d** obtained in 82% yield. decomp. pt. 90 °C. Found: C, 29.52; H, 4.15. $C_{20}H_{33}BCl_5F_4NP_2Pt$ calcd.: C, 29.70; H, 4.11%.

cis-[Pt(OCHO)(C_6Cl_5)(PEt_3)$_2$], **8d**. A methanol solution of 20.9 mg (0.30 mmol) NaOCHO was added to a suspension of **7d** in the same solvent. The resulting suspension was stirred for 1 h and filtered through Celite. The filtrate was evaporated to dryness under reduced pressure and the residue extracted with 10 ml $CHCl_3$. The solution was evaporated to a small volume and on addition of MeOH **8d** was precipitated as a white solid. Yield: 150 mg (85%), decomp. pt. 130 °C. Found: C, 31.65; H, 4.59; Cl, 24.60. $C_{19}H_{31}Cl_5O_2P_2Pt$ calcd.: C, 31.44; H, 4.30; Cl, 24.42%. ν(C=O) 1640 cm^{-1} (vs); ν(C–O) 1275 cm^{-1} (s).

cis-[PtH(C_6Cl_5)(PEt_3)$_2$], **9d**. A solution of 100 mg (0.14 mmol) **8d**, in $CHCl_3$/MeOH, was stirred for 2 h at room temperature and evaporated to a small volume under reduced pressure. Addition of MeOH to this residue gave the product as a white powder. Yield 60%, decomp. pt. 130 °. During this reaction the formation of some metallic platinum was observed. Found: C, 31.84; H, 4.68; Cl, 26.28. $C_{18}H_{31}Cl_5P_2Pt$ calcd.: C, 31.71; H, 4.58; Cl, 26.00%. ν(Pt–H) 2075 cm^{-1} (s).

cis-[Pt($SnCl_3$)(C_6Cl_5)(PEt_3)$_2$], **10d**. A suspension of 79.6 mg (0.42 mmol $SnCl_2$ in CH_2Cl_2 was added to a solution of 299.6 mg (0.42 mmol) **6d** in 5 ml CH_2Cl_2. The tin salt dissolved and a white solid began to precipitate. The suspension was stirred for 3 h, the solid filtered off and recrystallized from $CHCl_3$. The product was obtained as white crystals in 90% yield. decomp. pt 144 °C. Found: C, 24.10; H, 3.26; Cl, 31.00. $C_{18}H_{30}Cl_8P_2PtSn$ calcd.: C, 23.87; H, 3.33; Cl, 31.31%. ν(Sn–Cl) 320 (s) and 340 (s) cm^{-1} [27].

cis-[Pt(C_6Cl_5)(MeOH)(PEt_3)$_2$][BF_4], **11d**. 200 mg (0.28 mmol) **6d**, suspended in 10 ml MeOH were treated with 55 mg (0.28 mmol) $AgBF_4$ and the mixture stirred for 3 h at room temperature. After filtration through Celite the solution was evaporated to dryness under reduced pressure. A ^{31}P NMR spectrum of a $CDCl_3$ solution of this residue showed the presence of comparable amounts of two products, B and C, with the following parameters:

Product B: $\delta(^{31}P)$ (*trans* to C_6Cl_5) 12.21 ppm $^1J(^{195}Pt,^{31}P)$ 2085 Hz, $\delta(^{31}P)$ (*trans* to X) −2.96 ppm, $^1J(^{195}Pt,^{31}P)$ 4208 Hz, $^2J(^{31}P,^{31}P)$ 19 Hz.

Product C: $\delta(^{31}P)$ (*trans* to C_6Cl_5) 14.38 ppm, $^1J(^{195}Pt,^{31}P)$ 2102 Hz, $\delta(^{31}P)$ (*trans* to Y) −1.55 ppm, $^1J(^{195}Pt,^{31}P)$ 4198 Hz, $^2J(^{31}P,^{31}P)$ 19 Hz.

Thus both products are of the type *cis*-[PtX(orY)(C_6Cl_5)(PEt_3)$_2$] and the electronic nature of the donor atoms of X and Y must be very similar, probably oxygen. This behaviour parallels that observed during the halogenabstraction in compound **4d**. Products B and C rearrange slowly in solution to the pair of *trans* compounds **2d** and A which ultimately give only **2d**. Comparison of the ^{31}P NMR data for the dehalogenation reactions of **4d** and **6d** suggest that compound B is the expected product *cis*-[Pt(C_6Cl_5)(MeOH)(PEt_3)$_2$][BF_4], **11d**. The nature of products A and C is under investigation.

trans-[PtBr(C_6F_5)(PEt_3)$_2$], **4c**. Although this compound has been obtained from the reaction of *cis*-[$PtCl_2(PEt_3)_2$] and C_6F_5MgBr [28], it was prepared as follows: 354 mg (3 mmol) PEt_3 was added to a suspension of 411 mg (1 mmol) of [Pt(1,5-C_8H_2)$_2$] [29], in 20 ml toluene, which had been pre-cooled to $-80\,^\circ$C. 247 mg (1 mmol) of C_6F_5Br was added to the red solution of [$Pt(PEt_3)_3$] [30] obtained above and the solution was allowed to warm up to $0\,^\circ$C and stirred for 16 h. The solvent was evaporated under reduced pressure, the residue was extracted with Et_2O and the product crystallized out on cooling the solution to $-20\,^\circ$C. Yield 70%. Its physical properties agree with those reported elsewhere [28].

trans-[Pt(C_6F_5)(MeOH)(PEt_3)$_2$][BF_4], **2c**, was prepared in situ from **4c** as follows: 190 mg (0.98 mmol) $AgBF_4$, dissolved in 5 ml methanol are added to a solution of 678 mg (1 mmol) **4c** in methanol. The mixture is stirred for 1 h in the absence of light and filtered through Celite. The solution is reduced, evaporated under reduced pressure to a convenient volume and used for further studies after checking its purity by NMR measurements.

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