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Generation of "$[(Ph_3P)_2Pt]$" from $[(Ph_3P)_2Pt(H)Cl]$ under conditions of phase transfer catalysis: synthetic application

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Abstract

Trans-$[(Ph_3P)_2Pt(H)Cl]$ reacts with PhC≡CPh, *trans*-PhCH=CHPh, CH_2=$CHCOOCH_3$, PPh_3, CO, PhI, Ph_2Hg under Phase Transfer conditions (benzene—60% KOH—18-crown-6) to give $[(Ph_3P)_2Pt(Ph_2C_2)]$, $[(Ph_3P)_2Pt(PhCH{=}CHPh)]$, $[(Ph_3P)_2Pt(CH_2{=}CHCOOCH_3)]$, $[(Ph_3P)_3Pt]$, $[(Ph_3P)_2Pt(CO)_2]$, $[(Ph_3P)_2Pt(I)Ph]$, $[(Ph_3P)_2PtPh_2]$ respectively, in 71–96% yield. The availability and stability of the initial Pt-hydride as well as the simplicity of the reaction procedure and the isolation of the desired products, allow these reactions to be used for the preparative synthesis of platinum complexes. The reaction with CH_3I carried out under similar conditions results in a mixture of $[(Ph_3P)_2Pt(I)CH_3]$ (3–5%) and $[(Ph_3P)_2Pt(H)I]$ (95–97%). The latter compound is also formed in quantitative yield by the reaction of $[(Ph_3P)_2Pt(H)Cl]$ with KI. The $[(Ph_3P)_2Pt(H)Cl]$—benzene—60% KOH—18-crown-6 system is active in the symmetrization of PhHgCl but showed low activity in the hydrogenation and isomerisation of octene-1. The decomposition of $[(Ph_3P)_2Pt(H)Cl]$ in the benzene—aqueous alkali—phase transfer catalyst system in absence of substrate results in tris(triphenylphosphine)platinum as the main product and a mixture of unidentified compounds. Data obtained are interpreted in terms of several alternative mechanisms, one of which involves the formation, and further conversions of, bis(triphenylphosphine)platinum.

Introduction

The discovery and intensive practical development of the Phase Transfer Catalysis (PTC) in the last 20–25 years, has become one of the most important steps in the progress of synthetic organic chemistry [1–3]. α-Elimination, i.e. the generation of dihalocarbenes in the haloform-aqueous base-phase transfer catalyst systems, discovered by Makosza and Wawryzniewicz about 20 years ago [4], is one of the most widely used PTC reactions [1–3]. For example:

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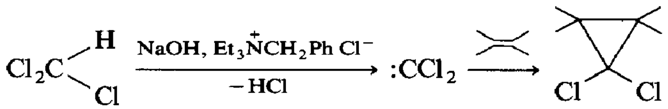
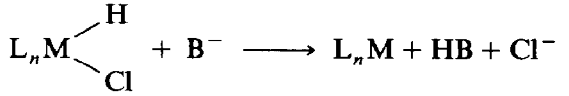


Makosza's technique provides obvious advantages over alternative methods of dihalocarbene generation because it has universal application, and is effective and simple [1–4].

Coordinatively unsaturated low valent transition metal complexes may be regarded as $\sigma^0\pi^2$ carbene analogues [5]. Obviously these complexes can be employed in the synthesis of various coordination compounds as well as in homogeneous catalysis. The application of such complexes to the activation of inert bonds, e.g. C-H bonds of hydrocarbons holds promise [6].

At present several examples of base-mediated α-eliminations of HCl from a transition metal atom are known [7]. However, the conditions of PTC which are being used at present in organometallic chemistry [1–3,8–12] and in the catalysis by transition metal complexes [8–10], have not been applied to reactions of the type:



$$\mathrm{L}_n\mathrm{M}\begin{smallmatrix}\mathrm{H}\\ \\ \mathrm{Cl}\end{smallmatrix} + \mathrm{B}^- \longrightarrow \mathrm{L}_n\mathrm{M} + \mathrm{HB} + \mathrm{Cl}^-$$

We recently showed [13] that dichlorohydridobis(triisopropylphosphine)iridium **1**, which appears to exist in solution in equilibrium with the dihydride **2** in the presence of H_2 [14], readily reacts with dihydrogen (20 °C, 1 atm H_2, 1–30 min) in the 50% NaOH/benzene/triethylbenzylammonium chloride system to give the pentahydride **3** in quantitative yield.

$$\begin{tikzcd} 2(\mathrm{Pr}^i_3\mathrm{P})_2\mathrm{Ir(H)Cl}_2 \arrow[r, shift left, "\mathrm{H}_2"] \arrow[d, "\mathrm{H}_2"', "-\mathrm{HCl}"] & 2(\mathrm{Pr}^i_3\mathrm{P})_2\mathrm{Ir(H)}_2\mathrm{Cl}_2 \arrow[l, shift left] \\ 2(\mathrm{Pr}^i_3\mathrm{P})_2\mathrm{IrH}_5 & \end{tikzcd}$$

(**1**) (**2**)

(**3**)

The reaction does not take place in the absence of phase transfer catalyst. The formation of **3** is not related to the generation of H^- from H_2 under the action of strong base. Evidently, the OH^- ion causes the reductive elimination of HCl from complexes **1** or **2** followed by H_2 addition to the resulting coordinatively unsaturated species [13].

Here we describe some transformations of chloro-hydrido platinum complex, viz. *trans*-$[(Ph_3P)_2Pt(H)Cl]$, in the benzene—aqueous alkali two-phase system in the presence of phase transfer catalyst. A preliminary communication on this has appeared [15].

Recently Jensen and Trogler reported the catalytic anti-Markovnikov hydration of alkenes in the olefin–$[(Me_3P)_2Pt(H)Cl]$—aqueous NaOH—$Et_3\overset{+}{N}CH_2Ph\ Cl^-$ systems and suggested that $[(Me_3P)_2Pt]$ is an active catalytic intermediate [16]. However, it was shown later that analytically pure samples of $[(Me_3P)_2Pt(H)Cl]$ showed no activity in these reactions [17]. Thus the catalytic effect observed by Jensen and Trogler [16] was probably caused by some impurities which were always present in the samples of $[(Me_3P)_2Pt(H)Cl]$ prepared by standard procedures [17].

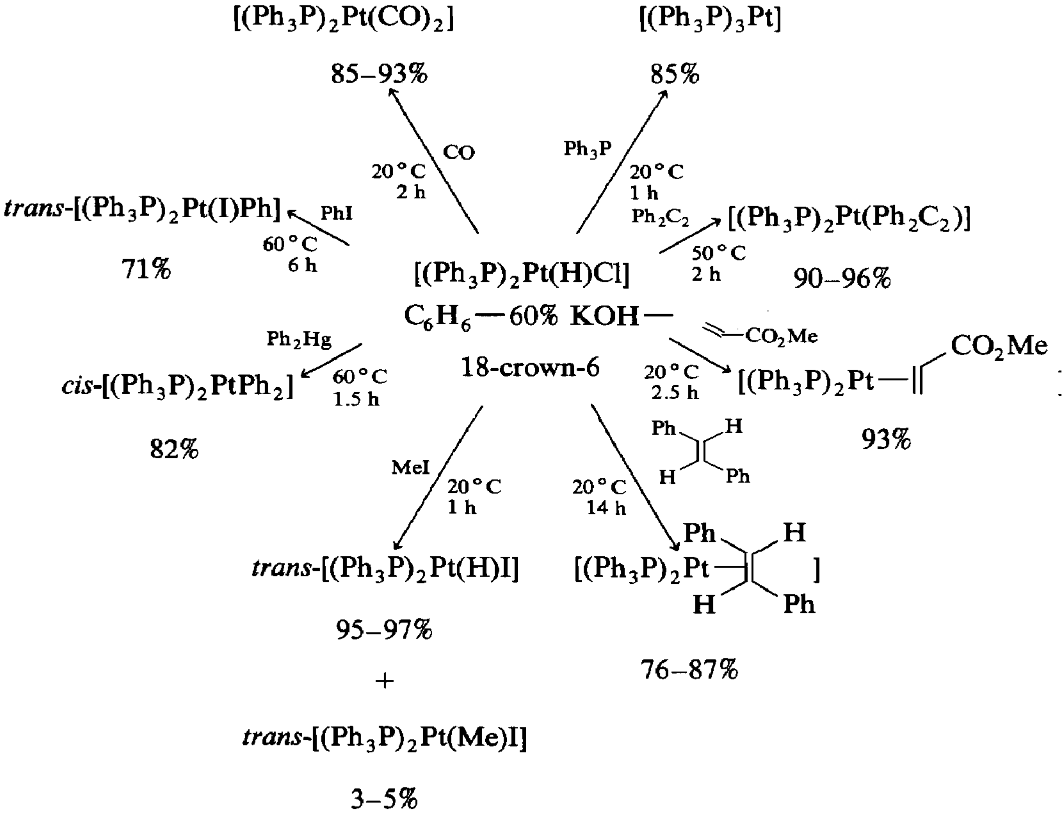
Results

Most of the reactions we carried out are summed up in Scheme 1. All the reactions were performed with vigorous stirring under an inert atmosphere. Yields are given for isolated, single compounds except for those from the reaction with methyl iodide. In that case the identification of the products and determination of their yields was performed by ^1H and ^{31}P NMR spectroscopy.

The selection of experimental conditions

Benzene was chosen as the organic phase for carrying out the reactions as it is inert, non-polar, water-insoluble liquid, and is a good solvent of $[(Ph_3P)_2Pt(H)Cl]$. Benzene is also one of the most widely used solvents in organic phase transfer reactions [1–3]. Concentrated aqueous solutions of NaOH or KOH as bases, and various quarternary ammonium salts or crown ethers as catalysts are usually used in Makosza's method to generate dihalocarbenes [1–3]. We carried out the reaction of $[(Ph_3P)_2Pt(H)Cl]$ with iodobenzene in benzene—50% NaOH—triethylbenzylammonium chloride and in benzene—60% KOH—18-crown-6 systems. In the crown ether system the reaction was found to be more facile, so we used a 60% solution of KOH as the base and 18-crown-6 as the catalyst for the rest of the reactions.

The reactions, which can be carried out in two-phase systems in absence of phase



Scheme 1

transfer catalysts are well known [1–3]. However, when the reactions are performed with tolan we found that a phase transfer catalyst is indispensable. Thus the reaction of $[(Ph_3P)_2Pt(H)Cl]$ with $PhC{\equiv}CPh$ in the 60% KOH—benzene system in the presence of 0.3 equivalents of 18-crown-6 is complete after 2 hours at 50 ° C, to give the corresponding tolan complex in > 90% yield. Under similar conditions but without a phase transfer catalyst only traces of the product are found in the reaction mixture, and the starting Pt-hydride remains practically unchanged. Similarly, $[(Ph_3P)_2Pt(H)Cl]$ is not oxidized in air with stirring in the 60% KOH—benzene system at 20 ° C, and after 10 hours the initial hydride can be isolated unchanged. However, in the presence of catalytic amounts of 18-crown-6, complete oxidation is observed within 6–8 hours; the only resonance in the $^{31}P\{^1H\}$ NMR spectrum of the benzene layer is a singlet at 26 ppm without ^{195}Pt satellites, corresponding to Ph_3PO. We failed to detect the molecular oxygen complex $[(Ph_3P)_2Pt(O_2)]$ in this reaction, probably because of the unstability of the latter in air [18] and its inevitable decomposition under the reaction conditions employed. Thus the reactions described here must be carried out in an inert atmosphere, and benzene and alkali solutions must also be oxygen-free.

It is noteworthy that *trans*-$[(Ph_3P)_2Pt(H)Cl]$ and its (1 : 1) ethanol adduct, formed directly in the synthesis [19], can be successfully used in the reactions.

Reactions with PhC≡CPh, trans-PhCH=CHPh, CH_2=$CHCOOCH_3$, Ph_3P and CO

Reactions with these ligands proceed smoothly as follows:

$$[(Ph_3P)_2Pt(H)Cl] + L \xrightarrow[\text{18-crown-6}]{\text{60\% KOH—C}_6\text{H}_6} \underset{76\text{–}96\%}{[(Ph_3P)_2PtL]}$$

$$L = PhC{\equiv}CPh,\ PhCH{=}CHPh,\ CH_2{=}CHCOOCH_3,\ Ph_3P,\ (CO)_2$$

After the reactions are complete the individual complexes can be readily isolated from the organic layer of the two-phase system.

The time required for the reaction to go to completion depends on the nature of the ligand. Thus, the reaction with triphenylphosphine at room temperature is over within 1–1.5 hours, whereas the reaction with *trans*-stilbene under similar conditions requires stirring for 14 hours. Reaction with stilbene at elevated temperature is unsatisfactory since the stilbene complex formed is unstable to heating and decomposes.

The tolan and stilbene complexes are well known [20] and we have identified them from their spectral data and melting points (see Experimental).

Interestingly, Sen and Halpern [21] observed only a very broad signal in the $^{31}P\{^1H\}$ NMR spectrum of $[(Ph_3P)_3Pt]$ (toluene solution) at room temperature; sharp signals were observed only at low temperatures. In contrast with these data there is rather a sharp singlet at 51 ppm with $J(P\text{–}Pt) = 4460$ Hz in the $^{31}P\{^1H\}$ NMR spectrum (benzene, 25 ° C) of the $[(Ph_3P)_3Pt]$ sample prepared by our technique. The widths of the peak and the ^{195}Pt satellites are about 30 and 60 Hz respectively. The $^{195}Pt\{^1H\}$ NMR spectrum of the same solution at 25 ° C shows a quartet ($\delta = -2943$ ppm) that has the same coupling constant and the width of spectral lines of about 300 Hz. However, even small quantities (1.5–5%) of PPh_3 added to the solution of $[(Ph_3P)_3Pt]$ lead to significant spectral-line broadening in the $^{31}P\{^1H\}$ NMR spectrum (see Fig. 1), and the signal in the $^{195}Pt\{^1H\}$ NMR

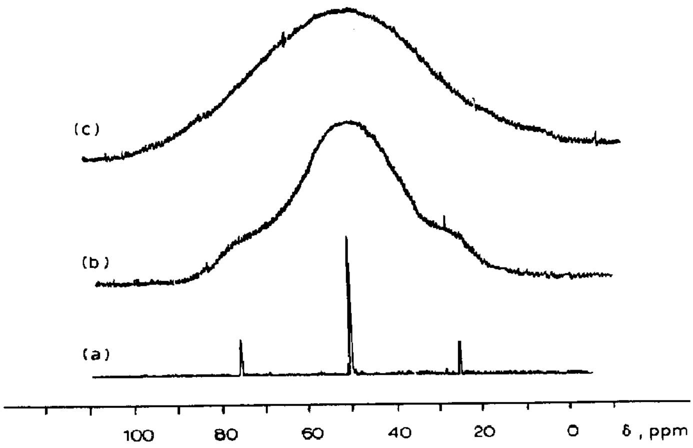


Fig. 1. $^{31}P\{^1H\}$ NMR spectra of $[(Ph_3P)_3Pt]$ (0.05 *M* benzene solution, 25 °C): (a) pure sample; (b) 0.015 equiv of PPh_3 added; (c) 0.05 equiv of PPh_3 added.

spectrum does not appear at all, which is probably caused by the intense ligand exchange occurring in the equilibrium:

$$[(Ph_3P)_3Pt] + Ph_3P \rightleftharpoons [(Ph_3P)_4Pt]$$

Thus the sharp signal, which was absent in our $^{31}P\{^1H\}$ NMR spectrum of $[(Ph_3P)_3Pt]$ solution at room temperature, as described by Sen and Halpern was probably caused by the presence of some excess of triphenylphosphine, or something similar, such as tetrakis(triphenylphosphine)platinum in the sample they used. In fact, the procedure used by Sen and Halpern to synthesize $[(Ph_3P)_3Pt]$ [21] is based on the elimination of Ph_3P from $[(Ph_3P)_4Pt]$ in ethanol under reflux [22]. Thus a small quantity of the impurity $[(Ph_3P)_4Pt]$ could well have remained in the product, which becomes all the more relevant in the knowledge that both $[(Ph_3P)_3Pt]$ and $[(Ph_3P)_4Pt]$ are insoluble in ethanol. The IR spectrum that we recorded for the carbonyl complex $[(Ph_3P)_2Pt(CO)_2]$ is identical with that described previously [23]. The $^{31}P\{^1H\}$ NMR spectrum of this complex (benzene, 25 °C) includes the broad (due to exchange processes) singlet ($\delta = 9.3$ ppm, $J(P-Pt) = 3330$ Hz). These data are consistent with those presented in [21] (toluene solution, -80 to -100 °C).

The typical $^{31}P\{^1H\}$ NMR spectrum of an ABX system is observed for the methyl acrylate complex (benzene, 25 °C): the two doublets from the nonequivalent phosphorous atoms split with different coupling constants on the ^{195}Pt nucleus (see Experimental), which indicates that rotation around the platinum–olefin bond is hindered at room temperature. Vinyl resonances appear in the ^1H NMR spectrum as three complex multiplets (1 : 1 : 1), one of which superposes the singlet from the methyl group.

Reactions with PhI and MeI

Reaction of iodobenzene with $[(Ph_3P)_2Pt(H)Cl]$ in the benzene—60% KOH—18-crown-6 system leads to the insertion of the $[(Ph_3P)_2Pt]$ fragment into the C–I bond:

$$[(Ph_3P)_2Pt(H)Cl] + PhI \xrightarrow[60\,°C,\ 6\ h]{60\%\ KOH—C_6H_6—18\text{-crown-}6} trans\text{-}[(Ph_3P)_2Pt(I)Ph]$$

$$71\%$$

However, the course of the reaction is changed significantly when PhI is replaced by MeI. The ^1H and $^{31}P\{^1H\}$ NMR data reveal that the σ-methyl derivative is obtained in 3–5% yield only, while the major product is *trans*-$[(Ph_3P)_2Pt(H)I]$ (95–97% yield).

$$[(Ph_3P)_2Pt(H)Cl] + MeI \xrightarrow[20\,°C,\ 1\ h]{60\%\ KOH—C_6H_6—18\text{-crown-}6}$$

$$trans\text{-}[(Ph_3P)_2Pt(I)Me] + trans\text{-}[(Ph_3P)_2Pt(H)I]$$

$$3\text{–}5\% \qquad\qquad 95\text{–}97\%$$

It is well known, that MeI, in contrast to PhI, readily undergoes nucleophilic substitution of iodide ion (S_N2), under conditions of PTC [1–3]:

$$MeI + OH^- \longrightarrow MeOH + I^-$$

$$MeOH + OH^- \rightleftharpoons MeO^- + H_2O$$

$$MeI + MeO^- \longrightarrow Me_2O + I^-$$

The released iodide ion appears to take part in ligand exchange, which occurs readily because of the strong *trans*-influence of the hydrido ligand. In fact, we have shown that $[(Ph_3P)_2Pt(H)Cl]$ when treated with KI under conditions of PTC, readily transforms into corresponding iodide:

$$[(Ph_3P)_2Pt(H)Cl] + KI \xrightarrow[20\,°C,\ 1\ h]{C_6H_6—H_2O—18\text{-crown-}6} [(Ph_3P)_2Pt(H)I]$$

$$100\%$$

Reactions with Ph_2Hg and PhHgCl

The insertion of $[(Ph_3P)_2Pt]$ fragment into organomercurials upon treatment with $[(Ph_3P)_3Pt]$ is well known [24]. We have found that $[(Ph_3P)_2Pt(H)Cl]$ can also be phenylated with Ph_2Hg under PTC:

$$[(Ph_3P)_2Pt(H)Cl] + Ph_2Hg \xrightarrow[18\text{-crown-}6]{60\%\ KOH—C_6H_6}$$

$$[(Ph_3P)_2Pt(Ph)HgPh] \xrightarrow[-Hg]{} [(Ph_3P)_2PtPh_2]$$

In order to obtain high yields of *cis*-$[(Ph_3P)_2PtPh_2]$ a 2-fold excess of diphenylmercury is required. In this case ca. 1 equivalent of metallic mercury is released and some Ph_2Hg remains unchanged. In addition a small amount of diphenyl is formed. A complex reaction mixture is formed when stoichiometric amounts of Ph_2Hg are used. The $^{31}P\{^1H\}$ NMR data indicate that the mixture contains only 10–15% of $[(Ph_3P)_2PtPh_2]$. Complete demercuration and diphenyl formation are also observed in this case.

The reaction with one equivalent of phenylmercury chloride is rather unusual. The $^{31}P\{^1H\}$ NMR data reveal that the expected σ-phenyl derivative $[(Ph_3P)_2Pt(Cl)Ph]$ is not formed and that metallic mercury (ca. 100%), diphenyl (10%) and *cis*-$[(Ph_3P)_2PtPh_2]$ (14%) are quantitatively isolated from the reaction mixture. We suggest that initially symmetrization of PhHgCl takes place, then the Ph_2Hg that forms reacts with the remaining $[(Ph_3P)_2Pt(H)Cl]$ as described above. Actually, bis(triphenylphosphine)diphenylplatinum and diphenyl * are not formed at all in the reaction when 10-fold excess of PhHgCl is used. The product of this conversion is diphenylmercury, i.e. the symmetrization of PhHgCl takes place thus:

$$PhHgCl \xrightarrow[55^\circ C,\ 0.5\ h]{[(Ph_3P)_2Pt(H)Cl]—60\%\ KOH—C_6H_6—18\text{-crown-}6} Ph_2Hg$$

After the reaction has gone to completion the $^{31}P\{^1H\}$ NMR spectrum of benzene layer shows only a singlet at 26 ppm, without ^{195}Pt satellites (apparently Ph_3PO), which indicates that during the symmetrization all the P–Pt bonds are cleaved.

From the experiment with the 10-fold excess of PhHgCl it follows that one mole of $[(Ph_3P)_2Pt(H)Cl]$ causes the symmetrization of about three moles of PhHgCl. So, it is natural that in the reaction with 1 equivalent of PhHgCl its symmetrization is followed by the formation of diphenylplatinum derivative. By special experiments we have shown that PhHgCl neither reacts with $[(Ph_3P)_2Pt(H)Cl]$ in benzene, nor undergoes symmetrization in the 60% KOH—benzene system in the presence of 18-crown-6.

Hydrogenation of octene-1

The formation of octane or isomeric octenes, even in trace amounts, was not observed upon stirring of a mixture of $[(Ph_3P)_2Pt(H)Cl]$, benzene, 60% KOH, 18-crown-6 and octene-1 for 4 hours under H_2 (1 atm) at 20 ° C. Under more severe conditions, viz. on stirring for 8 hours at 50–55 ° C, the reaction resulted in a mixture of starting octene-1, octane and *trans*-octene-2 in a ratio of ca. 20 : 5 : 1. In both cases the olefin to platinum complex ratio was ca. 7 : 1. Thus, the use of the $[(Ph_3P)_2Pt(H)Cl]$—benzene—aqueous alkali—phase transfer catalyst system is unlikely to be of any interest for hydrogenation of olefins.

Decomposition of $[(Ph_3P)_2Pt(H)Cl]$ in the benzene—60% KOH system in the presence of 18-crown-6

As we have mentioned before, no conversion of $[(Ph_3P)_2Pt(H)Cl]$ occurs in the benzene—60% KOH system takes place in absence of the phase transfer catalyst, whereas in the presence of 18-crown-6 in air complete oxidation of the hydride takes place. Under argon this reaction usually proceeds more slowly than many reactions with substrates, since the complete decomposition of the complex requires 15–20 hours under standard conditions at 20 ° C. At completion the aqueous layer remains colourless, while the organic phase becomes reddish-brown. The main product of the transformation is tris(triphenylphosphine)platinum, identified by the $^{31}P\{^1H\}$ NMR spectrum of benzene layer of the reaction mixture and subsequently isolated pure. The yield of $[(Ph_3P)_3Pt]$, based on phosphorous, is 50–60%; platinum metal is not formed, at least not as a precipitate. We failed to isolate and identify these reaction products that gave ^{31}P NMR resonances at 7.5, 10.8, 11.9 and 28.6 ppm.

Thus, the decomposition of $[(Ph_3P)_2Pt(H)Cl]$ under the conditions described is

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* Thus under the present reaction conditions diphenyl is formed by the reaction of $[(Ph_3P)_2Pt(H)Cl]$ with Ph_2Hg, but not with PhHgCl.

accompanied by a redistribution of phosphine ligands at the platinum atoms. A similar redistribution of phosphine ligands in the α-elimination of HCl from the iridium complex $[(Ph_3P)_2Ir(H)_2Cl(CO)]$ has been described [7b]:

$$(Ph_3P)_2Ir(H)_2Cl(CO) \xrightarrow[EtOH]{KOH} \underset{\text{ca. 50\%}}{(Ph_3P)_3Ir(CO)H}$$

+ mixture of unidentified carbonyl phosphine iridium complexes

Ugo and co-workers [7f] have reported the formation of $[(Ph_3P)_3Pt]$ and a mixture of unidentified products resulting from the decomposition of a compound they formulated as $[(Ph_3P)_2Pt]$ (see Discussion). Abis, Sen and Halpern [25] observed the formation of $[(Ph_3P)_3Pt]$ upon reductive elimination of methane from *cis*-$[(Ph_3P)_2Pt(H)CH_3]$. It was proposed that the intermediary formed, bis(triphenylphosphine)platinum, disproportionates to give $[(Ph_3P)_3Pt]$ and platinum metal.

$$cis\text{-}[(Ph_3P)_2Pt(H)CH_3] \xrightarrow[-CH_4]{} [(Ph_3P)_2Pt] \longrightarrow [(Ph_3P)_3Pt] + [Pt]$$

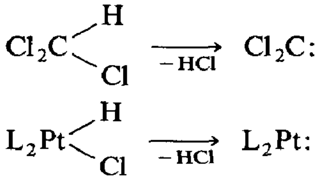
However, the authors [25] did not supply evidence to indicate whether the platinum metal was formed in this reaction.

Discussion

The reactions described above appear to be carbene or carbenoid-type transformations. They can be formally represented as the addition of carbene-like $[(Ph_3P)_2Pt]$ species to a substrate, or its insertion into C–I and C–Hg bonds. However, here, as in carbene chemistry, a variety of mechanisms and reaction pathways, which result in the same products, is possible. The mechanisms of the reactions involved would on their own be the subject of a special investigation. Here we consider and discuss only those reaction schemes which can account for the obtained results. One of these schemes involves the intermediate formation and further reactions of the intermediate, bis(triphenylphosphine)platinum, the other permits the data obtained to be interpreted without resorting to the concept of $[(Ph_3P)_2Pt]$ formation.

Mechanism involving $[(Ph_3P)_2Pt]$ formation

The α-elimination of HCl from the platinum atom of the $[(Ph_3P)_2Pt(H)Cl]$ complex and the generation of the $[(Ph_3P)_2Pt]$ carbene-like species, is similar to dihalocarbene formation from haloform [1–4], and probably occur in the reactions described above.



$$Cl_2C\begin{smallmatrix}H\\Cl\end{smallmatrix} \xrightarrow[-HCl]{} Cl_2C:$$

$$L_2Pt\begin{smallmatrix}H\\Cl\end{smallmatrix} \xrightarrow[-HCl]{} L_2Pt:$$

Furthermore, as with the carbene, the bis(triphenylphosphine)platinum formed reacts with the substrate present in the reaction mixture to give the final product:

$$[L_2Pt(I)Ph] \xleftarrow{PhI} [L_2Pt] \xrightarrow{PhC{\equiv}CPh} [L_2Pt(Ph_2C_2)]$$

The synthesis of $[(Ph_3P)_2Pt]$ was reported by Ugo and co-workers more than 20 years ago [7c]:

$$2[\mathrm{HPt(PPh_3)_3}]^+\mathrm{HSO^-_4} + \mathrm{KOH} + \mathrm{O_2} \xrightarrow{\mathrm{EtOH}}$$
$$2[\mathrm{(Ph_3P)_2Pt}] + 2\mathrm{Ph_3PO} + \mathrm{KHSO_4} + 2\mathrm{H_2O}$$

$$[\mathrm{(Ph_3P)_2Pt(H)Cl}] + \mathrm{BuLi} \longrightarrow [\mathrm{(Ph_3P)_2Pt}] + \mathrm{LiCl} + \mathrm{BuH}$$

The Italian chemists formulated the yellow solid (m.p. 157–160 °C) [$\mathrm{(Ph_3P)_2Pt}$], on the basis of elemental analysis and some ligand addition reactions [7c,7d]. This complex is very unstable and does not catalyze the hydrogenation and/or the isomerization of olefins. "However, subsequent attempts to prepare [$\mathrm{Pt(Ph_3P)_2}$] in *monomeric form* under conditions where it is sufficiently stable for direct detection and characterization, either in solution or as a solid, appear to have been unsuccessful" [21,25]. Recently the electrochemical reduction of *cis*-[$\mathrm{(Ph_3P)_2PtCl_2}$], to give a solution of [$\mathrm{(Ph_3P)_2Pt}$] has been reported [26]. Treatment of this solution with tolan results in a high yield of the corresponding acetylene complex [$\mathrm{(Ph_3P)_2Pt(Ph_2C_2)}$]. However with the exception of three similar reactions, no other methods, including spectroscopy, have been used to characterize this solution. Therefore, no evidence has been obtained in support of the existence of monomeric bis(triphenylphosphine)platinum in solution.

It is known that $\mathrm{L_2Pt}$ complexes, where L = tertiary phosphine, are rather stable and can be isolated and characterized (including X-ray diffraction study) only when L involves bulky alkyl groups, such as tert-butyl, iso-propyl, cyclohexyl, at the phosphorous atom [27]. The existence of such complexes provides evidence for the possibility of participation of bis(triphenylphosphine)platinum as an intermediate in our reactions. It should be noted that the idea of the probable intermediate participation of [$\mathrm{(Ph_3P)_2Pt}$] in a broad range of other reactions was reported some time ago [28].

Several paths of the [$\mathrm{L_2Pt}$] formation from [$\mathrm{L_2Pt(H)Cl}$] under action of hydroxide ion can be conceived. Path **A** is similar to the mechanism of dichlorocarbene generation from chloroform [1] and involves the deprotonation of hydride complex followed by elimination of $\mathrm{Cl^-}$ from the anion formed:

Path **A**

$$[\mathrm{L_2Pt(H)Cl}] + \mathrm{OH^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{L_2PtCl}]^- + \mathrm{H_2O} \qquad (1)$$

$$[\mathrm{L_2PtCl}]^- \overset{k_2}{\rightleftharpoons} [\mathrm{L_2Pt}] + \mathrm{Cl^-} \qquad (2)$$

Path **B** is similar to path **A**. The only difference being that the replacement of chloro ligand by hydroxo group in the chloro-hydrido complex precedes the deprotonation:

Path **B**

$$[\mathrm{L_2Pt(H)Cl}] + \mathrm{OH^-} \rightleftharpoons [\mathrm{L_2Pt(H)OH}] + \mathrm{Cl^-} \qquad (3)$$

$$[\mathrm{L_2Pt(H)OH}] + \mathrm{OH^-} \rightleftharpoons [\mathrm{L_2PtOH}]^- + \mathrm{H_2O} \qquad (4)$$

$$[\mathrm{L_2PtOH}]^- \rightleftharpoons [\mathrm{L_2Pt}] + \mathrm{H_2O} \qquad (5)$$

Path **C** also involves the replacement of $\mathrm{Cl^-}$ by $\mathrm{OH^-}$ in the starting hydride but is followed by the reductive elimination of water from the hydroxo-hydrido complex formed:

Path **C**

$$[L_2Pt(H)Cl] + OH^- \rightleftharpoons [L_2Pt(H)OH] + Cl^- \qquad (6)$$

$$[L_2Pt(H)OH] \rightleftharpoons [L_2Pt] + H_2O \qquad (7)$$

In order to obtain useful data, which would allow us to choose the most probable scheme for the generation of $[L_2Pt]$, we studied the possibility of substitution of the hydrido ligand in the $[(Ph_3P)_2Pt(H)Cl]$ complex in the $NaOD/D_2O—C_6H_6$, $NaOD/D_2O—C_6H_6$—18-crown-6 and $NaOD/D_2O—C_6D_6$—18-crown-6 systems. In no case was deuteration observed in the first 2–4 hours * under standard conditions according to IR and ^1H NMR spectroscopy (within the accuracy of the integral intensity measurement in ^1H NMR spectra; see Experimental) **. These data indicate that at least one of the stages in the **A**, **B**, or **C** paths should be practically irreversible. Obviously, only the second stage in the path **A** can be irreversible (no H/D exchange occurs if $k_2 \gg k_{-1}$), i.e. the elimination of Cl^- from the 16-electron anionic complex (equation 2). We regard this as unlikely.

We think that the paths **B** and **C** are more probable. The strong *trans*-influence of the hydrido ligand, observed in the reactions with KI and MeI, provides the opportunity for replacement of Cl^- by OH^- in *trans*-$[(Ph_3P)_2Pt(H)Cl]$. Since $[OH^-] \gg [Cl^-]$ under our conditions, the substitution (see equations 3 and 6) is practically irreversible, which explains the absence of the H/D exchange. It should be noted that the substitution of the chloro ligand by OH group in binuclear complexes of platinum, has already been carried out under PTC conditions [30], though, as a rule, the platinum atom is coordinated with the hard OH^- base rather reluctantly. The reaction stage (7) in path **C**, i.e. the reductive elimination of water from the hydroxo-hydrido complex of platinum, can also be irreversible. Yoshida, Otsuka and co-workers have investigated in detail the activation of water by $[L_2Pt]$ and $[L_3Pt]$ complexes (L = tertiary phosphine) and have shown that complexes with aliphatic phosphines undergo oxidative addition of water, whereas the less nucleophilic tris(triphenylphosphine)platinum does not participate in this reaction [31]. Still less nucleophilic bis(triphenylphosphine)platinum appears to be also incapable of undergoing oxidative addition by water.

Mechanisms not involving intermediate $[(Ph_3P)_2Pt]$ formation

Some of the reactions we have described can obviously proceed via other mechanisms, not involving the formation of bis(triphenylphosphine)platinum. It is

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* It is rather difficult to study H/D exchange for a longer time, as the starting hydride decomposes to yield products which give signals in the aromatic range of ^1H NMR spectra. This, in turn, prevents the accurate measurement of the relative integral intensities of aromatic and hydride proton signals of $[(Ph_3P)_2Pt(H)Cl]$.

** The absence of H/D exchange in the system containing C_6D_6 indicates that benzene C–H bonds are not activated under the conditions employed. Indeed, a rigid *cis*-coordination of phosphine ligands relative to the adding hydride and alkyl (aryl) fragments is necessary for the activation of C–H bonds by zero-valent platinum complexes $[L_2Pt]$. This can be achieved by using bidentate phosphines (L_2 = 1,2-bis(dicyclohexylphosphino)ethane) [29].

known that some ligands can reversibly displace Cl^- from the inner coordination sphere of *trans*-$[(Ph_3P)_2Pt(H)Cl]$. For example, when PPh_3 is added to a solution of *trans*-$[(Ph_3P)_2Pt(H)Cl]$ the following equilibrium is observed [7e]:

$$[(Ph_3P)_2Pt(H)Cl] + Ph_3P \rightleftharpoons [(Ph_3P)_3PtH]^+Cl^-$$

If alkali is added to the resulting solution exchange between Cl^- and OH^- in the outer coordination sphere occurs and then the irreversible (as the reverse process does not occur [31]) reductive elimination of water yields the final product [7e]:

$$[(Ph_3P)_3PtH]^+Cl^- + OH^- \rightleftharpoons [(Ph_3P)_3PtH]^+OH^- + Cl^-$$

$$[(Ph_3P)_3PtH]^+OH^- \longrightarrow [(Ph_3P)_3Pt] + H_2O$$

We think that this route predominates in the reactions studied by us with PPh_3 as well as, for example, those with CO and methyl acrylate which proceed quite readily. Ligand exchange in square planar platinum complexes usually proceeds via the formation of a 5-coordinate intermediate, which is stabilized by π-acceptor type ligands. In light of this and also taking into consideration steric factors, the reaction with methyl acrylate should proceed more readily than that with *trans*-stilbene, as was indeed observed. In addition, the acceptor properties of the ligand, can affect the case by which reductive elimination of water takes place from the cationic complex. However, this pathway is unlikely in the reaction without a substrate and also in the reactions with iodobenzene and diphenylmercury, and in these transformations bis(triphenylphosphine)platinum is a probable intermediate.

The role of phase transfer catalyst in our reactions is rather complicated. This catalyst can probably facilitate both deprotonation and ion or ligand exchange.

In conclusion we emphasize, that the possibility of other mechanisms and the simultaneous progress of the reaction with the same substrate along several different routes, nevertheless resulting in the same products, as in carbene chemistry, should not be excluded.

Experimental

All manipulations were performed under purified Ar, except where noted. All NMR data were recorded at ambient temperature on a Bruker WP-200 SY spectrometer. ^1H NMR spectra were recorded at 200.13 MHz; ^{31}P NMR spectra were recorded at 81.01 MHz; ^{195}Pt NMR spectra were recorded at 43.01 MHz. ^1H NMR shifts are relative to tetramethylsilane; the residual solvent peaks (C_6HD_5, δ 7.15; $CHCl_3$, δ 7.25) were used as internal reference. ^{31}P NMR shifts are relative to 85% H_3PO_4 at δ 0.0 with shifts downfield from the reference regarded as positive. ^{195}Pt NMR are relative to 5% aqueous K_2PtCl_4 at δ 0.0 with shifts downfield of the reference regarded as positive. Infrared spectra were recorded on a Carl Zeiss, Jena, UR-20 instrument. GLC measurements were performed with a Soviet-made Tsvet-129 instrument equipped with a 3m × 4mm GESE-30 on Chromaton-M Super packed column. TLC was carried out by use of Silufol UV 254 plates (Kavalier, Czechoslovakia). A magnetic stirring bar was used for the PTC reactions.

Methyl iodide was washed with $NaHSO_3$, water, then dried over $CaCl_2$, and distilled. Iodobenzene was purified by the same procedure and distilled under reduced pressure. Octene-1 and methyl acrylate were distilled before use. Triphenylphosphine was recrystallized from 95% ethanol and sublimed in vacuo. Benzene (UV grade, Chemapol, Czechoslovakia), 18-crown-6 ether (Sigma) and other compounds were used without purification. *trans*-$[(Ph_3P)_2Pt(H)Cl] \cdot EtOH$ [19], *trans*-$[(Ph_3P)_2Pt(H)Cl]$ [19], PhHgCl [32] and Ph_2Hg [33] were prepared by published procedures.

Benzene, aqueous alkali and all the solutions were degassed by three freeze–pump–thaw cycles before reaction. In most cases the reaction runs were monitored by TLC. TLC plates were developed by UV, in iodine vapour and/or over an open flame. For the latter, platinum-containing areas became black or dark brown probably as a result of platinum metal deposition. TLC monitoring of the reactions is recommended when reproducing the experiments, because the PTC reaction rate is primarily dependent on the efficiency of the stirring [1–3].

$[(Ph_3P)_2Pt(PhC{\equiv}CPh)]$ from $[(Ph_3P)_2Pt(H)Cl]$

A mixture of $[(Ph_3P)_2Pt(H)Cl]$ (0.20 g, 0.27 mmol), tolan (0.10 g, 0.56 mmol), 18-crown-6 ether (0.04 g, 0.15 mmol), benzene (3 ml) and 60% KOH (3 ml) was vigorously stirred at 50–55 °C for 2 h. The product was isolated in air. Benzene layer was separated off, and the aqueous solution was washed with benzene (2 × 5 ml). The combined benzene solutions were filtered through silica (40/100 μ) and concentrated to ca. 1 ml. The addition of ethanol (20 ml) precipitated the pale-yellow crystals of $[(Ph_3P)_2Pt(PhC{\equiv}CPh)]$. After 2 h the product was separated, washed with ethanol and dried in vacuo; yield 0.23 g (97%), m.p. (in air) 162–168 °C (dec, see ref. 28b). $^{31}P\{^1H\}$ NMR (benzene, 25 °C): δ 28.0 (s, $J(P–Pt) = 3465$ Hz, see ref. 34). $^{195}Pt\{^1H\}$ NMR (benzene, 25 °C): δ −3110.7 (t, see ref. 34). IR (Nujol mull): 1770 and 1740 cm^{-1} ($\nu(C{\equiv}C)$, see ref. 28b).

$[(Ph_3P)_2Pt(PhC{\equiv}CPh)]$ from $[(Ph_3P)_2Pt(H)Cl] \cdot EtOH$

The complex was prepared as described above from $[(Ph_3P)_2Pt(H)Cl] \cdot EtOH$ (0.10 g, 0.125 mmol), tolan (0.05 g, 0.28 mmol), 18-crown-6 ether (0.01 g, 0.04 mmol), benzene (2 ml) and 60% KOH (2 ml). Yield 0.105 g (94%).

$[(Ph_3P)_2Pt(PhCH{=}CHPh)]$

A mixture of $[(Ph_3P)_2Pt(H)Cl] \cdot EtOH$ (0.21 g, 0.27 mmol), *trans*-stilbene (0.236 g, 1.31 mmol), 18-crown-6 ether (0.03 g, 0.11 mmol), benzene (4 ml) and 60% KOH (2 ml) was vigorously stirred at 24 °C for 14 h. The orange-reddish organic layer was separated and treated with degassed ethanol (40 ml), and the mixture was cooled at ca. 10 °C overnight. The white or pale yellow crystals that had separated were washed with degassed ethanol (4 × 7 ml), pentane (2 × 8 ml) and dried in vacuo; yield 0.18–0.205 g (76–87%), m.p. (in air) 132–142 °C (dec, see ref. 35). $^{31}P\{^1H\}$ NMR (benzene, 25 °C): δ 29.5 (s, $J(P–Pt) = 3866$ Hz, see ref. 36).

$[(Ph_3P)_2Pt(CH_2{=}CHCOOCH_3)]$

A mixture of $[(Ph_3P)_2Pt(H)Cl] \cdot EtOH$ (0.15 g, 0.19 mmol), methyl acrylate (0.2 ml, 2.22 mmol), 18-crown-6 ether (0.01 g, 0.04 mmol), benzene (6 ml) and 60% KOH (2 ml) was stirred vigorously at 20 °C for 2.5 h. The pale-yellow organic layer was separated, and benzene was removed in vacuo. The residue was dissolved in degassed acetone (2 ml), and the solution was quickly filtered and treated with 10 ml of degassed pentane. After standing overnight at ca. 10 °C the white crystals were separated, washed with pentane (2 × 5 ml) and dried in vacuo; yield 0.14 g (93%), m.p. (in air) 86–91 °C (dec). ^{1}H NMR (benzene-d_6, 25 °C): δ 2.6 (m, 1H), 3.25 (s, 3H), 3.35 (m, 1H), 3.75 (m, 1H), 7.0 (m, 18H), 7.6 (m, 12H). ^{31}P{^{1}H} NMR (benzene, 25 °C): δ 30.5 (d, 1P, J(P–P) = 43 Hz, J(P–Pt) = 4070 Hz), 32.0 (d, 1P, J(P–P) = 43 Hz, J(P–Pt) = 3590 Hz). IR (Nujol mull): 1690 cm^{-1} (ν(CO)). Anal. Calcd for $C_{40}H_{36}O_2P_2Pt$: C, 59.62; H, 4.50. Found: C, 59.69; H, 4.40%.

[(Ph₃P)₃Pt]

A mixture of [(Ph$_3$P)$_2$Pt(H)Cl] · EtOH (0.203 g, 0.25 mmol), PPh$_3$ (0.065 g, 0.25 mmol), 18-crown-6 ether (0.01 g, 0.04 mmol), benzene (5 ml), and 60% KOH (2 ml) was stirred vigorously at 20 °C for 1 h. The clear yellow organic layer was separated and benzene was removed in vacuo. The yellow solid that remained was washed with ethanol (2 × 10 ml) and dried in vacuo; yield 0.21 g (85%), m.p. (in air) 124–128 °C (dec), (in vacuo) 190 °C (dec, see ref. 22). ^{31}P{^{1}H} NMR (benzene, 25 °C): δ 51.1 (s, J(P–Pt) = 4460 Hz, see ref. 21). ^{195}Pt{^{1}H} NMR (benzene, 25 °C): δ −2943.3 (q, J(Pt–P) = 4460 Hz). Anal. Calcd for $C_{54}H_{45}P_3Pt$: C, 66.05; H, 4.62. Found: C, 66.08; H, 4.60%.

[(Ph₃P)₂Pt(CO)₂]

A mixture of [(Ph$_3$P)$_2$Pt(H)Cl] · EtOH (0.20 g, 0.25 mmol), 18-crown-6 ether (0.02 g, 0.08 mmol), benzene (3 ml) and 60% KOH (1 ml) was stirred vigorously under CO at 20 °C for 1.5–2 h. The reddish-brown benzene layer was separated and treated with 40 ml of CO-saturated ethanol. After standing under CO for 3 h the solution became colourless and carbonyl phosphine complex precipitated as white or pale cream-coloured plates. Degassed water (4 ml) was added and the mixture was allowed to stand under CO at ca. 10 °C overnight. The crystals were separated, washed with ethanol (2 × 5 ml), pentane (2 × 5 ml) and dried in a stream of CO. Yield 0.165–0.180 g (85–93%). ^{31}P{^{1}H} NMR (benzene, 25 °C): δ 9.3 (br.s, J(P–Pt) = 3330 Hz, see ref. 21). IR (Nujol mull): 1980 (s), 1945 (s), 1910 (w) cm^{-1} (ν (CO), see ref. 23).

trans-[(Ph₃P)₂Pt(I)Ph]

A mixture of [(Ph$_3$P)$_2$Pt(H)Cl] (0.30 g, 0.40 mmol), iodobenzene (0.5 ml, 4.51 mmol), 18-crown-6 ether (0.06 g, 0.23 mmol), benzene (3 ml) and 60% KOH (3 ml) was stirred vigorously at 60 °C until the starting hydride had disappeared (6–8 h, monitoring with TLC or ^{1}H NMR). The product was isolated in air. The reaction mixture was diluted with water (5 ml) and extracted with hot benzene (7 × 10 ml). The combined warm benzene solutions were filtered through a silica (40/100 μ) layer and evaporated to dryness. The residue was recrystallized from hot benzene-hexane and dried in vacuo; yield 0.26 g (71%), m.p. (in air) 260–270 °C (dec, see ref. 37). ^{31}P{^{1}H} NMR (CH_2Cl_2, 25 °C): δ 21.5 (s, J(P–Pt) = 3090 Hz, see ref. 38). Anal. Calcd for $C_{42}H_{35}IP_2Pt$: C, 54.61; H, 3.82; I, 13.74; Pt, 21.12. Found: C, 55.15; H, 3.89; I, 13.88; Pt, 21.15%.

Reaction with CH₃I

A mixture of [(Ph$_3$P)$_2$Pt(H)Cl] · EtOH (0.12 g, 0.15 mmol), methyl iodide (0.2 ml, 3.31 mmol), 18-crown-6 ether (0.02 g, 0.08 mmol), benzene (2.5 ml) and 60% KOH (2 ml) was stirred vigorously at 20 °C for 1.5 h. The rest of the manipulations were carried out in air. The benzene layer was separated, and the aqueous solution was washed with benzene (3 × 5 ml). The combined benzene solutions were evaporated to dryness, and the residue was dissolved in $CHCl_3$ (20 ml) and filtered through silica (40/100 μ). Chloroform was evaporated to dryness and the residue was dried in vacuo; yield 0.127 g (3–5% of $[(Ph_3P)_2Pt(CH_3)I]$ and 95–97% of $[(Ph_3P)_2Pt(H)I]$, based on ^{31}P and ^{1}H NMR data). $^{31}P\{^1H\}$ NMR ($CHCl_3$, 25 ° C): δ 28.1 (s, 1P, $J(P-Pt) = 3060$ Hz, $[(Ph_3P)_2Pt(CH_3)I]$); 28.9 (s, ca. 20P, $J(P-Pt) = 2940$ Hz, $[(Ph_3P)_2Pt(H)I]$). ^1H NMR ($CDCl_3$, 25 ° C): δ −11.8 (t, ca. 10H, $J(P-H) = 11.5$ Hz, $J(Pt-H) = 1240$ Hz, Pt–H); 0.07 (t, 1H, $J(P-H) = 6.7$ Hz, $J(Pt-H) = 76.2$ Hz, $Pt-CH_3$, see ref. 39); 7.4 (m, ca. 180H, m,p-C_6H_5); 7.7 (m, ca. 120H, o-C_6H_5).

$[(Ph_3P)_2Pt(H)I]$

A mixture of $[(Ph_3P)_2Pt(H)Cl] \cdot EtOH$ (0.10 g, 0.12 mmol), KI (0.5 g, 3 mmol), 18-crown-6 ether (0.02 g, 0.08 mmol), benzene (3 ml) and water (3 ml) was stirred vigorously in air at 20 ° C for 1 h. The benzene layer was separated, and the aqueous one was washed with benzene (3 × 5 ml). The combined benzene solutions were filtered through silica (40/100 μ) and evaporated to dryness. The white, solid residue was washed with pentane (3 × 3 ml) and dried in vacuo; yield 0.105 g (99.5%), m.p. (in air) 185–190 ° C (dec). ^1H NMR ($CDCl_3$, 25 ° C): δ −11.8 (t, 1H, J (P–H) = 11.5 Hz, $J(Pt-H) = 1240$ Hz, Pt–H); 7.4 (m, 18H, m,p-C_6H_5); 7.7 (m, 12H, o-C_6H_5). $^{31}P\{^1H\}$ NMR (benzene, 25 ° C): δ 28.9 (s, $J(P-Pt) = 2940$ Hz). Anal. Calcd for $C_{36}H_{31}IP_2Pt$: C, 51.01; H, 3.69; I, 14.97; Pt, 23.02. Found: C, 50.97; H, 3.81; I, 14.61; Pt, 22.90%.

cis-$[(Ph_3P)_2PtPh_2]$

A mixture of $[(Ph_3P)_2Pt(H)Cl] \cdot EtOH$ (0.18 g, 0.22 mmol), diphenylmercury (0.16 g, 0.45 mmol), 18-crown-6 ether (0.015 g, 0.06 mmol), benzene (4 ml) and 60% KOH (2 ml) was stirred vigorously at 20 ° C for 2 h and then at 60 ° C for 1.5 h. By the end of the reaction the organic layer was light yellow and the aqueous layer was colourless; drops of metallic mercury were observed at the bottom of the flask. The rest of the operations were carried out in air. The amounts of diphenyl and unreacted diphenylmercury in the organic phayse were determined by TLC. The benzene layer was separated, and the aqueous one was washed with benzene (2 × 5 ml). The combined benzene solutions were filtered through silica (40/100 μ), concentrated to ca. 1 ml and treated with ethanol (7 ml). After 2 h white crystals that formed were separated, washed with ethanol (2 × 3 ml), acetone (2 × 3 ml), pentane (2 × 3 ml), and dried in vacuo; yield 0.16 g (82%), m.p. (in air) 140–150 ° C (dec, see ref. 40). $^{31}P\{^1H\}$ NMR (benzene, 25 ° C): δ 19.6 (s, $J(P-Pt) = 1730$ Hz, see ref. 41). Anal. Calcd for $C_{48}H_{40}P_2Pt$: C, 65.97; H 4.61. Found: C, 66.06; H, 4.84%.

Reaction with 1 equiv of PhHgCl

A mixture of $[(Ph_3P)_2Pt(H)Cl] \cdot EtOH$ (0.5 g, 0.63 mmol), PhHgCl (0.20g, 0.64 mmol), 18-crown-6 ether (0.03 g, 0.11 mmol), benzene (10 ml) and 60% KOH (4 ml) was stirred vigorously at 55 ° C for 1 h. $^{31}P\{^1H\}$ NMR spectrum of benzene layer showed no less than 10 resonances, including a broad singlet at 50 ppm ($[(Ph_3P)_3Pt]$), a singlet at 24.8 ppm ($J(P-Pt) = 3140$ Hz, unchanged $[(Ph_3P)_2Pt(H)Cl]$), and a singlet at 19.7 ppm ($J(P-Pt) = 1730$ Hz, $[(Ph_3P)_2PtPh_2]$, see previous experiment). The rest of the operations were carried out in air. The benzene layer was separated, and aqueous one was washed with benzene (2 × 10 ml). The combined benzene solutions were evaporated to dryness, and the residue was chromatographed on silica (40/100 μ)-packed 200 × 15 mm glass column with benzene as eluant, to give diphenyl (0.005 g, 10% calcd on PhHgCl) and [$(Ph_3P)_2PtPh_2$] (0.040 g, 14% calcd on PhHgCl) pure. Anal. Calcd for $C_{48}H_{40}P_2Pt$: C, 65.97; H, 4.61. Found: C, 66.04; H, 4.59%. Yield of mercury 0.12 g (94%).

Reaction with 10 equiv of PhHgCl

A mixture of [$(Ph_3P)_2Pt(H)Cl$] · EtOH (0.05 g, 0.06 mmol), PhHgCl (0.20 g, 0.64 mmol), 18-crown-6 ether (0.01 g, 0.04 mmol), benzene (3 ml) and 60% KOH (2 ml) was stirred vigorously at 55–60 °C for 1 h. $^{31}P\{^1H\}$ NMR spectrum of organic phase showed the only one resonance, viz., a singlet without ^{195}Pt satellites at 26 ppm. The rest of the operations were performed in air. The dark brown benzene layer was separated, and the aqueous one was washed with benzene (2 × 5 ml). Combined benzene solutions were evaporated to dryness, and the residue was extracted with hexane (TLC control). The combined hexane solutions were filtered through silica (40/100 μ), and the solvent was removed in vacuo. The residue, diphenylmercury, was sublimed in vacuo; yield 0.03 g, m.p. 123–124 °C (from hexane, see ref. 33).

Hydrogenation of octene-1

A mixture of [$(Ph_3P)_2Pt(H)Cl$] · EtOH (0.06 g, 0.07 mmol), octene-1 (0.08 ml, 0.51 mmol), 18-crown-6 ether (0.01 g, 0.04 mmol), benzene (1.5 ml) and 60% KOH (1.5 ml) was stirred vigorously under H_2 at 50–55 °C for 8 h. The organic layer was separated, distilled in vacuo and analyzed by GLC.

Decomposition of [$(Ph_3P)_2Pt(H)Cl$] in the C_6H_6—60% KOH—18-crown-6 system

A mixture of [$(Ph_3P)_2Pt(H)Cl$] · EtOH (0.20 g, 0.25 mmol), 18-crown-6 ether (0.02 g, 0.08 mmol), benzene (5 ml) and 60% KOH (2 ml) was stirred vigorously at 20 °C until all the starting hydride had disappeared (15–20 h, TLC control). The reddish-brown organic layer was separated, and the benzene was removed in vacuo. The residue was extracted with degassed pentane (5 × 50 ml), and the combined pentane solutions were evaporated to dryness. The tris(triphenylphosphine)platinum that remained ($>$ 90% pure by ^{31}P NMR) was washed with pentane (5 ml) and dried in vacuo; yield 0.105 g.

Attempted H/D exchange in [$(Ph_3P)_2Pt(H)Cl$]

(a). A mixture of [$(Ph_3P)_2Pt(H)Cl$] · EtOH (0.20 g, 0.25 mmol), benzene (6 ml) and a saturated solution of NaOD in D_2O (1.5 ml) was vigorously stirred in air at 20 °C. Portions (0.8–1.0 ml) of the organic phase were drawn 10 min, 30 min, 1 h, 3 h and 10 h after stirring was commenced. Each portion was evaporated and the residue was dried in vacuo. The IR spectra of all the samples studied were completely identical with the IR spectrum of the initial hydride in the range 1300–2400 cm^{-1}.

(b). A mixture of [$(Ph_3P)_2Pt(H)Cl$] · EtOH (0.06 g, 0.08 mmol), 18-crown-6 ether (0.02 g, 0.08 mmol), benzene-d_6 (3 ml) and a saturated solution of NaOD in D_2O (2 ml) was stirred vigorously at 20 °C. ^1H and $^{31}P\{^1H\}$ NMR spectra of organic phase were recorded 2 h and 4 h after stirring was commenced. No more than 15% and

30% of the initial hydride was found to have decomposed after 2 h and 4 h respectively, on the basis of ^{31}P NMR data. In both cases the ratio of the integral intensities of *o*-protons of triphenylphosphine ligands (8.0 ppm) and hydride protons of the initial complex (−15.1 ppm) in the ^{1}H NMR spectra was about 12 : 1.

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