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# Complexes of Long Alkyl Chain Tertiary Phosphines.
# Part 3. The Oxidative Addition of Methyl Iodide to Platinum(0) Tertiary Phosphine Complexes [1]

S. FRANKS and F. R. HARTLEY*

*Department of Chemistry and Metallurgy, The Royal Military College of Science, Shrivenham, Wiltshire, SN6 8LA, U.K.*

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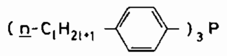
*The oxidative addition of methyl iodide to aged solutions of* $[PtL_2]$ *and* $[PtL_3]$ *complexes in benzene solution at 25 °C under pseudo first-order conditions has been followed spectrophotometrically. For all the tertiary phosphines studied except triphenylphosphine the reaction occurs in two steps which are due to rapid reaction of the* $[PtL_2]$ *present initially followed by slower reaction of* $[PtL_3]$*. Trialkylphosphines promote oxidative addition more than triarylphosphines, the rate of oxidative addition depending on L in the order* $P = P(C_6H_4Et\text{-}p)_3 < P(C_6H_4Me\text{-}p)_3 < P(n\text{-}C_{16}H_{33})_3 < P(n\text{-}C_8H_{17})_3$*. Triphenylphosphine complexes of platinum(0) are anomalous in showing both an induction period and only a single step.*

## Introduction

In previous papers we have described the syntheses of two series of tertiary phosphines $P(n\text{-}C_mH_{2m+1})_3$ where m = 10 to 19 and



where 1 = 3 to 9 together with the preparation of some of their complexes with the platinum group metals [1–4]. These tertiary phosphines and their transition metal complexes have rather different solubility properties to those previously available; in particular they are extremely soluble in aliphatic hydrocarbon and chlorinated aliphatic hydrocarbon solvents. Tertiary phosphine complexes have been widely used as homogeneous catalysts and the solvent plays a very important role in many homogeneous catalytic cycles. Since a very important step in many homogeneous catalytic cycles is oxidative addition it was of interest to determine how effective the new tertiary phosphines were at promoting oxidative addition to platinum(0). Accordingly we investigated the oxidative addition of methyl iodide to $[PtL_n]$ where L = tertiary phosphine and n = 3 or 4 (reaction 1). We have

$$PtL_n + CH_3I \rightarrow [PtL_2(CH_3)I] + (n-2)L \qquad (1)$$

previously reported on the ability of the present phosphines to promote oxidative addition at rhodium(I) [5].

## Experimental

The tertiary phosphines and their platinum(0) complexes were prepared as described previously [2–4]. Solutions of $PtL_n$ ($4 \times 10^{-4}$ mol $l^{-1}$) and methyl iodide (redistilled; 1 mol $l^{-1}$) in dry deoxygenated benzene were prepared and stored under an atmosphere of nitrogen. The solutions of the platinum(0) complexes were allowed to age in the dark until the equilibrium between $PtL_4$, $PtL_3$ and $PtL_2$ had been fully established (see part 1) [4]. The $PtL_n$ and methyl iodide solutions were then mixed under a nitrogen atmosphere. *CAUTION methyl iodide is a depressant and should only be handled in well-ventilated areas.* The absorbance at 358 or 360 nm (see Table I) was measured as a function of time using 1 cm quartz cells mounted in a constant temperature cell housing in a Unicam SP 1700B spectrophotometer. The temperature was maintained at 25.0 ± 0.1 °C using a Techne C100 circulating bath coupled to a Techne 1000 refrigeration unit.

It was demonstrated that neither solutions of methyl iodide in benzene nor the tertiary phosphines in benzene show any change in absorbance during the time of the present kinetic studies. Solutions of methyl iodide and triphenylphosphine react to form methyltriphenylphosphonium iodide; the second-order rate constant for this reaction is of the order of $10^{-5}$ l mol$^{-1}$ s$^{-1}$ [6]. In the present work the excess of methyl iodide present enabled the data to be analysed by a pseudo first order approach. Plots of $2.303\log(A_\infty - A_t)$ against time, where $A_\infty$ and $A_t$ were the absorbances at infinite time and time

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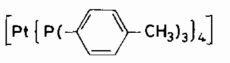
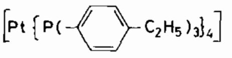
*Author to whom correspondence should be addressed.

TABLE I. Kinetic Data for the Oxidative Addition of Methyl Iodide to $[PtL_n]$ at 25.0 ± 0.1 °C.

| $[PtL_n]$ | Wavelength studied (nm) | $k_1$ ($s^{-1} \times 10^3$) | $k_2$ ($s^{-1} \times 10^3$) |
|---|---|---|---|
|  | 358 | 2.3 | 9.1 |
|  | 358 | 0.4 | 2.9 |
| $[Pt\{P(n\text{-}C_8H_{17})_3\}_4]$ | 360 | fast$^a$ | fast$^a$ |
| $[Pt\{P(n\text{-}C_{16}H_{33})_3\}_4]$ | 358 | 4.7 | 22.0 |
| $[Pt(PPh_3)_3]$ | 358 | 2.1$^b$ | |
| $[Pt(PPh_3)_4]$ | 358 | 1.9$^b$ | |

[a] Reaction was too fast to study by the present experimental technique; a slow residual reaction of methyl iodide with $[Pt\{P(n\text{-}C_8H_{17})_3\}_2(CH_3)I]$ to form $[Pt\{P(n\text{-}C_8H_{17})_3\}_2(CH_3)_2I_2]$ with a pseudo first-order rate constant of $4 \times 10^{-5}$ $s^{-1}$ was observed. [b] Only one rate constant was observed, see text.

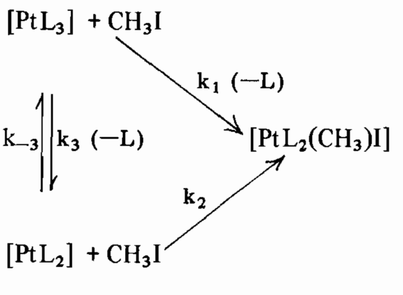
t, showed two linear regions linked by an inflection point.

## Results

It has been shown previously [4, 6–8] that $[PtL_4]$ is very extensively dissociated in solution and $[PtL_3]$ significantly so. Indeed a lower limit of >10 mol $l^{-1}$ has been reported for $K_D$ [8]. Accordingly in the aged solutions used in the present work the

$$[Pt(PPh_3)_4] \overset{K_D}{\rightleftharpoons} [Pt(PPh_3)_3] + PPh_3 \qquad (2)$$

concentration of $[PtL_4]$ will be effectively zero so that the reaction being studied is the oxidative addition of methyl iodide to $[PtL_3]$ and $[PtL_2]$ (Scheme). It would be expected from previous work



*Scheme*

that the oxidative addition of methyl iodide to the 14-electron $[PtL_2]$ complex would be much faster than to the 16-electron $[PtL_3]$ complex [6, 9]. If in addition the rate of dissociation of $[PtL_3]$, $k_3$, is slow relative to $k_2$ then a point of inflection in the plot of $2.303\log(A_\infty - A_t)$ against time would be expected. The initial rapid rate of reaction would correspond largely to the consumption of the $[PtL_2]$ initially present whilst the slower reaction would correspond to the reaction of methyl iodide with $[PtL_3]$ as well as with the $[PtL_2]$ being slowly formed from $[PtL_3]$.

When the situation in which $k_2 > k_1 > k_3$ (see Scheme) arises, the reaction may be considered as two parallel first-order reactions producing a common product (reactions 3 and 4). When, as in the present work, the formation of C is monitored

$$A \xrightarrow{k_1} C \qquad (3)$$

$$B \xrightarrow{k_2} C \qquad (4)$$

the calculation of $k_1$ and $k_2$ is not trivial. The rate equations

$$\frac{-d[A]}{dt} = k_1[A] \qquad (5)$$

$$\frac{-d[B]}{dt} = k_2[B] \qquad (6)$$

integrate to yield

$$[A] = [A_o]e^{-k_1t} \qquad (7)$$

$$[B] = [B_o]e^{-k_2t} \qquad (8)$$

where $[A_o]$ and $[B_o]$ are the initial concentrations of A and B. But

$$[C] = [A_o] - [A] + [B_o] - [B] \qquad (9)$$

and if it is assumed that the large excess of methyl iodide forces the reaction to go to completion, then

$$[C_\infty] = [A_o] + [B_o] \qquad (10)$$

where $[C_\infty]$ is the final concentration of C, whence

$$[C] = [C_\infty] - [A_o]e^{-k_1t} - [B_o]e^{-k_2t} \qquad (11)$$

and

$$\log([C_\infty] - [C]) = \log([A_o]e^{-k_1t} + [B_o]e^{-k_2t}) \qquad (12)$$

If only one reactant, A or B, were present or if $k_1$ and $k_2$ were of similar value, then a plot of log $([C_\infty] - [C])$ against time would be linear. However if both reactants are present and if $k_1 \neq k_2$ then such a plot will, in general, be a curve [10]. If one species, B, is more reactive than the other (A), then when the more reactive species has disappeared,

$$\log[A] = \log([C_\infty] - [C]) = \log[A_o] - \frac{k_1t}{2.303} \qquad (13)$$

from which $[A_o]$ and $k_1$ may be evaluated from the intercept and slope respectively of the plot of log $([C_\infty] - [C])$ against time. Once $k_1$ is known $k_2$ may be obtained from the early part of the plot obtained using equation 12. In this way the rate constants $k_1$ and $k_2$ in Table I were obtained. With $[Pt\{P(n\text{-}C_8H_{17})_3\}_4]$ the rate of the initial reaction with methyl iodide was too fast for either $k_2$ or $k_1$ to be determined by the present technique. A slow residual reaction due to oxidative addition of methyl iodide to $[Pt\{P(n\text{-}C_8H_{17})_3\}_2(CH_3)I]$ was observed with a pseudo first-order rate constant of $4 \times 10^{-5}$ $s^{-1}$.

When the tertiary phosphine was triphenylphosphine two significant differences were observed as compared to the situations with the other phosphines. Firstly an induction period was observed and secondly the plot of $\log([C_\infty] - [C])$ against time showed no point of inflection. The induction period is interesting. Previously [4] we found that when $[PtL_4]$ complexes were dissolved in benzene the absorbances at 330 and 360 nm decreased steadily with time as soon as the solutions had been made up for all the phosphines except triphenylphosphine. For triphenylphosphine an induction period preceded the increase in absorbance with time that arose from dissociation of triphenylphosphine ligands. The fact that an induction period precedes both phosphine dissociation and oxidative addition of methyl iodide to $[Pt(PPh_3)_n]$ suggests that some transitional species must be formed through which the reaction takes place. If a similar species were formed from both $[Pt(PPh_3)_3]$ and $[Pt(PPh_3)_2]$ then the $k_1$ and $k_2$ rates in the scheme would be very similar giving rise to the observed linear plot. Alternatively it is conceivable that the reaction of methyl iodide with triphenylphosphine platinum(0) complexes takes place by an entirely different mechanism to that of the other tertiary phosphine platinum(0) complexes.

In deriving the results in Table I we have neglected the following points:

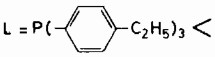
(i) Reaction of the tertiary phosphine with methyl iodide has been ignored because it takes place at a rate two orders of magnitude slower than the present reactions [6].

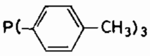
(ii) The $k_2$ rate constant in Table I is a composite rate constant involving both $k_2$ and $k_3$ in the Scheme. However since $k_3$ values are two orders of magnitude lower than $k_2$ the contribution of $k_3$ will be negligible [4].

(iii) Further reaction of $[PtL_2(CH_3)I]$ with methyl iodide to form $[PtL_2(CH_3)_2I_2]$ is very slow for all tertiary phosphines except $P(n\text{-}C_8H_{17})_3$ under the present conditions; no significant absorbance change occurs during the timescale of the present experiments. Accordingly this reaction may be ignored except when $L = P(n\text{-}C_8H_{17})_3$ when it has a pseudo first-order rate constant of $5 \times 10^{-5}$ $s^{-1}$.

## Discussion

The rate of oxidative addition of methyl iodide to $[PtL_2]$ varied with the nature of L in the order



$<$ 

$< P(n\text{-}C_{16}H_{33})_3 <$

$P(n\text{-}C_8H_{17})_3$. The order triarylphosphine < trialkylphosphine reflects an increase in the basicity of the tertiary phosphine ligand which promotes nucleophilic attack by platinum on the carbon atom of methyl iodide. Within the trialkyl- and triarylphosphine series an increase in alkyl chain length decreases the rate of oxidative addition. This is possibly steric in origin although the steric bulk of $P(C_6H_4Et\text{-}p)_3$ would not be expected to be significantly greater than that of $P(C_6H_4Me\text{-}p)_3$; the observed result may therefore arise from specific solvation effects. The rate of oxidative addition of methyl iodide to $[PtL_3]$ followed a similar trend to that observed for $[PtL_2]$.

Although the interpretation of the single rate constant observed with triphenylphosphineplatinum(0) complexes is open to more than one explanation (see above), it is significant that the rate constants derived for $[Pt(PPh_3)_3]$ and $[Pt(PPh_3)_4]$ are similar although smaller than those observed with the other triaryl phosphines.

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