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# ALKANE SOLUBLE TRANSITION METAL COMPLEXES

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RMCS Technical Report D/R/2

| Accession For | |
|---|---|
| NTIS GRA&I | ☑ |
| DTIC TAB | ☐ |
| Unannounced | ☐ |
| Justification | |
| By | |
| Distribution/ | |
| Availability Codes | |
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This report includes the 3rd semi-annual report covering the period

April 7th 1983 to October 6th 1983 as well as the final report covering the

complete period   April 15th 1979   to October 6th 1983.  The research

reported in this document has been made possible through the support and

sponsorship of the US Government through its European Research Office.  This

report is intended only for the internal management use of the Grantee and

the US Government.

# CONTENTS

# Chapter 1
## Introduction

The direct use of alkanes as starting materials for the synthesis of a wide range of petrochemicals is a major goal in Chemistry.[1] Alkanes are by their very nature unreactive and thus routes for the activation of alkanes are being actively sought[2-4]. One promising route is the use of transition metal complexes to effect this activation. However many of the complexes investigated have been insoluble in alkanes with the result that a suitable solvent medium has had to be used. Of necessity the solvent used is potentially more susceptible to activation than the desired alkane. Accordingly we have adopted a rather different approach in that we have synthesised two series of long chain tertiary phosphine and tertiary phosphine oxide ligands :-

$R_3P$

$(R'\!\!-\!\!\langle\bigcirc\rangle\!\!-)_3P$

$R_3PO$

$(R'\!\!-\!\!\langle\bigcirc\rangle\!\!-)_3PO$
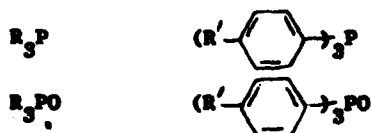
R groups are straight chain alkyl groups with chain lengths in the range $C_{10}$ to $C_{20}$; $R'$ groups are also straight chain alkyl groups in the range $C_3$ to $C_8$. As expected, these ligands confer high alkane solubility to their transition metal complexes.

A range of platinum, palladium and rhodium complexes containing these long alkyl chain tertiary phosphines have been prepared and characterised. Particular interest was focussed initially on the ability of these complexes to undergo oxidative-addition since this is believed to be a key step in the activation of alkanes. During the course of this work it was discovered that not only were the rhodium(I) complexes $[RhCl(CO)(PR_3)_2]$ very effective at promoting the oxidative-addition of alkanes, but also that this might provide a valuable approach to the degradation of mustard.

The unique extreme solubility of the transition metal complexes of long alkyl chain tertiary phosphines leads to some interesting possibilities in using these complexes to catalyse organic syntheses. This has been investigated by examining the hydroformylation of 1-hexene in the presence of $[RhCl(CO)(PR_3)_2]$ where the presence of para-alkyl substituents in the phenyl rings of triphenylphosphine was

1.

found to enhance the ratio of normal: branched aldehyde formed.    A second catalytic

system that has been studied in detail is the selective reduction of the di-  and

tri-olefins methyl linoleate and methyl linolenate to the corresponding mono-olefins

in the presence of tin(II) chloride and $\left[MCl_2(PR_3)_2\right]$ where M = Pd and Pt.  The

presence of para-alkyl substituents on the phenyl rings of triphenylphosphine

increases the activity of the platinum(II) complexes.  The activity of the

platinum(II) complexes is further enhanced by omitting the solvent that is normally

used, and relying instead on the solubility of the platinum(II) complex in the

poly-olefin substrate.

Chapters 2 - 5 of this report are based on the papers previously published in

the open literature together with papers currently submitted, whilst chapters 6 and

7 report work carried out in the last three months of the grant.  Chapter 8 provides

an overall summary.

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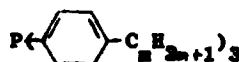    C. Kemball) 1977, 335.

# Chapter 2

## The Preparation and Characterisation of Long Alkyl Chain
## Tertiary Phosphines

The preparation and characterisation of the two series of long alkyl chain
tertiary phosphines, 1 and 2, are described in two papers[1,2]. Since the

$$P(C_nH_{2n+1})_3 \qquad\qquad P(\!\!-\!\!\langle\phantom{x}\rangle\!\!-\!\!C_nH_{2n+1})_3$$

n=10-19             n = 2-9
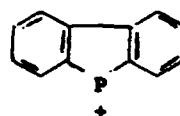
1             2          3

phosphines 1 and 2 are air sensitive low melting waxy solids, it was convenient

to oxidise them to the more stable, more crystalline tertiary phosphine oxides,

$R_3PO$, whose preparations and characterisations are also described. Mass

spectrometry proved to be a very valuable technique for characterising both

the tertiary phosphines and tertiary phosphine oxides. In the course of this it

was found that the aryl phosphines, 2, all gave $[M]^+$ as the base peak except for

$PPh_3$ itself which gives 3 as the base peak. For the oxides $[M-H]^+$ gives the base

peak for all but one phosphine. This is described in reference 3. References

1, 2 and 3 are reproduced as the remaining pages of this chapter.

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# The Preparation and Properties of Tertiary Phosphines and Tertiary Phosphine Oxides with Long Alkyl Chains

By Stephen Franks, Frank R. Hartley,* and David J. A. McCaffray, Department of Chemistry and Metallurgy, The Royal Military College of Science, Shrivenham, Swindon, Wiltshire SN6 8LA

A series of tertiary phosphines and tertiary phosphine oxides with straight-chain alkyl groups of between ten and nineteen carbon atoms have been prepared. The tertiary phosphines are waxy, very air-sensitive solids, whereas the tertiary phosphine oxides are more crystalline, are stable in air, and do not show the deliquescence associated with the lower members of the series with alkyl chains containing between one and seven carbon atoms. The compounds were characterised by microanalysis, i.r., ¹H, and ³¹P n.m.r. spectra, and mass spectrometry. The trialkylphosphines were found to form readily complexes [ML$_2$Cl$_2$] with palladium(II) and platinum(II) and the trialkylphosphine oxides formed complexes with elements, such as nickel(II) and copper(II), in the first transition series.

TERTIARY phosphines are very good ligands for transition metals, and tertiary phosphine oxides for lanthanide and actinide elements. It was therefore of interest to prepare complexes of these ligands with long straight-chain alkyl groups, P(n-C$_n$H$_{2n+1}$)$_3$ and PO(n-C$_n$H$_{2n+1}$)$_3$, since such complexes would be expected to be freely soluble in hydrocarbon solvents which is desirable for many applications, including the preparation of homogeneous catalysts for the activation of alkanes and the preparation of new reagents for the solvent-extraction of metals. Accordingly we report here the preparation and characterisation of the complete series of tertiary phosphines and tertiary phosphine oxides with straight-chain alkyl groups comprising between ten and nineteen carbon atoms.

Prior to this work the only compounds which are reported here that have previously been described are P(n-C$_{10}$H$_{21}$)$_3$,[1,2] P(n-C$_{12}$H$_{25}$)$_3$,[3] P(n-C$_{14}$H$_{29}$)$_3$,[4] P-(n-C$_{18}$H$_{37}$)$_3$,[1] and PO(n-C$_{12}$H$_{25}$)$_3$[3] and none of these have been fully characterised.

## EXPERIMENTAL

*Preparation of the Trialkylphosphines.*—The trialkylphosphines are extremely sensitive to oxygen. Accordingly all steps in their preparation and characterisation were effected under an atmosphere of nitrogen. The trialkylphosphines were prepared from the corresponding alkyl bromides by reacting the Grignard reagent with phosphorus trichloride in tetrahydrofuran solution. The solutions were hydrolysed with a deoxygenated saturated aqueous solution of ammonium chloride.[5] The organic layer was syringed off into a Schlenk tube and dried over anhydrous sodium sulphate. The tetrahydrofuran was distilled off *in vacuo*, leaving the crude phosphine which was dried *in vacuo* at 80 °C for 24 h, followed by recrystallisation from chloroform and ethanol. The lower members were found to be extremely difficult to recrystallise due to their waxy states, but the higher members were easier to handle and were obtained in higher purity. Appearances, yields, and m.p.s are recorded in Table 1. All the alkyl bromides were available commercially except n-undecyl bromide and n-heptadecyl bromide which were prepared from the corresponding alcohols by the action of hydrobromic acid.[6]

*Preparation of the Trialkylphosphine Oxides.*—The trialkylphosphines were treated under nitrogen with a slight excess of hydrogen peroxide (6% w/v),[5] calculated on the basis of the reaction PR$_3$ + H$_2$O$_2 \rightarrow$ POR$_3$ + H$_2$O. The trialkylphosphine oxides were extracted with chloroform, dried over anhydrous sodium sulphate, precipitated by the addition of ethanol, and recrystallised from acetone. Appearances, yields, m.p.s, and microanalytical data are given in Table 2.

*Characterisation of the Trialkylphosphines.*—The waxy state of the lower trialkylphosphines, coupled with the extreme sensitivity to oxygen, rendered purification and characterisation very difficult. Good microanalytical data were only obtained for the higher members of the series (see Table 1). Accordingly, complete characterisation

### TABLE 1
Physical and analytical data for the trialkylphosphines

| Phosphine | Colour | Appearance | Yield [a] | M.p. (°C) | ¹H N.m.r.[b] chemical shifts | | $M^+$ Found (Calc.) | Analysis Found (Calc.) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | C | H |
| P(n-C$_{10}$H$_{21}$)$_3$ | Cream | Soft wax | 70% | 37—40 [c,d] | 0.86 | 1.27 | 454 (454) | | |
| P(n-C$_{11}$H$_{23}$)$_3$ | Cream | Soft wax | 69% | 40—41 | 0.88 | 1.27 | | | |
| P(n-C$_{12}$H$_{25}$)$_3$ | Cream | Soft wax | 57% | 44—45 [d] | 0.88 | 1.27 | 538 (538) | | |
| P(n-C$_{13}$H$_{27}$)$_3$ | White | Hard wax | 61% | 45—47 | 0.88 | 1.27 | 580 (580) | | |
| P(n-C$_{14}$H$_{29}$)$_3$ | White | Hard wax | 76% | 49—52 [d] | 0.88 | 1.27 | 622 (622) | | |
| P(n-C$_{15}$H$_{31}$)$_3$ | White | Hard wax | 79% | 49—53 | 0.88 | 1.27 | 664 (664) | | |
| P(n-C$_{16}$H$_{33}$)$_3$ | White | Crystalline solid | 76% | 59—61 [c,d] | 0.88 | 1.27 | 706 (706) | 79.9 (81.5) | 13.7 (14.1) |
| P(n-C$_{17}$H$_{35}$)$_3$ | White | Crystalline solid | 75% | 60—61 | 0.88 | 1.27 | 748 (748) | 81.1 (81.7) | 14.0 (14.1) |
| P(n-C$_{18}$H$_{37}$)$_3$ | White | Crystalline solid | 72% | 62—64 | 0.88 | 1.27 | 790 (790) | 81.0 (81.9) | 14.4 (14.1) |
| P(n-C$_{19}$H$_{39}$)$_3$ | White | Crystalline solid | 68% | 60—62 | 0.88 | 1.27 | 832 (832) | 81.8 (82.1) | 14.1 (14.2) |

[a] Yield based on PCl$_3$. [b] Recorded in CDCl$_3$ solution; δ in p.p.m. from SiMe$_4$. [c] See ref. 1. [d] See ref. 6.

## TABLE 2

### Physical and analytical data for the trialkylphosphine oxides

| Phosphine oxide | Colour | Appearance | Yield (%)[a] | M.p. (°C) | N.m.r. chemical shifts ¹H[b] | | ³¹P[c] | M⁺ Found (Calc.) | Analysis Found (Calc.) C | H |
|---|---|---|---|---|---|---|---|---|---|---|
| PO(n-C₁₀H₂₁)₃ | White | Waxy solid | 85 | 37 | 0.88 | 1.27 | −42.64 | 470 (470) | 76.1 (76.5) | 13.2 (13.5) |
| PO(n-C₁₁H₂₃)₃ | White | Waxy solid | 80 | 40—41 | 0.88 | 1.27 | −45.25 | 512 (512) | 76.6 (77.2) | 13.4 (13.6) |
| PO(n-C₁₂H₂₅)₃ | White | Crystalline solid | 78 | 50—52[d] | 0.88 | 1.27 | −44.41 | 554 (554) | 76.2 (77.0) | 13.2 (13.6) |
| PO(n-C₁₃H₂₇)₃ | White | Crystalline solid | 80 | 59—60 | 0.88 | 1.27 | −44.45 | 596 (596) | 77.2 (76.5) | 13.2 (13.7) |
| PO(n-C₁₄H₂₉)₃ | White | Crystalline solid | 81 | 57—58 | 0.88 | 1.27 | −43.94 | 638 (638) | 77.1 (76.9) | 13.6 (13.7) |
| PO(n-C₁₅H₃₁)₃ | White | Crystalline solid | 78 | 60—61 | 0.88 | 1.27 | −46.50 | 680 (680) | 79.1 (79.3) | 13.7 (13.8) |
| PO(n-C₁₆H₃₃)₃ | White | Crystalline solid | 79 | 60—61 | 0.88 | 1.27 | −46.06 | 722 (722) | 79.3 (79.7) | 13.7 (13.8) |
| PO(n-C₁₇H₃₅)₃ | White | Crystalline solid | 86 | 74—75 | 0.88 | 1.27 | −42.64 | 764 (764) | 79.6 (80.0) | 13.7 (13.8) |
| PO(n-C₁₈H₃₇)₃ | White | Crystalline solid | 94 | 73—75 | 0.88 | 1.27 | −44.43 | 806 (806) | 80.1 (80.3) | 13.6 (13.9) |
| PO(n-C₁₉H₃₉)₃ | White | Crystalline solid | 93 | 69—71 | 0.88 | 1.27 | −46.01 | 848 (848) | 81.1 (80.6) | 14.0 (13.9) |

[a] Yield based on trialkylphosphine. [b] Recorded in CDCl₃ solution containing SiMe₄ as internal standard. [c] Recorded in CDCl₃ solution using TMP as external standard. [d] See ref. 3.

depended on a combination of physical techniques together with the characterisation, including microanalysis, of the corresponding trialkylphosphine oxide.

The i.r. spectra (4 000—900 cm⁻¹), obtained without the need for a mulling agent, showed the absence of bands attributable to P=O or P—O stretching modes indicating the absence of significant amounts of oxidation products. Strong absorption bands at 3 000—2 900 cm⁻¹ (C–H stretching modes in CH₂), 2 870—2 810 cm⁻¹ (C–H stretching modes in CH₃), 1 490—1 400 and 1 385—1 360 cm⁻¹ (C–H deformation modes), and 730—710 cm⁻¹ (CH₂ rocking modes), which are all consistent with the presence of trialkylphosphines,[7] were observed. No bands assignable to P–C stretching modes were observed. Such bands are expected[7,8] between 750 and 650 cm⁻¹ and are either too weak to be observed or are obscured by the strong CH₂ rocking modes.

The ¹H n.m.r. spectra showed multiplets at δ 1.27 and a triplet at δ 0.88 (downfield from SiMe₄) assigned to the methylene and methyl groups, respectively, of the long alkyl chains. Integrated intensities of these two peaks were consistent with the expected number of protons per alkyl chain. The absence of any further proton signals provided evidence of purity.

The mass spectra all showed the expected molecular ion. The fragmentation patterns were characteristic of the trialkylphosphines; no unexpected peaks were observed, nor were peaks containing oxygen, therefore the mass spectra provided further evidence of purity.

Attempts to use gas–liquid chromatography to provide an estimate of purity[9,10] were unsuccessful because decomposition occurred below the temperature necessary for elution. Thus using a 3 ft column of 10% SE 30 on 80—100 mesh Chromosorb WHP, a temperature programme from 160—300 °C at 8 °C min⁻¹, and both a flame-ionisation and a phosphorus detector, a number of peaks were obtained, at relatively short retention times, that did not contain phosphorus, together with a peak due to a phosphorus-containing compound after a relatively long interval of time; for P(C₁₀H₂₁)₃ this latter peak was observed after 17 min corresponding to a column temperature of 300 °C.

*Characterisation of the Trialkylphosphine Oxides.*—Good microanalytical data were obtained for all members of the series. The i.r. spectra, recorded in Nujol and hexachlorobutadiene mulls, showed a strong absorption band centred at about 1 148 cm⁻¹ which was assigned to the P=O stretching vibration;[7,8] in other respects the spectra resembled those of the trialkylphosphines. The ¹H n.m.r. spectra were essentially identical to those of the trialkylphosphines in showing a multiplet at δ 1.27 due to the methylene protons and a triplet at δ 0.88 due to the terminal methyl protons. The absence of any further resonances, together with the fact that the relative integrated intensities of the two peaks were consistent with the anticipated formulae, was taken as an indication of purity. The phosphorus-31 n.m.r. spectra in CDCl₃ showed a single resonance in the range 43—46 p.p.m. downfield from trimethyl phosphate, which is consistent with the values reported previously for other members of the series.[6,11,12] In addition the single phosphorus resonance provided further evidence of purity.

The mass spectra all showed the expected molecular ion and the fragmentation patterns were characteristic of trialkylphosphine oxides, with no unexpected peaks.

*Measurements.*—Microanalytical data were determined in the Chemistry Department at University College, London. Mass spectra were recorded on a Hitachi–Perkin-Elmer RMU-7M mass spectrometer using a VG 2035 data system at the Materials Quality Assurance Directorate, Woolwich, London. Hydrogen-1 n.m.r. spectra were recorded in CDCl₃ solution containing tetramethylsilane as an internal standard, using a Perkin-Elmer R32 spectrometer. Phosphorus-31 n.m.r. spectra were recorded in CDCl₃ solution using a Brucker WH 90 spectrometer (10-mm phosphorus probe, 36.4 MHz). All chemical shifts were measured relative to trimethyl phosphate (TMP) as external standard.

I.r. spectra were recorded in the range 4 000—250 cm⁻¹ and 4 000—200 cm⁻¹ using Perkin-Elmer spectrometers, models 457 and 577, respectively. Solids were run as mulls, using Nujol or hexachlorobutadiene as the mulling agent, and liquids as thin films using potassium bromide plates for the range 4 000—400 cm⁻¹ and CsI or polythene plates below 450 cm⁻¹. All spectra were calibrated with a

standard polystyrene film. Gas-liquid chromatographic data were recorded using a Packard 419 gas-liquid chromatograph, equipped with a flame-photometric detector, a phosphorus probe, and a Curie point pyrolyser, for rapid injection of sample.

## RESULTS

The trialkylphosphines were all low-melting waxy solids that were extremely soluble in hexane and chlorinated solvents such as dichloromethane, chloroform, carbon tetrachloride, and 1,2-dichloroethane, and moderately soluble in tetrahydrofuran, benzene, and other aromatic solvents, hot alcohols such as methanol and ethanol, and warm acetone. They are, however, insoluble in cold methanol, ethanol, and acetone. These solubility characteristics are very similar to those of the alkyl bromides from which they are prepared, as well as of any decomposition products including the corresponding trialkylphosphine oxides.

ion peak; (ii) peaks due to the loss of olefins from the parent ion [two olefins are lost, $C_nH_{2n}$ through reaction (1) and $C_{n-1}H_{2n-2}$ through (2); the ion formed by reaction (1) is

$$P(C_nH_{2n+1})_3 \longrightarrow PH(C_nH_{2n+1})_2 + C_nH_{2n} \qquad (1)$$

$$PH(C_nH_{2n+1})_2 \longrightarrow PH(2e)(C_nH_{2n+1}) + C_{n-1}H_{2n-2} \qquad (2)$$

dominant in most of the spectra]; (iii) ions at $m/e$ = and 76 due to $PHMe_2$ and $PMe_3$, respectively; and (iv) ions such as $CH_3^+$, $C_2H_5^+$, $C_3H_7^+$, $C_4H_9^+$, $C_5H_{11}^+$, etc., and $C_2H_3^+$, $C_3H_5^+$, $C_4H_7^+$, $C_5H_9^+$, etc., with slightly less of each alkenyl ion than of the corresponding alkyl ion. These ions are typical of those observed in the mass spectra of n-alkanes where they reach a maximum at around $C_3H_7^+$ and $C_4H_9^+$ and thereafter tail off rapidly in intensity,[17] as observed here. With branched-chain alkanes a very different pattern is observed. The mass spectra are thus consistent with the presence of
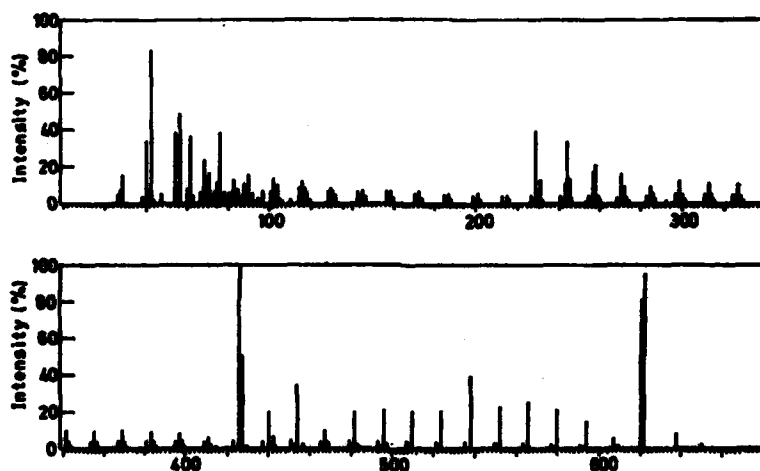


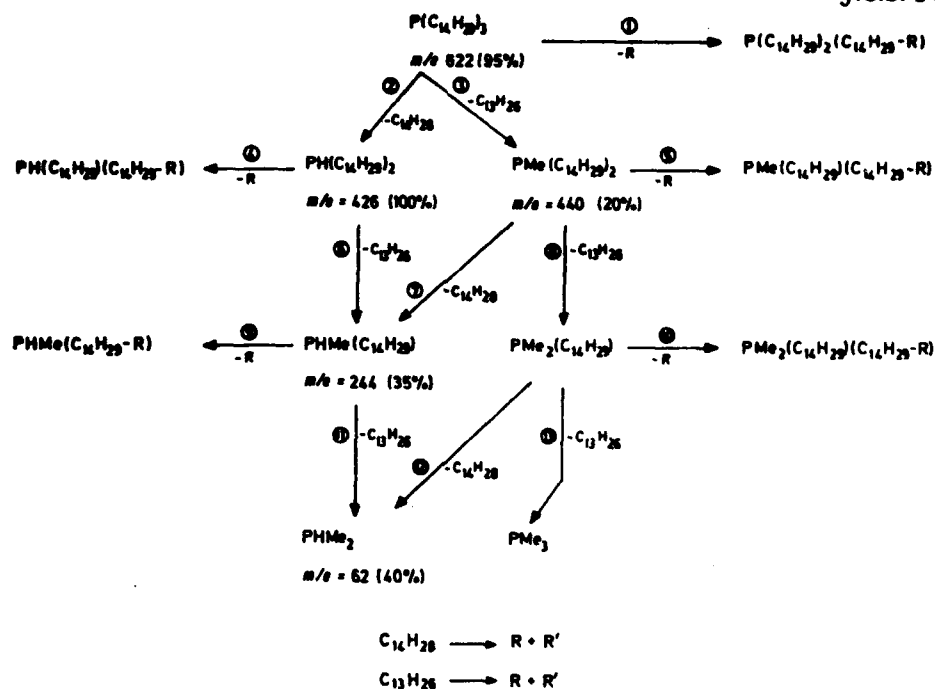FIGURE 1 Mass spectrum of $P(C_{14}H_{29})_3$

Accordingly purification is difficult and necessitates multiple fractional recrystallisation. The trialkylphosphines are very sensitive to air, which results in the formation of a large number of oxidation products. Thus the $^{31}P$ n.m.r. spectrum of $P(C_{14}H_{29})_3$ after standing in chloroform solution in air for several hours, showed no absorption due to tris(tetradecyl)phosphine (ca. 30 p.p.m. upfield from TMP), but bands downfield from TMP at −45.68 (5), −42.90 (1.5), −29.90 (2), −27.45 (1), and −27.00 p.p.m. (2.5) where the figures in parentheses are the relative intensities. These bands are consistent with the formation of a series of oxidation products, $P(OR)_{3-n}R_n$ ($n$ = 1 or 2) and $P(O)(OR)_{3-n}R_n$ ($n$ = 0, 1, 2, or 3) as observed previously for the air oxidation of tri-n-butylphosphine.[18,19]

The mass spectra of the long straight-chain trialkylphosphines were similar in appearance to the mass spectrum of the second member of the series, $PEt_3$.[20] However, since the spectra of the higher members of the series do not appear to have been reported,[20] and since there are some differences as compared with $PEt_3$, it is opportune to report the spectra in some detail. A typical mass spectrum is shown in Figure 1. The spectra show: (i) a strong parent-

linear alkyl tertiary phosphines. The fragments observed can be explained by the fragmentation pattern given in the Scheme. It is apparent from the relative abundances of the products that the principal fragmentation route for $P(C_{14}H_{29})_3$ involves P−C bond cleavage with loss of the olefin $C_{14}H_{28}$ and formation of $PH(C_{14}H_{29})_2$. This is consistent with the relative energies of the P−C and C−C bonds of ca. 276 and ca. 348 kJ mol$^{-1}$, respectively.[4,12,13]

The trialkylphosphine oxides are stable in air. They are solids that are more crystalline than the corresponding phosphines, and are thus easier to handle and purify. The phosphine oxides are very soluble in chlorinated solvents and saturated hydrocarbons, such as hexane, and moderately soluble in aromatic solvents, tetrahydrofuran, warm alcohols such as methanol and ethanol, and warm acetone. They are however insoluble in cold methanol, ethanol, and acetone. These solubility characteristics are very similar to those of the trialkylphosphines. In contrast to the lower members of the series[4,20] [i.e. those below $PO(C_9H_{19})_3$] the long-chain trialkylphosphine oxides were not deliquescent at all.

The mass spectra of the long straight-chain trialkyl-

$P(C_{14}H_{29})_3$

$m/e\ 622\ (95\%)$

① → $P(C_{14}H_{29})_2(C_{14}H_{29}\text{-R})$
$-R$

② $-C_{14}H_{28}$

③ $-C_{13}H_{26}$

$PH(C_{14}H_{29})(C_{14}H_{29}\text{-R})$ ← ④ ← $PH(C_{14}H_{29})_2$     $PMe(C_{14}H_{29})_2$ → ⑤ → $PMe(C_{14}H_{29})(C_{14}H_{29}\text{-R})$
$-R$      $m/e = 426\ (100\%)$     $m/e = 440\ (20\%)$    $-R$

⑥ $-C_{13}H_{26}$     ⑧ $-C_{13}H_{26}$

⑦ $-C_{14}H_{28}$

$PHMe(C_{14}H_{29}\text{-R})$ ← ⑨ ← $PHMe(C_{14}H_{29})$     $PMe_2(C_{14}H_{29})$ → → $PMe_2(C_{14}H_{29})(C_{14}H_{29}\text{-R})$
$-R$      $m/e = 254\ (35\%)$         $-R$

⑩ $-C_{13}H_{26}$     ⑪ $-C_{13}H_{26}$

⑫ $-C_{14}H_{28}$

$PHMe_2$         $PMe_3$

$m/e = 62\ (40\%)$

$C_{14}H_{28} \longrightarrow R + R'$

$C_{13}H_{26} \longrightarrow R + R'$

SCHEME   Fragmentation pattern of $P(C_{14}H_{29})_3$; the percentage abundances of the uniquely determined species are shown in parentheses; $R = C_nH_{2n+1}$, $R' = C_nH_{2n-1}$

phosphine oxides are very similar in appearance to those of the corresponding phosphines, with the difference that all the ions containing phosphorus are sixteen mass units heavier due to the presence of an oxygen atom. This is consistent with the greater bond energy of the P=O than P–C bond, ca. 523 kJ mol⁻¹ (ref. 21) and ca. 276 kJ mol⁻¹ (refs. 5 and 18) respectively. A typical mass spectrum is shown in Figure 2.

The trialkylphosphines (L) were found to displace readily ligands such as cyclo-octadiene (COD) from complexes of palladium(II) and platinum(II) to give compounds of general formula [ML₂Cl₂] corresponding to those formed by lower

$$[M^{II}(COD)Cl_2] + 2L \longrightarrow [M^{II}L_2Cl_2] \qquad (3)$$
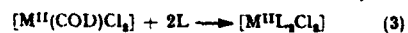
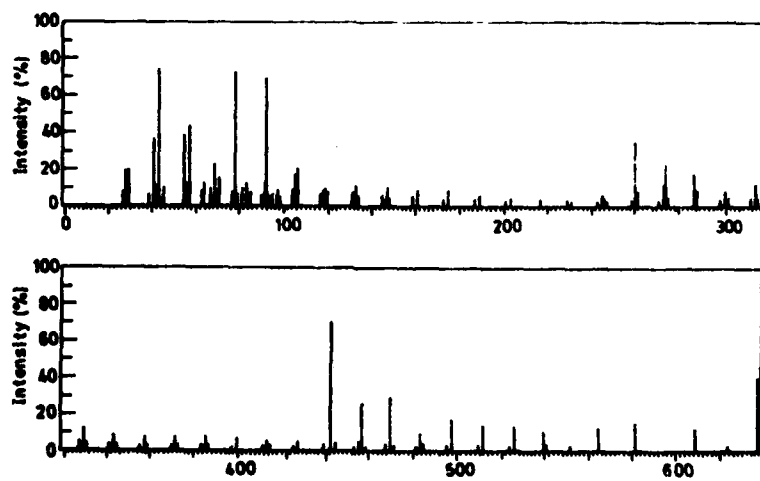members of the series.[21] The long-chain trialkylphosphine oxides (L') complex with first-row transition metal elements



FIGURE 2   Mass spectrum of $PO(C_{14}H_{29})_3$

such as nickel(II) and copper(II), in a similar manner to shorter-chain trialkylphosphine oxides.[16] The characteristic colour of the nickel–phosphine oxide complexes may be used for the detection of tertiary phosphine oxides.[20,22]
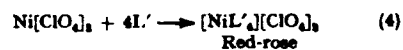
$$Ni[ClO_4]_2 + 4I.' \longrightarrow [NiL'_4][ClO_4]_2 \quad (4)$$
$$\text{Red-rose}$$

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8.

# Preparation and Properties of Tertiary p-Alkylarylphosphines containing Straight-chain Alkyl Groups

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A series of tris(p-alkylaryl)phosphines with straight chain alkyl groups, $P(p\text{-}C_6H_4\text{-}C_nH_{2n+1})_3$ where $n = 2—9$, have been prepared by reaction of phosphorus trichloride with the Grignard reagent derived from the corresponding p-bromoalkylbenzene. When $n = 2$ and 3 the phosphines are crystalline solids, but for $n > 3$ they are viscous oils up to $n = 9$, which is a waxy solid. The phosphines have been characterised by microanalysis, and i.r., $^1H$ and $^{31}P$ n.m.r., and mass spectrometry. The p-substituted-arylphosphines are more sensitive than triphenylphosphine to air; aerial oxidation converts them exclusively into the corresponding phosphine oxide, in contrast to trialkyl-phosphines which are oxidised to a complex mixture of products. The complexing ability of the new phosphines $(PAr_3)$ is demonstrated by their ready displacement of 1,5-cyclo-octadiene (cod) from $[M(cod)Cl_2]$ (M = Pd and Pt) to yield trans-$[Pd(PAr_3)_2Cl_2]$ and cis-$[Pt(PAr_3)_2Cl_2]$, respectively.

TERTIARY phosphines are very good ligands for transition metals, and tertiary phosphine oxides for lanthanide and actinide elements. In a previous paper [1] we reported the preparation of such compounds with long straight-chain alkyl groups from which it is possible to prepare complexes that are freely soluble in hydrocarbon solvents, a property that is desirable for many applications including the preparation of homogeneous catalysts for the activation of alkanes and for the hydrogenation, isomerisation, hydroformylation, and hydrosilylation of

sensitive to oxygen both in solution and in the solid state The sensitivity depended upon the length of the alkyl chain attached to the phenyl rings. Therefore, all steps in their preparation and characterisation were effected under a nitrogen atmosphere.

The tris(p-alkylaryl)phosphines were prepared by treating the Grignard reagent of the corresponding p-bromo-alkylbenzenes with phosphorus trichloride in tetrahydro-furan solution. The lower members of the series were found to be crystalline solids which were purified by re-crystallisation. However, the higher members ($n > 3$) were

TABLE 1

Physical, analytical, and spectroscopic data for the triarylphosphines $P(p\text{-}C_6H_4R)_3$

| R | Colour | Appearance | Yield [a] (%) | M.p. (°C) | B.p. (°C) [b] | $^{31}P$ n.m.r. chemical shift [c] | Molecular ion M [d] | Analysis (%) Found (calc.) C | H |
|---|---|---|---|---|---|---|---|---|---|
| $C_2H_5$ | White | crystalline solid | 83 | 99 | | +10.6 | 346 | 82.5 (83.2) | 7.9 (7.9) |
| $C_3H_7$ | White | crystalline solid | 71 | 45—48 | | +10.5 | 388 | 82.9 (83.5) | 8.5 (8.6) |
| $C_4H_9$ | Yellow | viscous oil | 67 | | 212 (0.005) | +10.6 | | 83.7 (83.7) | 9.1 (9.1) |
| $C_5H_{11}$ | Yellow | viscous oil | 69 | | 296 (0.35) | +10.6 | 472 | 83.2 (83.9) | 9.3 (9.6) [d] |
| $C_6H_{13}$ | Yellow | viscous oil | 66 | | Not distilled | | | | |
| $C_7H_{15}$ | Yellow | viscous oil | 58 | | 280 (0.005) [e] | +10.8 | 556 | | |
| $C_8H_{17}$ | Yellow | viscous oil | 63 | | Not distilled | +10.7 | | | |
| $C_9H_{19}$ | Yellow-green | viscous waxy solid | 81 | | Not distilled | +10.8 | 640 | | |

[a] Yield based on $PCl_3$. [b] Boiling point under reduced pressure, shown in mmHg in parentheses. [c] Measured relative to trimethyl-phosphate as an external standard, which lies $-4.242$ p.p.m. down-field from 85% $H_3PO_4$ (Lady Richards, personal communication) All values refer to solutions in $CDCl_3$. [d] Phosphorus: 6.7 (found), 6.6 (calculated). [e] Resulted in some decomposition of phosphine

alkenes, as well as for the solvent-extraction of metals. In a number of these applications there are known to be significant differences between the properties of the complexes of aliphatic and aromatic tertiary phosphines. For example [Rh(PR₃)₃Cl] complexes are much less effective as catalysts for the hydrogenation of olefins when R is an alkyl group than when it is an aryl group.[2,3] Accordingly, in the present paper we describe the synthesis of a series of tris(p-alkylaryl)phosphines and their corresponding phosphine oxides, $P(p\text{-}C_nH_{2n+1}C_6H_4)_3$ and $O=P(p\text{-}C_nH_{2n+1}C_6H_4)_3$ in which $n = 2—9$, all of which are reported for the first time.

## EXPERIMENTAL

Tris(p-alkylaryl)phosphines, $P(p\text{-}C_6H_4\text{-}C_nH_{2n+1})_3$ ($n = 2—9$).—The tris(p-alkylaryl)phosphines were found to be

found to be viscous liquids or waxy solids, and these, where possible, were purified by distillation. Appearances, yields, and analytical and spectroscopic data are recorded in Table 1.

Tris(p-alkylaryl)phosphine Oxides, $O=P(p\text{-}C_6H_4\cdot C_nH_{2n+1})_3$ ($n = 2—9$).—The tris(p-alkylaryl)phosphines were treated under nitrogen with a slight excess of 6% w/v hydrogen peroxide to yield the tris(p-alkylaryl)phosphine oxides, which were either recrystallised from acetone or heated at 80 °C in vacuo for 12 h to remove any excess of solvent. Appearances, melting points, and spectroscopic data are given Table 2.

p-Bromoalkylbenzenes. $p\text{-}BrC_6H_4\text{-}C_nH_{2n+1}$ ($n = 4—9$) — The p-bromoalkylbenzenes were not commercially available and so were prepared by the action of the Grignard reagent of an alkyl bromide on p-bromobenzaldehyde to produce an alcohol which was then dehydrated and hydrogenated to

give the desired product.[4] p-Bromobenzaldehyde was treated with an excess of the alkylmagnesium halide in diethyl ether solution to yield the p-bromophenyl alcohol, which was then heated over freshly pulverized, fused potassium hydrogensulphate at 185 °C for 8 h or until the dehydration was complete. The dehydrated product was dis-

any solvent. Physical and microanalytical data are given in Table 4.

*Materials.*—Complexes [Pt(cod)Cl$_2$] [5] and [Pd(cod)Cl$_2$] [6] were prepared by standard procedures. The method of Clark was preferred for the platinum complex because it is easier and gives a whiter product. However the platinum(II)

### TABLE 2

Physical, analytical, and spectroscopic data for the triarylphosphine oxides $O=P(p\text{-}C_6H_4R)_3$

| R | Appearance | M.p. (°C) | $^{31}$P N.m.r. chemical (p.p.m.) [a] | Molecular ion $M^+$ | Analysis (%) Found (calc.) | | |
|---|---|---|---|---|---|---|---|
| | | | | | C | H | P |
| $C_3H_5$ | White crystalline solid | 148—152 | −30.7 | 362 | 79.0 (79.5) | 8.6 (8.6) | 8.6 (8.6) |
| $C_3H_7$ | White crystalline solid | 110—112 | −36.3 | 404 | 79.6 (80.2) | 8.1 (8.2) | 7.8 (7.7) |
| $C_5H_{11}$ | Yellow oil | | −36.3 | 488 | 80.6 (81.1) | 9.1 (9.3) | 5.7 (6.3) |
| $C_7H_{15}$ | Yellow oil | | −35.3 | 572 | | | |
| $C_9H_{19}$ | Yellow oil | | −36.2 | 656 | | | |

[a] Chemical shifts measured relative to trimethyl phosphate as an external standard, which lies −4.242 p.p.m. down-field from 85% $H_3PO_4$ (Lady Richards, personal communication). All values refer to solutions in $CDCl_3$.

tilled under reduced pressure to yield the p-bromoalkenyl-benzene, which was then dissolved in absolute ethanol (100 ml) and hydrogenated over Adam's catalyst (platinum oxide, $PtO_2\cdot2H_2O$). Distillation gave the p-bromoalkylbenzene in good yield. Boiling points of all intermediates, together with yields, are given in Table 3.

*p-Bromopropylbenzene.*—This may be prepared by the above route, but it is more easily prepared by the reaction of allyl bromide with the mono-Grignard reagent of 1,4-di-

complex prepared according to ref. 6 gives excellent micro-analytical data.

*Measurements.*—Microanalyses were determined in the Chemistry Departments at University College London and the University of Kent. Mass spectra were recorded on a Hitachi–Perkin-Elmer RMU-7M mass spectrometer using a VG 2035 data system at the Materials Quality Assurance Directorate, Woolwich, London. Phosphorus-31 n.m.r. spectra were recorded in $CDCl_3$ solution using a Brucker WH-

### TABLE 3

Physical data for p-bromoalkylbenzenes and precursors

| p-Bromoalkylphenyl alcohol | | p-Bromoalkenylbenzene | | | p-Bromoalkylbenzene | | | Overall yield [e] (%) |
|---|---|---|---|---|---|---|---|---|
| Formula | Yield [a] (%) | Formula | Yield [b] (%) | B.p. (°C) [c] | Formula | Yield [d] (%) | B.p. (°C) [c] | |
| | | $p\text{-}BrC_6H_4\text{-}CH_2CH=CH_2$ | 79 | 98 (0.12) | $p\text{-}BrC_6H_4C_3H_7$ | 93 | 56 (0.5) | |
| $p\text{-}BrC_6H_4CH(OH)C_2H_7$ | 86 | $p\text{-}BrC_6H_4\text{-}CH=CH\text{-}C_2H_5$ | 73 | 96 (0.2) | $p\text{-}BrC_6H_4C_4H_9$ | 96 | 66 (0.03) | 60 |
| $p\text{-}BrC_6H_4CH(OH)C_4H_9$ | 73 | $p\text{-}BrC_6H_4\text{-}CH=CH\text{-}C_3H_7$ | 70 | 105 (0.05) | $p\text{-}BrC_6H_4C_5H_{11}$ | 96 | 85 (0.1) | 49 |
| $p\text{-}BrC_6H_4CH(OH)C_5H_{11}$ | 76 | $p\text{-}BrC_6H_4\text{-}CH=CH\text{-}C_4H_9$ | 71 | 130 (0.3) | $p\text{-}BrC_6H_4C_6H_{13}$ | 94 | 86—88 (0.05) | 51 |
| $p\text{-}BrC_6H_4CH(OH)C_6H_{13}$ | 63 | $p\text{-}BrC_6H_4\text{-}CH=CH\text{-}C_5H_{11}$ | 74 | 120 (0.15) 100 (0.2) | $p\text{-}BrC_6H_4C_7H_{15}$ | 96 | 96 (0.15) 95 (0.20) | 46 |
| $p\text{-}BrC_6H_4CH(OH)C_7H_{15}$ | 71 | $p\text{-}BrC_6H_4\text{-}CH=CH\text{-}C_6H_{13}$ | 79 | 113 (0.35) | $p\text{-}BrC_6H_4C_8H_{17}$ | 86 | 104 (0.15) | 43 |
| $p\text{-}BrC_6H_4CH(OH)C_9H_{17}$ | 74 | $p\text{-}BrC_6H_4\text{-}CH=CH\text{-}C_7H_{15}$ | 83 | 138 (0.1) | $p\text{-}BrC_6H_4C_9H_{19}$ | 94 | 107 (0.2) 112 (0.35) | 58 |

[a] Yield based on p-bromobenzaldehyde. [b] Yield based on alcohol. [c] B.p. under reduced pressure, shown in mmHg in parentheses. [d] Yield based on alkenylbenzene. [e] Yield of p-bromoalkylbenzene based on p-bromobenzaldehyde.

bromobenzene, followed by hydrogenation of the resulting alkene to yield the desired product.[6]

*Compounds* [M(PAr$_3$)$_2$Cl$_2$] *where* M = Pd, Pt, Ar = p-$C_6H_4\text{-}C_nH_{2n+1}$.—All experiments were performed under a nitrogen atmosphere to prevent oxidation of the phosphine and decomposition of any intermediate complexes. Chloroform solutions of the phosphine PAr$_3$ (2 equiv.) and the cyclo-octadiene (cod) complex [M(cod)Cl$_2$] (1 equiv.) were mixed together and stirred for 4 h to yield [M(PAr$_3$)$_2$Cl$_2$]. The solutions were taken to dryness and, where possible, recrystallised from ethanol-chloroform (6 : 4). The higher members of this series could only be obtained as viscous oils. These were purified by pouring them onto a column of alumina (Brockman activity I, neutral) and eluting with chloroform-methanol (6 : 4). The solvent was removed and the complex heated at 50 °C *in vacuo* for 12 h to remove

90 spectrometer (10-mm phosphorus probe, 36.4 MHz). All $^{31}$P chemical shifts were measured relative to trimethyl phosphate as an external standard. $^1$H n.m.r. spectra were recorded in $CDCl_3$ solution containing SiMe$_4$ as an internal standard using a Perkin-Elmer R32 spectrometer.

I.r. spectra were recorded in the range 4 000—200 cm$^{-1}$ using Perkin-Elmer spectrometers, models 457 and 577. Solids were run as mulls, using Nujol or hexachlorobutadiene as the mulling agent, and liquids as thin films using potassium bromide plates for the range 4 000—400 cm$^{-1}$ and CsI plates below 400 cm$^{-1}$. All spectra were calibrated with a standard polystyrene film.

## RESULTS AND DISCUSSION

The tris(p-alkylaryl)phosphines were prepared by treating phosphorus trichloride with the Grignard reagent

derived from the corresponding $p$-bromoalkylbenzene. The $p$-bromoalkylbenzenes are not commercially available and so it was necessary to develop a satisfactory procedure for making the pure *para*-isomer in good yield. We [1] and others [7] have noted previously that, when preparing very soluble compounds of the present type, it is essential to use very pure starting materials to minimise the amount of purification needed at the end. This is because the products and their impurities have very similar properties, making separation difficult.

$p$-Halogenoalkylbenzenes have been prepared either by reaction of chlorobenzene with a terminal alkene in the presence of concentrated sulphuric acid [8] or chlorobenzene with an alkyl bromide in the presence of aluminium tribromide or finely divided aluminium.[9] However, we

the *para*-isomer in high yield. Reaction of an alkyl Grignard reagent with an arylaldehyde yields a secondary alcohol, which is then dehydrated to the alkenylbenzene and hydrogenated to the alkylbenzene.[4] The materials used in this preparation are all readily available, isomeric mixtures are not formed and the final product is therefore easily purified, by fractional distillation. The best yields are obtained when a slight excess of the Grignard reagent is used. $p$-Bromopropylbenzene can be prepared in this way but it is more easily prepared as described in the Experimental section.

After completion of this work our attention was drawn to the synthetic procedure of Manassen and Dror,[13] based upon the reaction of bromobenzene with an acyl chloride in the presence of aluminium trichloride, fol-

TABLE 4

Physical properties, spectroscopic, and analytical data for $[M\{P(C_6H_4R)_3\}_2Cl_2]$

| R | M | Colour, appearance | M.p. (°C) | $\nu$(M–Cl)/cm$^{-1}$ | $^{31}$P N.m.r. | | Analysis (%) Found (calculated) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\delta$/p.p.m.[a] | $J_{Pt-P}$/Hz | C | H | Cl | P |
| $C_2H_5$ | Pd | Yellow, crystalline solid | ca. 230 (decomp.) | 360 | −18.6 | | 65.8 (66.3) | 6.4 (6.3) | 8.3 (8.2) | 7.9 (7.1) |
| | Pt | Cream, crystalline solid | 268 (decomp.) | 295, 320 | −9.2 | 3 695 | 59.8 (60.1) | 5.7 (5.7) | 7.6 (7.4) | |
| $n$-$C_3H_7$ | Pd | Yellow, crystalline solid | 166 (decomp.) | 360 | −18.9 | | 67.5 (67.9) | 6.8 (7.0) | 7.5 (7.4) | 8.0 (7.5) |
| | Pt | Cream, crystalline solid | 95 | 295, 320 | −9.3 | 3 696 | 61.7 (62.8) | 6.3 (6.4) | 6.8 (6.9) | 5.8 (6.9) |
| $n$-$C_4H_9$ | Pd | Yellow, crystalline solid | 164 | 360 | −18.7 | | 69.7 (69.4) | 7.8 (7.6) | 6.9 (6.8) | 5.8 (5.9) |
| | Pt | Cream, crystalline solid | 136—138 (decomp.) | 295, 320 | −9.2 | 3 696 | 62.9 (63.9) | 6.8 (7.0) | 6.1 (6.3) | 5.3 (5.5) |
| $n$-$C_5H_{11}$ | Pd | Yellow, crystalline solid | 118 | 360 | −18.7 | | 70.0 (70.6) | 7.9 (8.1) | 6.1 (6.3) | 6.1 (5-5) |
| | Pt | Yellow, hard wax | | 295, 320 | −9.3 | 3 694 | 62.5 (65.4) | 7.2 (7.5) | 6.2 (5.9) | 4.9 (5.1) |
| $n$-$C_6H_{13}$ | Pd | Dark wax | | 365 | −18.6 | | 69.9 (71.7) | 8.0 (8.5) | 5.4 (5.9) | |
| $n$-$C_7H_{15}$ | Pd | Dark oil | | 365 | −18.6 | | 74.4 (74.1) | 9.5 (9.5) | 4.7 (4.9) | 4.8 (4.8) |

[a] Chemical shifts measured relative to trimethyl phosphate as external standard. All spectra were recorded in CDCl₃.

found that both routes give rise to mixtures of isomers that are very difficult to separate on a preparative scale for all but the lower alkyl groups. It is well known that the halogenation of alkylbenzenes proceeds quite rapidly under varying reaction conditions.[10,11] In the presence of acid catalysts and at low temperatures halogenation of the aromatic ring occurs, but again a mixture of *ortho*- and *para*-isomers is formed. It has been shown that silver trifluoroacetate catalyses the reaction between iodine and both benzene and toluene to form iodobenzene and $p$-iodotoluene respectively.[12] We have extended this reaction to the iodination of heptylbenzene and have formed the *para*-substituted product exclusively. However the yield is low and a large excess of alkylbenzene must be present in the system, which presents difficulties in the separation of the product from the reaction mixture.

Although all the above procedures are simple one-step processes they each have obvious disadvantages. The difficulties in separating the *para*-isomer, together with the low yields which are often obtained, render these processes unsuitable for large-scale procedures. Accordingly, it was decided to use a three-stage synthesis to prepare the $p$-halogenoalkylbenzenes which gave solely

lowed by a Wolff–Kischner reduction of the acyl group to an alkyl group using alkaline hydrazine. The product is claimed to be solely the *para*-isomer with no *ortho*-contaminant. However, although the overall yield is not given, the original discoverers [14] report that the acylation step yields only 30% of the desired product together with 25% of PhCOR. By contrast, overall yields in the present synthesis of $p$-bromoalkylbenzenes are 46—60% (Table 3).

*Characterisation of the Tris(p-alkylaryl)phosphines.*—Good microanalyses were obtained for the lower members of the series; however, the high members could not be distilled without decomposition, and therefore the waxy state of these phosphines coupled with the increased sensitivity to oxygen when compared with triphenylphosphine rendered purification and characterisation difficult. Accordingly a complete characterisation of the whole series depended on a combination of physical techniques, as well as characterisation of derivatives including the phosphine oxides (Table 2) and the bis(phosphine)dichloro-palladium(II) and platinum(II) complexes (Table 4). The mass spectra showed the presence of the expected molecular ions (Table 1).

The i.r. spectra (4 000—200 cm$^{-1}$) showed the absence

of bands attributable to P=O or P–O stretching modes, indicating the absence of significant amounts of oxidation products. The spectra were very similar to those of the para-bromoalkylbenzenes from which they were prepared. No bands assignable to P–C stretching modes were observed, which is in agreement with their absence in the spectra of trialkylphosphines characterised previously.[1,15,16]

The relative intensities of the signals in the ¹H n.m.r. spectra (Table 5) were consistent with the proposed number of protons in each molecule. The ³¹P n.m.r. spectra in deuteriochloroform (Table 1) showed a single resonance ca. +10.66 p.p.m. up-field from trimethyl-phosphate (ca. 6.4 p.p.m. upfield from 85% $H_3PO_4$) which is consistent with the values reported previously for other tertiary aromatic phosphines.[17,18] In addition the

### TABLE 5

¹H N.m.r. chemical shifts * for the triarylphosphines

| Phosphine | Me | CH₂ not adjacent to aromatic ring | CH₂ adjacent to the aromatic ring | Aromatic protons |
|---|---|---|---|---|
| P(p-C₆H₄–C₂H₅)₃ | 1.20 | | 2.60 | 7.20 |
| P(p-C₆H₄–C₃H₇)₃ | 0.95 | 1.65 | 2.60 | 7.20 |
| P(p-C₆H₄–C₅H₉)₃ | 0.92 | 1.50 | 2.60 | 7.20 |
| P(p-C₆H₄–C₅H₁₁)₃ | 0.88 | 1.28 | 2.60 | 7.20 |
| P(p-C₆H₄–C₆H₁₃)₃ | 0.88 | 1.27 | 2.60 | 7.20 |
| P(p-C₆H₄–C₇H₁₅)₃ | 0.88 | 1.27 | 2.60 | 7.20 |
| P(p-C₆H₄–C₉H₁₇)₃ | 0.88 | 1.27 | 2.60 | 7.20 |
| P(p-C₆H₄–C₉H₁₉)₃ | 0.88 | 1.27 | 2.60 | 7.20 |

* All spectra recorded in CDCl₃ using SiMe₄ as internal standard.

single phosphorus resonance provided further evidence of purity. Upon oxidation to the phosphine oxide, O=P(p-C₆H₄R)₃, the chemical shift moves down-field by ca. 37 p.p.m. (Table 2), which is consistent with results observed with other triaryl- and trialkyl-phosphines.[1,19–21]

*Properties of the Tris(p-alkylaryl)phosphines.*—The triarylphosphines were either crystalline solids or viscous oils that were extremely soluble in hexane and chlorinated solvents such as dichloromethane, chloroform, and carbon tetrachloride, and moderately soluble in tetrahydro-furan, diethyl ether, and aromatic solvents such as benzene and toluene. The lower members of the series were found to be soluble in ethanol but this ability decreased as the length of the alkyl group on the phenyl rings increased. The higher members of the series are insoluble in cold ethanol, methanol, and other polar solvents. The corresponding phosphine oxides were also found to have similar physical properties and solubility characteristics.

These new phosphines were found to be sensitive to oxygen both as solids or oils, and in solution, whereas triphenylphosphine has been shown to be stable towards oxidation as a solid and in solution, and in fact has been used as an oxidation inhibitor in solutions of other oxygen-sensitive phosphines.[22] Unlike trialkylphosphines, which yield a mixture of products on oxidation in air (auto-oxidation),[1,23] these new triarylphosphines appear to give exclusively the phosphine oxide. The oxidation properties were studied using ³¹P n.m.r.

spectroscopy. Tri(p-ethylphenyl)phosphine was allowed to stand in air for several days, after which significant amounts of the phosphine oxide could be detected ca. 36 p.p.m. downfield from the parent phosphine. Only two peaks were observed in the spectra. Similar results were found using tris(p-propylphenyl)phosphine. The sensitivity of the para-substituted triarylphosphines towards oxidation appeared to increase as the alkyl chain on the phenyl ring increased in length. This may be due to an increase in the aliphatic character of the phosphine, which results from changes in the stereochemistry of the molecule due to the presence of the long alkyl chains. Electronic factors may be ruled out because the ethyl and nonyl groups should not differ appreciably in their electron-donor properties at the phosphorus atom.

*Palladium(II) and Platinum(II) Complexes.*—The tris-(p-alkylaryl)phosphines were found to readily displace co-ordinated dienes and other weak donor-ligands from complexes of palladium and platinum to yield bis(phosphine)dichloro-complexes. I.r. and ³¹P n.m.r. spectroscopy indicate that the palladium complexes have the *trans*-configuration whereas the platinum(II) complexes are *cis* (Table 4).[24] It is noteworthy that in each series the melting or decomposition points decrease as the alkyl group increases in length; this is immediately apparent from the physical appearance of the complexes, those with longer alkyl chains being waxy solids whereas those with shorter alkyl chains are crystalline. Clearly as the alkyl chain gets longer it becomes more difficult to pack the molecules into a crystal.

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13.

# The Mass Spectra of Some *para* Substituted Triarylphosphines and Triarylphosphine Oxides

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The mass spectra are reported for a series of tris(p-alkylaryl)phosphines and the corresponding phosphine oxides. The phosphines all give [M]⁺˙ as the base peak except when the phenyl groups are not para substituted. For the oxides [M−H]⁺ gives the base peak with one exception for which [M]⁺˙ is the most abundant ion.

Triarylphosphines are good ligands for transition metals, and triarylphosphine oxides for lanthanide and actinide elements. We have recently described the preparation and complexes of a series of tris(*p*-alkylaryl)phosphines which were synthesized in order to prepare metal complexes with rather different solubility properties to triphenylphosphine complexes.[1,2] In the course of characterizing the new phosphines their mass spectra were found to show significant differences from the mass spectrum of triphenylphosphine. These differences are described in the present paper. A detailed examination of the corresponding phosphine oxides is also included because, with the exception of triphenylphosphine oxide itself, these oxides have not been investigated by mass spectrometry.

Extensive mass spectral studies of triphenylphosphine and its oxide have been carried out previously.[3] Studies with deuterated analogues of triphenylphosphine revealed that scrambling on the ring sites does not occur. Cyclization can occur to give heterocyclic ions through the loss of a hydrogen atom *ortho* to the phosphorus atom. The effect of a methyl substituent on the aromatic ring of triphenylphosphine has been investigated.[4] The mass spectrum of the *para* derivative shows many of the features of triphenylphosphine itself in the formation of heterocyclic ions. The mass spectrum of tris(*p*-chlorophenyl)phosphine has been examined by other workers but no spectral assignments are published.[5]

The compounds under investigation in this work can be represented by structures **1** and **2** for the phosphines and phosphine oxides respectively, where X = H, Cl, $CH_3$, $C_2H_5$, $n$-$C_3H_7$, $n$-$C_7H_{15}$, $n$-$C_9H_{19}$ and $OCH_3$. Initial studies at medium resolution for X = Cl and $C_2H_5$ coupled with the results outlined above for
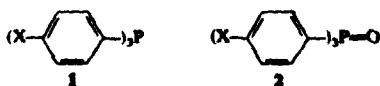
X = H and $CH_3$ suggest that common fragmentation pathways exist for both sets of compounds. The presence of the related ions can also be inferred from the low resolution studies of the remaining compounds.

The general structures of ions obtained with the phosphines are shown in Table 1. The normalized intensities of each set of ions are also shown. The most notable feature is that the base peak is the molecular ion [M]⁺˙ in all cases except when X = H. Both electron-withdrawing substituents (X = Cl) and electron-donating substituents (X = alkyl or $OCH_3$) give [M]⁺˙ as the base peak, suggesting that the electron densities on the phosphorus atoms are similar in both cases. The ³¹P nuclear magnetic resonance (NMR) chemical shifts of these compounds are all similar in agreement with this deduction.[1] The anomalous behaviour observed in the phosphine series when X = H is not observed with the phosphine oxides. For the alkyl substituents X = $C_2H_5$ to $n$-$C_9H_{19}$ the length of the substituent alkyl chain has little effect on the distribution of the ions in Table 1.

A similar treatment for the phosphine oxides in terms of general ion structures is shown in Table 2. With the exception of $n$-$C_9H_{19}$, the base peak involves the loss of a hydrogen radical from the molecular ion [M−H]⁺. Care must be taken to account for the isotopic contribution of [M−H]⁺ to [M]⁺˙. The loss of a single substituent group from the molecular ion [M−X]⁺ is more favourable for the phosphine oxides than for the corresponding phosphines. This suggests a weakening of the X-aryl bond in the former, which may be due to the lower resonance stabilization of the aromatic ring coupled to phosphorus(V). However, ³¹P NMR studies suggest that the X-substituent does not affect the electron density on the phosphorus atom to any degree.[1] Some of the ions in Table 2 are also seen in the phosphines themselves. Thus, the oxygen atom may be undergoing new bond formation with the aromatic rings to produce some of these ions.

The accurate masses of some of the ions in the spectrum of tris(*p*-chlorophenyl)phosphine oxide are of interest. A strong peak at $m/z$ 170 is observed

(X—⟨ ⟩—)₃P    (X—⟨ ⟩—)₃P=O

**1**          **2**

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Table 1. Ions produced in the mass spectra of triarylphosphines (X-C6H4)3P

| ion\X | H | Cl | CH3 | C2H5 | n-C3H7 | n-C7H15 | n-C9H19 | OCH3 |
|---|---|---|---|---|---|---|---|---|
| [M]+• | 33 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| [M-X]+ | 11 | 3 | 2 | 1 | 2 | 1 | 1 | 1 |
| (X-C6H4)2P+ | 6 | 27 | 29 | 6 | 2 | 3 | 13 | 26 |
| (dibenzophosphole) | 100 | 20 | 55 | 1 | 1 | 1 | 1 | 5 |
| (X...)2 | 1 | 4 | 17 | 4 | 2 | 1 | 2 | 16 |
| [XC6H4P]+• | 26 | 91 | 76 | 26 | 4 | 4 | 0 | 76 |

Table 2. Ions produced in the mass spectra of triarylphosphine oxides (X-C6H4)3P=O

| ion\X | H | Cl | CH3 | C2H5 | n-C3H7 | n-C7H15 | n-C9H19 | OCH3 |
|---|---|---|---|---|---|---|---|---|
| [M]+• | 26 | 46 | 36 | 41 | 37 | 60 | 100 | 54 |
| [M-H]+ | 100 | 100 | 100 | 100 | 100 | 100 | 63 | 100 |
| [M-X]+ | — | 24 | 4 | 10 | 19 | 7 | 7 | 1 |
| (X-C6H4)2P=O | 19 | 42 | 17 | 18 | 20 | 32 | 28 | 33 |
| (X...X with O) | 15 | 14 | 9 | 4 | 2 | 4 | 2 | 8 |
| (X-C6H4)2P+ | 10 | 58 | 23 | 21 | 26 | 33 | 19 | 73 |
| (X...)2 | 4 | 8 | 3 | 6 | 2 | 12 | 19 | 5 |

which shows no chlorine isotope peaks at low resolution. The accurate mass of this ion suggests $C_{11}H_7P$ to be the elemental composition. Two possible structures are $a$ and $b$. The origin of this ion is unclear, although its formation is thought to involve the oxygen atom of the starting molecular ion since it is not seen in the spectrum of the corresponding phosphine. Accurate
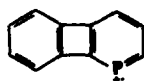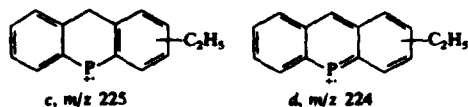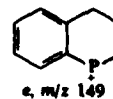


a, m/z 170
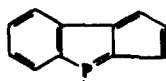


b, m/z 170

mass studies on (p-C2H5C6H4)3P show evidence of reactions occurring at the sidechain. The ions c, d and e at m/z 225, 224 and 149 respectively show how sidechain reactions may produce heterocyclic ions.



c, m/z 225



d, m/z 224



e, m/z 149

## EXPERIMENTAL

Triphenylphosphine, triphenylphosphine oxide (Aldrich Chemical Co Ltd), tri(p-tolyl)phosphine and tri-(p-methoxyphenyl)phosphine (Kodak Ltd) were examined as supplied. A range of triarylphosphines (p-$XC_6H_4$)3P, where X = Cl, C2H5, n-C3H7, n-C7H15 and n-C9H19, were synthesized by a Grignard method as

15.

described previously.[1] The oxides $(p\text{-}XC_6H_4)_3P=O$, where $X = C_2H_5$, $n\text{-}C_3H_7$, $n\text{-}C_7H_{15}$ and $n\text{-}C_9H_{19}$ were prepared by oxidation of the corresponding phosphine in acetone using 6% w/v hydrogen peroxide.[1] The oxides with $X = Cl$, $OCH_3$ and $CH_3$ were also prepared in this fashion: their $^{31}P$ NMR chemical shifts were 22.7, 24.9 and 25.9 ppm downfield from trimethylphosphate respectively.

Low resolution mass spectra $(M/\Delta M = 1000)$ were recorded using either a Perkin-Elmer-Hitachi RMU7 M mass spectrometer or a VG Micromass 305F mass spectrometer, operating at 70 eV with an ion source temperature of 250 °C. The accelerating voltages were 3.2 and 4.0 kV respectively. The data were collected using a VG 2035 data system. Observed metastable transitions were within ±0.2 u of the calculated values throughout.

Medium resolution mass spectra $(M/\Delta M = 7500)$ were recorded using a Kratos MS 50 mass spectrometer operating at 70 eV; the data were collected using a Kratos DS 50 data system.

$^{31}P$ NMR spectra were recorded in deuterochloroform solution using a JEOL FX 90Q NMR spectrometer operating at 36.2 MHz.

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Received 11 March 1981; accepted 26 March 1981

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16.

# Chapter 3

## The Preparation and Characterisation of Transition
## Metal Complexes of Long Alkyl Chain Tertiary Phosphines

The long alkyl chain tertiary phosphines have been used to prepare a series

of platinum, palladium and rhodium complexes, full details of which are given in

reference 1. A summary given in reference 2, was reported at the Chemical Systems

Laboratory Conference in November 1982[2]. All the complexes as expected are very

soluble in non-polar solvents. Accordingly their purification is not easy.

Preparative routes have therefore been developed that minimise by-product formation

or give by-products that are readily separated from the complexes.

As part of the work described in Chapter 5 it was desirable to use trans-

$[RhI(CO)(PAr_3)_2]$, where Ar = aryl. An attempt to prepare this from the well

characterised, stable chloro-complex trans-$[RhCl(CO)(PAr_3)_2]$ by halide metathesis

quickly showed that the iodo-complex is less stable than its chloro-analogue.

A detailed investigation of the preparation, characterisation and study of

the behaviour in solution of $[RhI(CO)(PAr_3)_2]$ is described in reference 3.

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# Complexes of Long Alkyl Chain Tertiary Phosphines.
## Part I. The Preparation and Characterisation of Platinum Metal Complexes of Long-Chain Tertiary Phosphine Ligands

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Received June 6, 1980

*The long chain tertiary phosphine ligands (P(C$_n$-H$_{2n+1}$)$_3$ and P(C$_6$H$_4$-C$_m$H$_{2m+1}$)$_3$ have been used to prepare the following series of platinum, palladium and rhodium complexes: cis-[PtL$_2$Cl$_2$], trans-[PdL$_2$Cl$_2$], trans-[PtL$_2$HCl] (L = trialkylphosphine only), [PtL$_4$] and trans-[RhL$_2$Cl(CO)]. The complexes are very soluble in chlorinated solvents and both aliphatic and aromatic hydrocarbons as well as tetrahydrofuran, but either insoluble or only slightly soluble in polar solvents such as alcohols, acetone and diethylether. Many of the complexes are crystalline solids whose purification merely requires care; however a number are waxes or oils and both the preparative routes used and the work up procedures for these must be chosen with extreme care. In addition to the monomeric trans-[PdL$_2$Cl$_2$] complexes trialkylphosphines yield dark coloured palladium(II) products that are believed to be a mixture of several isomers of the ortho-metallated chloride bridged dimers [Pd{P(C$_n$H$_{2n+1}$)$_2$C$_n$H$_{2n}$}Cl]$_2$ which differ in the sizes of their Pd–P–C rings together with some unmetallated chloride bridged dimer [Pd{P(C$_n$-H$_{2n+1}$)$_3$}Cl$_2$]$_2$.*

## Introduction

We have recently described the preparation of two series of tertiary phosphines, trialkylphosphines, P(C$_n$H$_{2n+1}$)$_3$ where n = 10–19 inclusive [1] and tris-(p-alkylaryl)phosphines P(C$_6$H$_4$C$_m$H$_{2m+1}$)$_3$ where m = 2–9 inclusive [2]. Herein we describe the preparation of a number of complexes of those phosphines with platinum, palladium and rhodium. These complexes were prepared because it was anticipated that they would have unusual solubilities, in particular very high solubilities in hydrocarbon solvents. Complexes with unusual solubilities are of interest for a number of reasons:

1. Solvents play an important part in the mechanism of chemical reactions in solution. Hence it was of interest to prepare complexes with very high solubilities in non-polar solvents to see in what way the catalytic ability of these complexes differed from their less soluble homologues.

2. There has been increasing interest in recent years in the possibility of activating alkanes to chemical reaction through coordination to transition metals [3]. Since alkanes are extremely unreactive and less reactive than virtually all other organic compounds it seemed profitable to prepare potential catalyst precursors that would be freely soluble in alkanes without the need for the presence of a further, more reactive organic compound.

3. Complexes with high solubilities in hydrocarbon solvents may be of value in the solvent extraction of metals, as stationary phases in gas chromatography, as additives in organic materials such as plastics and paints where, for example, they may prevent fouling of ships' bottoms by prevention of algae and barnacle growth.

## Experimental

### Materials

[Pt(COD)Cl$_2$] [4] [Pd(COD)Cl$_2$] [5] and [Pt(COD)$_2$] [6, 7] were prepared by standard procedures. The method of Clark [4] was preferred for the platinum(II) complex because it is easier and gives a whiter product. However the platinum(II) complex prepared according to reference 5 gave excellent microanalytical data. [Rh$_2$Cl$_2$(CO)$_4$] was prepared as follows[†]: Rhodium trichloride tri-hydrate was spread evenly along a narrow ceramic boat. The salt was then moistened with a few drops of distilled

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[†]This experimental procedure was devised by Dr. D. J. A. McCaffrey in our laboratories. It is a modification and improvement of that in reference 8.

water.(This preparation has been found not to proceed using the dry salt). The boat was then placed in a heated glass tube which was surrounded by a mixture of refluxing toluene and xylene such that the temperature was kept at approximately 125 °C. Carbon monoxide was passed over the heated moist RhCl$_3$·3H$_2$O at such a rate as to cause sublimation of the final product to the end of the glass tube. Care must be taken to avoid 'blowing' the product out of the end of the tube which is protected by an oil bubbler. The whole apparatus was well lagged with cotton wool, a) to help the reflux of the solvent system, and b) to cause condensation of the water further along the glass tube than the product. After a reaction time of 24 hours the apparatus was carefully dismantled and any excess moisture was wiped from the end of the tube. The product does not require further purification. Yield 60%.

### cis-[PtL$_2$Cl$_2$]

Solutions of two equivalents of tertiary phosphine and one equivalent of [Pt(COD)Cl$_2$] in chloroform were reacted under nitrogen for two hours at room temperature. In the case of the triarylphosphines the solutions were evaporated to dryness and where possible recrystallised from a mixture (60:40) of ethanol and chloroform. The higher members of the series could only be obtained as either waxes or viscous oils. These were purified chromatographically on alumina (Brockman activity I, neutral) eluting with a 60:40 mixture of chloroform and methanol. The solvent was removed and the product dried at 50 °C in vacuo overnight. In the case of the trialkylphosphines the products, where possible, were precipitated from solution by the addition of an equal volume of methanol. The trioctylphosphine complex was purified by column chromatography to yield a yellow wax. Physical, spectroscopic and analytical data are given in Tables I and II.

### trans-[PdL$_2$Cl$_2$]

The palladium(II) complexes were synthesised by an identical route to that used for the platinum(II) complexes. In general the former were less crystalline and therefore more difficult to purify. With the longer chain trialkylphosphines column chromatography was used to separate a dark red waxy material from the pale yellow to pale brown [PdL$_2$Cl$_2$]. The proportion of the dark red waxy material increased with increasing phosphine alkyl chain length to the extent that virtually no [PdL$_2$Cl$_2$] was formed with phosphines that have fifteen or more carbon atoms in their chains. Physical spectroscopic and analytical data for [PdL$_2$Cl$_2$] are given in Tables III and V and for the dark red waxy materials in Table IV.

### trans-[Pt(PR$_3$)$_2$HCl]

Trans-[Pt(PR$_3$)$_2$HCl] R = alkyl were prepared by hydrazine hydrate reduction of the corresponding cis-[Pt(PR$_3$)$_2$Cl$_2$] in a solution of chloroform and ethanol, the chloroform being necessary because of insufficient solubility in ethanol alone [9]. Physical, spectroscopic and analytical data are given in Table VI.

### [PtL$_n$]

A solution of the triaryl- or trialkyl-phosphine (4 mmol) and [Pt(COD)$_2$] (1 mmol) was stirred in dry hexane under nitrogen for two hours before evaporation to dryness [10]. The products were further dried in vacuo for 24 hours at room temperature. Physical, spectroscopic and analytical data are given in Table VII.

### trans-[RhL$_2$Cl(CO)]

Trans-[RhL$_2$Cl(CO)] complexes were prepared from [Rh$_2$Cl$_2$(CO)$_4$] following the literature preparation [11] but using the minimum volume of chloroform possible. The complexes, where crystalline, were recrystallised from ethanol–chloroform mixtures. Physical, spectroscopic and analytical data are given in Tables VIII and IX.

### Halide Metatheses

A number of bromide and iodide complexes are reported in Tables I, II, V and IX. These were prepared by treating the chloride complexes with excess lithium bromide or sodium iodide in acetone.

### Kinetics of the Dissociation of [PtL$_n$] in Solution

A 4 × 10$^{-4}$ mol l$^{-1}$ solution of [PtL$_n$] in benzene was prepared under nitrogen. The absorbance at 358 nm was recorded as a function of time at 25.0 °C. When n = 4, plots of log (A$_t$ − A$_∞$) against time, where A$_t$ and A$_∞$ are the absorbances at time t and at equilibrium, showed two distinct regions for which apparent rate constants k$^{obs}$ and k$'^{obs}$ can be evaluated (Fig. 1). For [Pt(PPh$_3$)$_3$] only a single straight line plot was obtained. The two regions observed for the tetrakis complexes were therefore ascribed to sequential loss of a phosphine (reaction 1).

$$PtL_4 \underset{+L,\ k_{-1}}{\overset{-L,\ k_1}{\rightleftharpoons}} PtL_3 \underset{+L,\ k_{-2}}{\overset{-L,\ k_2}{\rightleftharpoons}} PtL_2 \tag{1}$$
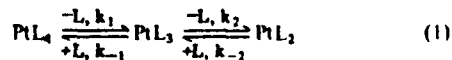
The first stage involves a first order reaction opposed by a second order reaction (2).

$$PtL_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PtL_3 + L \tag{2}$$
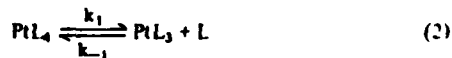
for which the integrated rate equation is [12]:

$$\ln\left\{\frac{C_o^2 - C_e C}{(C - C_e)C_o}\right\} = k_1^{obs}\left\{\frac{C_o + C_e}{C_o - C_e}\right\} t \tag{3}$$
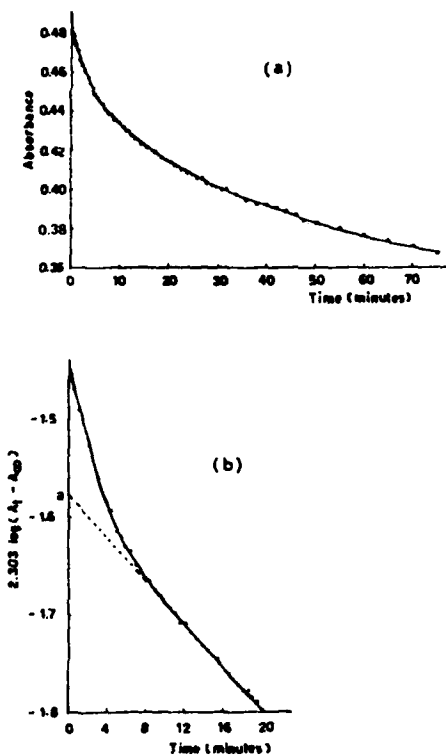
Fig. 1. The dissociation of a $4 \times 10^{-4}$ mol $l^{-1}$ solution of $[Pt\{P \text{—} \langle \bigcirc \rangle \text{—} CH_3)_3\}_4]$ in benzene at 25 °C. (a) Plot of absorbance against time. (b) Plot of 2.303 log($A_t - A_\infty$) against time.

where $C_o$, $C_e$ and $C$ are the concentrations of $[PtL_4]$ initially, at equilibrium and at time t and ($C_o - C$) is the concentration of both $PtL_3$ and L at time t. Since for L = $PPh_3$, $k_1/k_{-1} > 10$ mol $l^{-1}$ [13], then for $C_o = 4 \times 10^{-4}$ mol $l^{-1}$, $C_e$ is essentially zero. Equation 3 therefore reduces to

$$\ln(C_o/C) = k_1^{obs} t \qquad (4)$$

which was used to evaluate $k_1^{obs}$ by noting that C = $A/\epsilon l$ and $C_o = A_o/\epsilon l$ where $\epsilon$ is the molar absorbance and $l$ the cell length.

For the second stage of the reaction with the tetrakis complexes, the starting solution effectively contains one equivalent of $[PtL_3]$ and one equivalent of free L (reaction 5)

$$PtL_3 + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} PtL_2 + 2L \qquad (5)$$
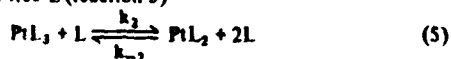
for which the integrated rate equation (see Appendix) is:

$$\left\{ \frac{B}{\sqrt{(B^2 C_o'^2 + 6BC_o' + 1)}} \right\}$$

$$\ln \left\{ \frac{\frac{1}{2B}\sqrt{(1 + 6BC_o' + B^2 C_o'^2)} + C' - (1 + 3BC_o')/2B}{\frac{1}{2B}\sqrt{(1 + 6BC_o' + B^2 C_o'^2)} - C' + (1 + 3BC_o')/2B} \right\}$$

$$= Bk_2^{obs} t + \text{const.} \qquad (6)$$

where

$$B = (C_e')/(C_o' - C_e')(2C_o' - C_e') \qquad (7)$$

in which $C_o'$, $C_e'$ and $C'$ are the concentrations of $[PtL_3]$ initially, at equilibrium and at time t. $k_2^{obs}$ values were determined from equation 6, by noting that $C_o' = A_o/\epsilon' l$ and $C_e' = A/\epsilon' l$ and taking the value of $A_o$ for this second stage by extrapolation of the second stage of the plot in Fig. 1 back to zero time (point a). Values of $k^{obs}$, $k'^{obs}$, $k_1^{obs}$ and $k_2^{obs}$ are summarised in Table X.

*Measurements*

Microanalytical data were determined in the Chemistry Department at University College, London. $^1$H nmr spectra were recorded in $CDCl_3$ solution containing TMS as an internal standard using a Perkin-Elmer R32 spectrometer. $^{31}$P nmr spectra were recorded in $CDCl_3$ solution using a Brucker WH90 spectrometer; TMS was used as an internal standard for the former, trimethylphosphate (TMP), which lies 4.242 ppm downfield from 85% $H_3PO_4$ [14], was used as an external standard for the latter. $^{13}$C nmr spectra were recorded by the Physical Chemistry Measurements Unit at Harwell in $CDCl_3$ using TMS as an internal standard.

Infrared spectra were recorded as nujol and hexachlorobutadiene mulls in the range 4000–200 $cm^{-1}$ using a Perkin-Elmer model 577 spectrometer calibrated with a standard polystyrene film. U/v–visible spectra were recorded on a Unicam SP 1700B Spectrophotometer in 1 cm cells mounted in a water-jacketted cell-housing fed by a Techne C100 circulating bath coupled to a Techne 1000 refrigeration unit.
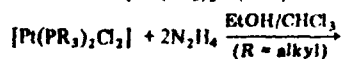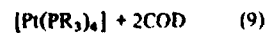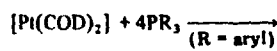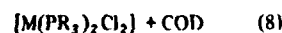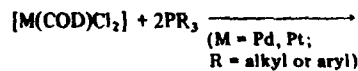
**Results and Discussion**

All the complexes prepared in this work have very similar solubility properties both to each other and to the starting phosphines. Thus they are very soluble in chlorinated solvents, aliphatic hydrocarbons such

TABLE I. Physical, Spectroscopic and Analytical Data for [Pt{P(C$_n$H$_{2n+1}$)$_3$}$_2$X$_2$].

| P(C$_n$H$_{2n+1}$)$_3$ | X | Configuration | Appearance | M.pt (°C) | Infrared[a] ν(Pt–X) (cm$^{-1}$) | $^{31}$P nmr Chemical shift (ppm)[b] | $J_{Pt-P}$ (Hz) | Analytical Data Found (Calculated) C | H | X | P |
|---|---|---|---|---|---|---|---|---|---|---|---|
| P(C$_3$H$_9$)$_3$ | Cl | cis | White prisms | 142 | 305, 283 | +4.9 | 3518 | 42.0(43.0) | 7.8(8.1) | 11.1(10.6) | – |
| P(C$_8$H$_{17}$)$_3$ | Cl | cis | Yellow wax | –30 | 305, 283 | +1.8 | 3513 | 55.7(57.2) | 10.6(10.1) | 7.3(7.2) | 6.4(6.3) |
| P(C$_{13}$H$_{27}$)$_3$ | Cl | cis | Cream crystalline solid | 42 | 305, 283 | c | | 64.5(65.2) | 11.2(11.4) | 4.7(4.9) | – |
| P(C$_{14}$H$_{29}$)$_3$ | I | trans | Yellow crystalline solid | 42–44 | c | +10.9 | 2252 | 56.6(58.2) | 10.0(10.1) | 15.4(15.8) | 4.4(3.9) |
| | Cl | cis | Cream crystalline solid | 31–33 | 305, 283 | +3.5 | 3515 | 66.1(66.7) | 11.3(11.6) | 4.3(4.7) | – |
| | I | trans | Yellow crystalline solid | 46–48 | c | +10.8 | 2252 | 59.4(59.5) | 10.3(10.4) | – | – |
| P(C$_{16}$H$_{33}$)$_3$ | Cl | cis | Cream crystalline solid | 50 | 305; 283 | +4.9 | 3514 | 66.9(68.6) | 11.7(11.9) | 4.2(4.3) | – |
| P(C$_{18}$H$_{37}$)$_3$ | Cl | cis | Cream crystalline solid | 62 | 305, 283 | c | | 68.3(70.2) | 11.9(12.1) | 3.9(3.8) | – |
| | I | trans | Yellow crystalline solid | 60–62 | c | | 3514 | 61.7(63.9) | 10.9(11.0) | 13.1(12.5) | 4.1(3.1) |

[a]Recorded as major mulls. [b]Chemical shifts in CDCl$_3$ measured relative to TMP as external standard. [c]ν(M–X) for all iodide complexes are assumed to be <200 cm$^{-1}$.
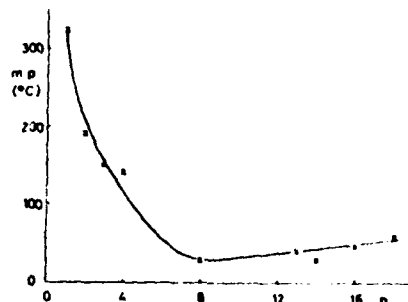


Fig. 2. The effect of chain length on the melting point of cis-[Pt{P(C$_n$H$_{2n+1}$)$_3$}$_2$Cl$_2$].

as hexane, cyclohexane and petroleum ether, benzene, toluene and tetrahydrofuran and slightly soluble in acetone. The trialkylphosphine complexes did not dissolve in polar solvents such as ethanol, methanol and diethylether, but the triarylphosphine complexes were slightly soluble in these solvents when the *para*-alkyl group was small but decreased in solubility as it increased in size. All the complexes were relatively low melting solids, waxes or oils. This coupled with their extreme solubility properties made purification difficult. Accordingly, since for each series of complexes a wide range of preparative routes have been described in the literature, the methods used were those involving the least amount of purification (reactions 8–11). In reactions 8 and 9 the only by-product is

$$[M(COD)Cl_2] + 2PR_3 \xrightarrow[\substack{(M = Pd, Pt; \\ R = alkyl \text{ or } aryl)}]{}$$

$$[M(PR_3)_2Cl_2] + COD \qquad (8)$$

$$[Pt(COD)_2] + 4PR_3 \xrightarrow[(R = aryl)]{}$$
$$[Pt(PR_3)_4] + 2COD \qquad (9)$$

$$[Rh_2Cl_2(CO)_4] + 4PR_3 \xrightarrow[(R = alkyl \text{ or } aryl)]{}$$

$$2trans\text{-}[Rh(PR_3)_2Cl(CO)] + 2CO \qquad (10)$$

$$[Pt(PR_3)_2Cl_2] + 2N_2H_4 \xrightarrow[(R = alkyl)]{EtOH/CHCl_3}$$

$$trans\text{-}[Pt(PR_3)_2HCl] + NH_4Cl + \tfrac{1}{2}N_2 + NH_3 \qquad (11)$$

cyclooctadiene (COD) which is sufficiently volatile to be removed by pumping *in vacuo*. In reaction 11 the oxidation products of hydrazine are nitrogen which is obviously volatile, ammonia and ammonium chloride which are extracted into aqueous hydrochloric acid.
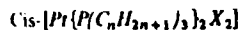
Cis-$[Pt\{P(C_nH_{2n+1})_3\}_2X_2]$

Cis-$[Pt\{P(C_nH_{2n+1})_3\}_2Cl_2]$ were prepared by reaction 8. Microanalytical results (Table I) were good except for the waxy material which could not be recrystallised but was purified by column chromatography. The melting-points initially decrease sharply as n increases, reaching a minimum at about n = 8; thereafter there is a slight increase in melting-point with increase in chain length (Fig. 2). A cis-configuration was suggested by the infrared spectra ($\nu_{Pt-Cl}$ = 305 and 283 cm⁻¹, cf. cis-$[Pt(PEt_3)_2Cl_2]$ 303 and 281 cm⁻¹) [15]. The complexes do not isomerise on heating, instead they decompose. ³¹P nmr spectra involve a triplet with ¹⁹⁵Pt–³¹P coupling constants between 3513 and 3518 Hz (X = Cl) which is typical of a cis-configuration and should be compared to a coupling constant of about 2400 Hz for trans-complexes [16-18]. ³¹P chemical shifts for X = Cl were in the range +2 to +5 ppm upfield from TMP which was again consistent with values reported elsewhere for cis-complexes [16].

The iodo-complexes, which were prepared by heating the chloro-complexes with excess sodium iodide in acetone, have a trans-configuration (¹⁹⁵Pt–³¹P coupling constants at 2252 Hz). Since the sterically less demanding chloride ligands form cis-complexes, this cis to trans-isomerisation on halide substitution would appear to be a consequence of electronic factors. Since cis to trans-isomerisation is sometimes promoted by excess nucleophile it was of interest to see if refluxing the cis-dichloro complexes with excess lithium chloride in acetone would promote isomerisation; it did not. The pure cis-isomer was recovered after 24 hours of refluxing.

The bis(trialkylphosphine) complexes can also be prepared by displacing acetonitrile from $[Pt(MeCN)_2Cl_2]$; however in this case a mixture of cis- and trans-isomers was obtained. These are virtually impossible to separate because of their very similar physical properties.

Cis-$[Pt\{P(C_6H_4C_mH_{2m+1})_3\}_2X_2]$

Cis-$[Pt\{P(C_6H_4C_mH_{2m+1})_3\}_2X_2]$ were prepared by reaction 8. Microanalytical results (Table II) were in good agreement with the proposed formulae. For m = 2 to 4 the chlorides were white crystalline solids after dissolution in the minimum volume of hot ethanol followed by crystallisation by storing in an ice-box for a week. For m = 5 to 9, however, they were yellow waxes or oils which were purified by column chromatography. This decrease in melting-point with increasing alkyl chain length indicates the increasing difficulty of packing the molecules into a crystal. The infrared spectra of the chloro complexes had two bands in the Pt–Cl stretching region at 295 and 320 cm⁻¹ (cf. cis-$[Pt(PPh_3)_2Cl_2]$, 280 and 303 cm⁻¹) [19] indicating a cis-configuration. This was further confirmed by ³¹P nmr data

TABLE II. Physical, Spectroscopic and Analytical Data for cis-$[Pt\{P(C_6H_4R)\}_2X_2]$

| R | X | Appearance | M. pt. (°C) | Infrared[a] ν(Pt-Cl) (cm⁻¹) | ³¹P nmr[b] δ (ppm) | $J_{Pt-P}$ (Hz) | Analytical Data Found (Calculated) C | H | X | P |
|---|---|---|---|---|---|---|---|---|---|---|
| C₂H₅ | Cl | White needles | 268 (dec) | 295, 320 | -9.2 | 3695 | 59.8(60.1) | 5.7(5.7) | 7.6(7.4) | — |
| | Br | Yellow crystalline solid | 243-4 | c | -8.9 | 3641 | 54.0(55.0) | 5.2(5.2) | 16.7(15.3) | — |
| | I | Yellow crystalline solid | 202-4 | c | -6.7 | 3484 | 47.4(50.5) | 4.9(4.8) | 19.7(22.2) | — |
| C₃H₇ | Cl | White crystalline solid | 86 | 295, 320 | -9.3 | 3696 | 61.7(62.8) | 6.3(6.4) | 6.8(6.9) | 5.8(6.0) |
| C₄H₉ | Cl | White needles | 136-8 | 295, 320 | -9.2 | 3698 | 62.9(63.9) | 6.8(7.0) | 6.1(6.3) | 5.3(5.5) |
| | Br | Yellow crystalline solid | 118 | c | — | — | 59.6(59.3) | 6.3(6.5) | 12.8(13.1) | — |
| | I | Yellow crystalline solid | 116 | c | — | — | 52.9(55.0) | 6.1(6.0) | 20.1(19.4) | — |
| C₆H₁₁ | Cl | Yellow hard wax | — | 295, 320 | -9.3 | 3694 | 63.5(65.4) | 7.2(7.5) | 6.2(5.9) | 4.7(4.7) |
| C₉H₁₉ | Cl | Yellow oil | — | 295, 320 | — | — | — | — | — | 4.9(5.1) |

[a] Recorded as nujol mulls. [b] Chemical shifts measured in CDCl₃ relative to TMP as external standard. [c] ν(M-X) for all bromide and iodide complexes are assumed to be <200 cm⁻¹.

TABLE III. Physical, Spectroscopic and Analytical Data for *trans*-[Pd{P(C$_n$H$_{2n+1}$)$_3$}$_2$Cl$_2$].

| P(C$_n$H$_{2n+1}$)$_3$ | Appearance | M. pt. (°C) | Infrared $\nu$(Pd–Cl) (cm$^{-1}$) | $^{31}$P nmr chemical shift$^b$ $\delta$ (ppm) | Analytical Data Found (calculated) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | X | P |
| P(C$_4$H$_9$)$_3$ | Yellow prisms | 65 | 355 | –4.1 | 49.2(49.5) | 9.5(9.4) | 11.9(12.2) | 10.5(10.7) |
| P(C$_8$H$_{17}$)$_3$ | Yellow oil | ~10 | 355 | –7.3 | 63.4(61.3) | 11.0(11.7) | 8.3(8.1) | 7.7(7.0) |
| P(C$_{13}$H$_{27}$)$_3$ | Yellow crystals | 40° (dec) | 355 | –7.4 | 68.8(69.9) | 11.8(12.2) | 5.0(5.3) | – |
| P(C$_{16}$H$_{33}$)$_3$ | Yellow-brown crystals | 40° (dec) | 355 | –4.3 | 69.8(70.9) | 12.1(12.3) | 4.9(5.0) | 5.0(4.4) |

$^a$Infrared spectra recorded as nujol mulls. $^b$All chemical shifts measured in CDCl$_3$ solution relative to TMP as external standard.

where chemical shifts of between –9.2 and –9.3 ppm downfield from TMP with $^{195}$Pt–$^{31}$P coupling constants between 3694 and 3698 Hz were observed for the chloro-complexes consistent with previous literature reports for similar complexes [16–18]. $^1$H nmr spectra merely served to confirm the presence of the phosphine ligands and the absence of any significant amount of organic impurity.

*Trans*-[Pd{P(C$_n$H$_{2n+1}$)$_3$}$_2$Cl$_2$]

When one equivalent of [Pd(COD)Cl$_2$] was treated with two equivalents of trialkylphosphine in chloroform under nitrogen an instantaneous reaction occurred which on evaporation to dryness yielded a dark solid. Repeated recrystallisation from hexane and ether yielded a yellow or yellow-brown solid, shown below to be *trans*-[Pd{P(C$_n$H$_{2n+1}$)$_3$}$_2$Cl$_2$] and a dark red or brown waxy product which became more crystalline as the alkyl chain increased in length. The reaction may be summarised as:

[Pd(COD)Cl$_2$] + P(C$_n$H$_{2n+1}$)$_3$ →

$$\textit{trans-}[Pd\{P(C_nH_{2n+1})_3\}_2Cl_2] +$$
(yellow)

+ dark red or brown complex        (12)
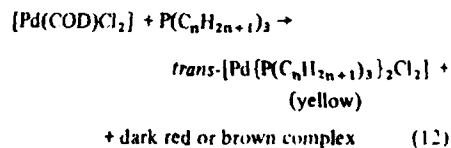
As the chain length of the trialkylphosphine increased in length so the proportion of the dark red product increased, so that it became impossible to isolate the yellow monomeric complex when the alkyl chain had fifteen or more carbon atoms.

The yellow *trans*-[Pd{P(C$_n$H$_{2n+1}$)$_3$}$_2$Cl$_2$] were either oils or crystalline solids whose microanalyses were consistent with their proposed formulae (Table III). On heating they decomposed rather than melted. In the palladium–chlorine stretching region of the infrared spectrum they showed a single band at 355 cm$^{-1}$ (cf. *trans*-[Pd(P$_n$Bu$_3$)$_2$Cl$_2$], $\nu_{Pd-Cl}$ = 355 cm$^{-1}$) [20] indicative of a *trans*-geometry. This geometry was confirmed by their $^{31}$P nmr spectra where again a single band between –4.1 and –7.3 ppm downfield from TMP was observed in agreement with previous results with lower homologues [17, 18, 21]. $^1$H nmr merely served to indicate the presence of trialkylphosphine and the absence of another organic material which might have been present as impurity.

The dark solids obtained from reaction 12 were purified by column chromatography. Their infrared spectra showed a number of bands in the palladium–chlorine stretching region, particularly between 265 and 310 cm$^{-1}$ together with a weak band at 355–357 cm$^{-1}$. The latter possibly arises from a terminal Pd–Cl stretching vibration in the dimeric chloride bridged [Pd{P(C$_n$H$_{2n+1}$)$_3$}Cl$_2$]$_2$, *1*, (cf. [Pd(P$^n$Pr$_3$)Cl$_2$]$_2$ has $\nu_{Pd-Cl}$ at 356 (terminal Cl), 299 (bridging

TABLE IV. Physical, Spectroscopic and Analytical Data for the Dark Products Obtained from Reaction 5.

| Phosphine | Appearance | Infrared (cm⁻¹)ᵃ | ³¹P nmr δ (ppm)ᵇ | Analytical Data Found | | | | Calculated Analyses | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | Cl | P | | C | H | Cl | P |
| P(C₁₃H₂₇)₃ | Dark red wax | 265 str 275 str 289 str 297 str 308 str 357 str | -2.99 | 61.5 | 10.0 | 5.1 | | (i) Monomeric [Pd{P(C₁₃H₂₇)₃}₂Cl₂] | 69.9 | 12.2 | 5.3 | |
| | | | | | | | | (ii) Dimeric [Pd{P(C₁₃H₂₇)₃}₃Cl₂]₂ | 61.8 | 10.8 | 9.3 | |
| | | | | | | | | (iii) *o-Metallated dimer* [Pd{P(C₁₃H₂₇)₂(C₁₃H₂₆)}Cl]₂ | 64.9 | 11.2 | 4.9 | |
| P(C₁₆H₃₃)₃ | Dark brown solid | 250–300 br strᶜ | | 64.6 | 11.5 | 3.7 | 4.8 | (i) Monomeric [Pd{P(C₁₆H₃₃)₃}₂Cl₂] | 72.4 | 12.5 | 4.4 | 3.9 |
| | | | | | | | | (ii) Dimeric [Pd{P(C₁₆H₃₃)₃}₃Cl₂]₂ | 65.2 | 11.3 | 8.0 | 3.5 |
| | | | | | | | | (iii) *o-Metallated dimer* [Pd{P(C₁₆H₃₉)₂(C₁₆H₃₂)}Cl]₂ | 68.0 | 11.6 | 4.2 | 3.6 |

ᵃBands in the region 250–360 cm⁻¹ in spectra recorded as nujol mulls, which it was not possible to identify individual bands. ᵇChemical shift in CDCl₃ solution measured relative to TMP as an external standard. ᶜA broad band in
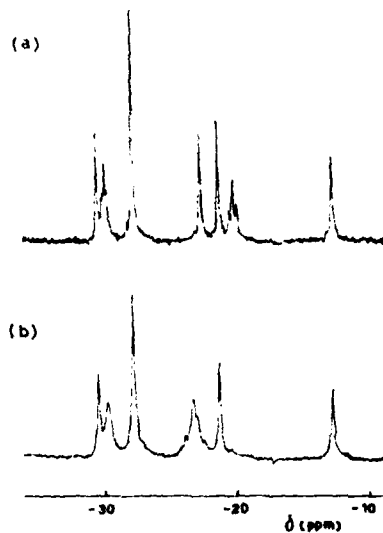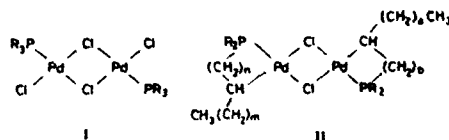


Fig. 3. ¹³C nmr spectra of (a) *trans*-[Pd{P(C₈H₁₇)₃}₂Cl₂] and (b) *cis*-[Pt{P(C₈H₁₇)₃}₂Cl₂] in CDCl₃ solution.

Cl *trans* to Cl) and 253 cm⁻¹ (bridging Cl *trans* to PⁿPr₃)) [22]. The dark colours are consistent with structure *I* since [Pd(PPr₃)Cl₂]₂ is deep orange [23]. However *I* does not appear to be the sole dark product formed by reaction 12



since there are too many bands in the infrared spectra of the products (Table IV) and the microanalytical data do not fit. In particular the chlorine analyses indicate that the product has only half as much chlorine as expected for *I*. We believe that a considerable amount of *o-metallation* may have taken place to yield *II*. Since the alkyl chain may metallate at several points giving different sized Pd–P–C rings each with a different degree of strain, a number of Pd–Cl stretching vibrations in the region 250 to 300 cm⁻¹ would be expected [24, 25]. ¹H nmr spectroscopy is not very helpful in determining the structures of the dark red compounds because the spectra merely show the bands expected if the phosphine ligands were present. The ³¹P nmr spectrum of the product containing P(C₁₃H₂₇)₃ shows a single absorption at -3 ppm downfield from TMP which is significantly different to the -7.4 ppm shift observed in *trans*-[Pd{P(C₁₃H₂₇)₃}₂Cl₂]. The presence of a single band argues

TABLE V. Physical, Spectroscopic and Analytical Data for trans-[Pd{P←⬡-R}₃]₂X₂]

| R | X | Appearance | M. pt. (°C) | Infrared ν(Pd—Cl) (cm⁻¹)ᵃ | ³¹P nmr δ (ppm)ᵇ | Analytical Data Found (Calculated) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | X | P |
| $C_3H_5$ | Cl | Yellow crystalline solid | ~230(dec) | 360 | -18.6 | 65.8(66.3) | 6.4(6.3) | 8.3(8.2) | 7.9(7.1) |
| | Br | Yellow-orange crystalline solid | 244(dec) | c | -17.2 | 56.7(60.1) | 5.8(5.7) | 16.5(16.7) | 6.6(6.5) |
| | I | Orange crystalline solid | ~180(dec) | c | -7.9 | 53.9(54.8) | 5.25(5.2) | 24.1(24.1) | 6.3(5.9) |
| $C_3H_7$ | Cl | Yellow crystalline solid | 166(dec) | 360 | -18.9 | 67.5(67.9) | 6.8(7.0) | 7.5(7.4) | 8.0(7.5) |
| $C_4H_9$ | Cl | Yellow crystalline solid | 164 | 360 | -18.7 | 69.7(69.4) | 7.8(7.6) | 6.9(6.8) | 5.8(5.9) |
| | Br | Yellow-orange crystalline solid | 102 | c | | 64.2(63.9) | 7.2(7.0) | 13.5(14.2) | 5.6(5.5) |
| | I | Orange crystalline solid | 158–160 | c | | 57.1(59.0) | 6.2(6.4) | 22.7(20.8) | 5.8(5.1) |
| $C_5H_{11}$ | Cl | Yellow crystalline solid | 118 | 360 | -18.7 | 70.0(70.6) | 7.9(8.1) | 6.1(6.3) | 6.1(5.5) |
| | Br | Yellow-orange crystalline solid | 104 | c | | 64.9(65.4) | 7.2(7.5) | 13.0(13.2) | 5.4(5.1) |
| | I | Orange crystalline solid | 106(dec) | c | | 58.5(60.7) | 6.9(7.0) | 18.4(19.4) | 5.0(4.7) |
| $C_6H_{13}$ | Cl | Dark wax | - | 365 | -18.6 | 69.0(71.7) | 8.0(8.5) | 5.4(5.9) | - |
| $C_8H_{19}$ | Cl | Dark oil | - | 365 | -18.6 | 74.4(74.1) | 9.5(9.5) | 4.7(4.9) | 4.8(5.3) |

ᵃRecorded as nujol mulls. ᵇChemical shifts measured in CDCl₃ relative to TMP as external standard. ᶜν(M–X) for all bromide and iodide complexes are assumed to be <200 cm⁻¹.



Fig. 4. ¹³C nmr spectrum of trans-[Pd{P(C₁₃H₂₇)₃}₂Cl₂] in CDCl₃ solution.

for the presence of a single species with only minor contamination. This would suggest II with only trace of I, since all the species II with different sized rings might well be expected to have very similar ³¹P nmr chemical shifts.

¹³C nmr was used in an attempt to elucidate the structures of the dark materials from reaction 12. However since the spectra were complex it was necessary first to record and assign the spectra of simple complexes. The ¹³C nmr spectra of [M(PR₃)Cl₂], M = Pd, Pt, R = Et, Pr, ⁿBu and [M(PⁿBu₂ᵗBu)₂Cl₂] have been described previously [26, 27]. We recorded the spectra of [M{P(C₈H₁₇)₃}₂Cl₂] (Fig. 3) and trans-[Pd{P(C₁₃H₂₇)₃}₂Cl₂] (Fig. 4). The peaks in these spectra were assigned (Table XI) by comparison with those in the literature [26, 27] which show that as the carbon atoms become more remote from phosphorus there is an initial downfield shift, which then reverses to become an upfield shift. Assignment is further aided by the observation that the ³¹P ¹³C coupling is much larger for odd than even numbered carbon atoms. When the ³¹P–³¹P coupling is large as in the trans-complexes the early odd-numbered carbon atoms give rise to a 1:2:1 triplet due to virtual coupling whereas in the cis-complexes where ³¹P ³¹P coupling is much less only a doublet is observed. The ¹³C nmr spectra of the dark products of reaction

12 with $P(C_{13}H_{27})_3$ and $P(C_{16}H_{33})_3$ are shown in Fig. 5 and summarised in Table XI. It is apparent that the dark red product formed from $P(C_{13}H_{27})_3$ has a very similar ^{13}C nmr spectrum to that of *trans*-$[Pd\{P(C_{13}H_{27})_3\}_2Cl_2]$ except that the signals corresponding to the first, third and eleventh carbon atoms are broad. Whilst it is possible that the broadening of the signals due to the first and third carbon atoms is a consequence of one third of the alkyl chains being *o*-metallated and giving rise to signals near but not coincident with the unmetallated chains, the ^{13}C nmr spectrum does not prove the presence of *o*-metallation. The spectrum obtained from the dark product of reaction 12 with $P(C_{16}H_{33})_3$ was unexpected (Fig. 5) in that the signals corresponding to the first, third and fourteenth carbon atoms were of very low intensity in relation to the other signals. As in the case of $P(C_{13}H_{33})_3$ they were also broad.

In conclusion it is not possible to unambiguously assign a structure to the dark red products of reaction 12. However, we believe that they are primarily a mixture of *o*-metallated isomers of different ring sizes, *II*, together with a small amount of unmetallated dimer, *I*. The separation of these products will be extremely difficult, if not impossible, due to their very similar physical characteristics.

## Trans-$[Pd\{P(C_6H_4C_mH_{2m+1})_3\}_2X_2]$

*Trans*-$[Pd\{P(C_6H_4C_mH_{2m+1})_3\}_2X_2]$ were prepared by reaction 8. Microanalytical results (Table V) were in good agreement with the proposed formulae. For m = 2–5 the products were crystalline, more crystalline and with higher melting (decomposition) points than their platinum analogues. This made recrystallisation of the palladium complexes easier without the need to put the ethanolic solutions in an ice-box at all. For m = 6–9 the complexes were waxes and oils which were purified by column chromatography. The physical states of the higher members resembled those of their alkyl analogues, for example *trans*-$[Pd\{P(C_6H_{17})_3\}_2Cl_2]$ and *trans*-$[Pd\{P(C_6H_4C_9H_{19})_3\}_2Cl_2]$ were both oils of similar viscosity. In the palladium–chlorine stretching region of the infrared they showed a single absorbance at 360–365 cm$^{-1}$ indicative of a *trans*-configuration (cf. *trans*-$[Pd(PPh_3)_2Cl_2]$ has a $\nu_{Pd-Cl}$ at 357 cm$^{-1}$) [20]. In their ^{31}P nmr spectra the chloro-complexes showed a single resonance between $-18.6$ and $-18.9$ ppm downfield from TMP, which is again consistent with a *trans*-configuration [17, 18, 21]. This is a little over 9 ppm downfield from the ^{31}P chemical shift in the *cis*-platinum(II) analogues. The ^{31}P chemical shifts move upfield on replacing Cl by Br and again on replacing Br by I. [1]H nmr spectra merely served to confirm the presence of the phosphine ligands and the absence of any significant amount of organic impurity.

TABLE VI. Physical, Spectroscopic and Analytical Data for the Hydride Complexes *trans*-$[Pt\{P(C_nH_{2n+1})_3\}_2HCl]$.

| $P(C_nH_{2n+1})_3$ | Appearance | M. pt. (°C) | Infrared[a] | | ^{1}H NMR[b] | | | | ^{31}P NMR[c] | | Analytical Data Found ((Calculated)) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $\nu(M-Cl)$ (cm$^{-1}$) | $\nu(M-H)$ (cm$^{-1}$) | $\delta$ (ppm) | $J_{P-H}$ (Hz) | $J_{Pt-H}$ (Hz) | $J_{Pt-H}$ (Hz) | $\delta$ (ppm) | $J_{Pt-P}$ (Hz) | C | H | Cl |
| $P(C_{13}H_{27})_3$ | Cream crystalline solid | 40 | 283 | 2170 | $-16.5$ | 15 | 1270 | Not observed[d] | $-11.4$ | 2693 | 65.4(67.2) | 11.3(11.7) | 2.3(2.5) |
| $P(C_{14}H_{29})_3$ | Cream crystalline solid | 52–54 (dec) | 275 | 2170 | $-16.6$ | 15 | 1316 | Not observed[d] | | | 66.7(68.3) | 11.7(11.9) | 2.0(2.4) |
| $P(C_{16}H_{33})_3$ | Cream crystalline solid | 54(dec) | 275 | 2170 | $-16.5$ | 15 | Not observed[d] | | | | | | |
| $P(C_{18}H_{37})_3$ | Cream crystalline solid | 54(dec) | 275–280 | 2170–2175 | $-16.6$ | 15 | Not observed[d] | | | | 69.8(71.5) | 11.8(12.4) | 2.2(2.0) |

[a]Nujol mulls. [b]Chemical shifts measured in CDCl$_3$ solution relative to TMS as an internal standard. [c]Chemical shifts measured in CDCl$_3$ solution relative to TMP as an external standard. [d]Due to insufficient solubility.

TABLE VII. Physical, Spectroscopic and Analytical Data for [PtL$_n$].

| L | n | Appearance | $^{31}$P NMR Chemical Shift δ (ppm)$^a$ | Analytical Data Found (Calculated) | | |
|---|---|---|---|---|---|---|
| | | | | C | H | P |
| P+⬡)$_3$ | 3 | Bright yellow crystalline | | 65.0(66.1) | 4.5(4.6) | 9.7(9.5) |
| P+⬡)$_3$ | 4 | Pale yellow crystalline solid | b | 67.8(69.5) | 4.9(4.9) | 9.8(10.0) |
| P+⬡CH$_3$)$_3$ | 4 | Yellow crystalline solid | −26.3 | 70.1(71.4) | 6.1(6.0) | 8.2(8.8) |
| P+⬡C$_2$H$_5$)$_3$ | 4 | Yellow crystalline solid | −26.4 | 75.1(73.0) | 6.9(6.9) | 8.7(7.9) |
| P+⬡C$_4$H$_9$)$_3$ | 4 | Red wax | | | | |
| P(C$_8$H$_{17}$)$_4$ | 4 | Yellow oil | | 67.0(68.7) | 11.8(12.3) | 8.0(7.4) |
| P(C$_{16}$H$_{33}$)$_3$ | 4 | Cream crystalline solid | | 76.0(76.3) | 12.8(13.2) | |

$^a$Chemical shifts in C$_6$D$_6$ solution relative to TMP as an external standard. $^b$Insoluble in C$_6$D$_6$ at 25 °C.

Trans-[Pt{P(C$_n$H$_{2n+1}$)$_3$}$_2$HCl]

Trans-[Pt{P(C$_n$H$_{2n+1}$)$_3$}$_2$HCl] were prepared by reaction 4. Microanalytical results (Table VI) were in good agreement with the proposed formulae. The complexes all had low melting (decomposition) points which were similar to those of the corresponding cis-[Pt{P(C$_n$H$_{2n+1}$)$_3$}$_2$Cl$_2$]. The infrared spectra showed single strong absorptions in the Pt–H and Pt–Cl stretching regions at 2170 cm$^{-1}$ and between 275 and 283 cm$^{-1}$ respectively (cf. trans-[Pt(PEt$_3$)$_2$HCl], $\nu_{Pt-H}$ = 2183 cm$^{-1}$, $\nu_{Pt-Cl}$ = 269 cm$^{-1}$) [19, 28]. $^1$H nmr showed a hydride resonance that was a triplet of triplets at −16.5 to −16.6 ppm upfield from TMS, with J$^{195}$P$_{t-}$$^1$H = 1270–1316 Hz and J$^{31}$P$_{-}$$^1$H = 15 Hz (cf. trans-[Pt(PEt$_3$)$_2$HCl], $^1$H chemical shift = −16.9 ppm, J$^{195}$P$_{t-}$$^1$H = 1276 Hz and J$^{31}$P$_{-}$$^1$H = 14.5 Hz) [29]. The $^{31}$P nmr spectrum of trans-[Pt{P(C$_{13}$H$_{27}$)$_3$}$_2$HCl] showed a resonance at −11.4 ppm downfield from TMP with a Pt–P coupling constant of 2693 Hz which was consistent with a trans-configuration [16–18]. The absence of any other bands in the $^1$H and $^{31}$P nmr spectra was taken as an indication of purity.

[PtL$_4$] where L = P(C$_n$H$_{2n+1}$)$_3$ or P(C$_6$H$_4$C$_m$H$_{2m+1}$)$_3$

The zerovalent complexes [PtL$_4$] were prepared from [Pt(COD)$_2$] according to reaction 9. Most of the complexes obtained (Table VII) were yellow crystalline solids although [Pt{P(C$_8$H$_{17}$)$_3$}$_4$] was a yellow viscous oil, and the attempted preparation of Pt{P(C$_6$H$_4$C$_4$H$_9$)$_3$}$_4$] yielded a red sticky gum which was extremely difficult to handle. Satisfactory microanalytical data (Table VII) were obtained for all but the latter complex. All were air sensitive but capable of storage under nitrogen. The infrared spectra showed little other than the presence of

the phosphine and the absence of cyclooctadiene. The $^{31}$P nmr spectra of the P(C$_6$H$_4$Me)$_3$ and P(C$_6$H$_4$-Et)$_3$ complexes in benzene solution showed broad singlets at about −26.3 ppm downfield from TMP consistent with the results of previous workers [13]. There was no $^{195}$Pt–$^{31}$P coupling observable at ambient temperature due to rapid phosphine dissociation.

When the [PtL$_4$] complexes were dissolved in benzene solution all but that with L = P(C$_6$H$_4$C$_4$H$_9$)$_3$ gave yellow solutions with an absorbance peak at about 330 nm and a shoulder at 360 nm. The absorbance decreased with time; for [Pt(PPh$_3$)$_4$] there was an initial induction period but for all the other complexes the decrease in absorbance began as soon as the solution was made up. When this decrease was monitored (see experimental section) it was apparent that two steps were involved, an initial fairly rapid step ascribed to the loss of one phosphine ligand, followed by a slower step that was ascribed to loss of a second phosphine ligand. In support of this [Pt(PPh$_3$)$_3$] gave only a single step when dissolved in benzene solution. It was of interest to obtain comparative rate data for the two steps for several of the different phosphines since this provides a measure of the relative ability of the phosphines to promote coordinative unsaturation. The results in Table X indicate that for 4 × 10$^{-4}$ mol l$^{-1}$ solutions, the values of k$_1^{obs}$ for loss of the first phosphine (reaction 1) are in the order P(C$_{16}$H$_{33}$)$_3$ > PPh$_3$ > P+⬡CH$_3$)$_3$ and for loss of the second phosphine k$_2^{obs}$ (reaction 1) are in the order P+⬡CH$_3$)$_3$ > P(C$_{16}$H$_{33}$)$_3$ > PPh$_3$. Although no measures of the steric bulk of P(C$_{16}$H$_{33}$)$_3$ are available, we believe from other trialkyl phosphines that it is unlikely to have a greater steric bulk than PPh$_3$ [30]. Accordingly we believe the significantly faster rate of loss

TABLE VIII. Physical, Spectroscopic and Analytical Data (or *trans*-[Rh{P(C$_n$H$_{2n+1}$)$_3$}$_2$Cl(CO)].

| P(C$_n$H$_{2n+1}$)$_3$ | Appearance | M. pt. (°C) | Infrared$^a$ | | $^{31}$P NMR$^b$ | | Analytical Data Found (Calculated) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | ν(Rh–Cl) | ν(C≡O) (cm$^{-1}$) | δ (ppm) | J$_{Rh-P}$ (Hz) | C | H | Cl | P |
| P(C$_4$H$_9$)$_3$ | Yellow-orange oil | – | 300 | 1955 | –13.0 | 116 | 52.0(51.6) | 9.5(9.7) | 6.1(6.3) | 11.8(11.0) |
| P(C$_5$H$_{17}$)$_3$ | Orange oil | – | 300 | 1950 | –13.1 | 116 | 64.2(64.8) | 11.0(11.3) | 4.3(3.9) | |
| P(C$_{14}$H$_{29}$)$_3$ | Cream-brown crystalline solid | 40(dec) | 310 | 1940 | | | 71.1(72.3) | 12.1(12.4) | 2.5(2.5) | |
| P(C$_{16}$H$_{33}$)$_3$ | Cream-brown crystalline solid | 42(dec) | 310 | 1940 | –13.0 | 116 | 71.9(73.7) | 12.6(12.6) | 2.3(2.2) | 4.1(3.9) |
| P(C$_{18}$H$_{37}$)$_2$ | Cream-brown crystalline solid | 56(dec) | 310 | 1940 | –13.1 | 115 | 73.2(74.6) | 12.1(12.8) | 2.4(2.0) | 4.4(3.5) |

$^a$Infrared spectra recorded as nujol mulls. $^b$Chemical shifts were measured in deuterochloroform solution relative to TMP as an external standard.
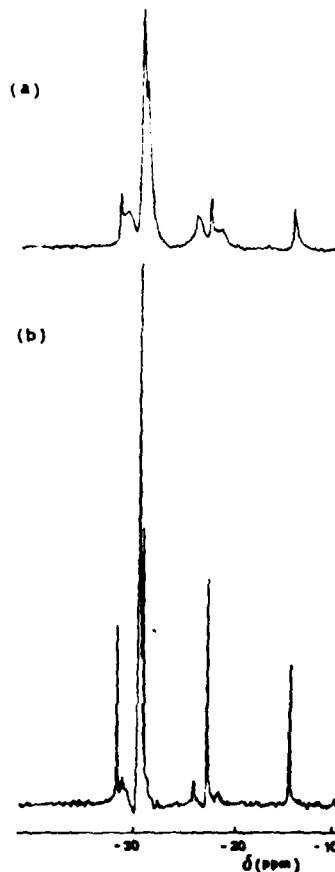


Fig. 5. $^{13}$C nmr spectra in CDCl$_3$ solution of the dark coloured palladium(II) products from reaction 12. (a) P(C$_{13}$H$_{27}$)$_3$, (b) P(C$_{16}$H$_{33}$)$_3$.

of the first phosphine ligand from [Pt {P(C$_{16}$H$_{33}$)$_3$}$_4$] compared to the triarylphosphines is a consequence of the greater σ-donor ability of the trialkylphosphine which results in an undue excess of electron density at the platinum so destabilising the {PtL$_4$} species in accordance with Pauling's electroneutrality principle. The rates of loss of the second phosphine ligand are all very similar so that it would be unjustified to attempt to rationalise these.

Trans-[RhL$_2$Cl(CO)] where L = P(C$_n$H$_{2n+1}$)$_3$ and P(C$_6$H$_4$C$_m$H$_{2m+1}$)$_3$

*Trans*-[RhL$_2$Cl(CO)] were prepared by displacement of CO from [RhCl(CO)$_2$]$_2$ (reaction 10). The lower members of the alkyl series were oils which

TABLE IX. Physical, Spectroscopic and Analytical Data for trans-[Pt{P-⟨ ⟩-P)₃}₂XCl)]

| R | X | Appearance | M. pt. (°C) | Infrared[a] $\nu$(M–X) | $\nu$(C=O) (cm⁻¹) | ³¹P NMR[b] $\delta$ (ppm) | $J_{Rh-P}$ (Hz) | Analytical Data Found (Calculated) C | H | X | P |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_2H_5$ | Cl | Yellow crystalline solid | 194–196(dec) | 317 | 1963 | −24.1 | 126 | 68.0(68.5) | 6.3(6.3) | 4.3(4.1) | 7.5(7.2) |
| | I | Yellow crystalline solid | 154–156(dec) | e | 1965 | | | 63.9(65.5) | 6.8(7.0) | 10.7(11.3) | 6.4(5.5) |
| $C_3H_7$ | Cl | Yellow crystalline solid | 138 | 310 | 1973 | | | 69.7(70.0) | 6.8(6.8) | 3.8(3.8) | 7.0(6.6) |
| $C_4H_9$ | Cl | Yellow crystalline solid | 136 | 310 | 1968 | −24.1 | 126 | 71.1(71.3) | 7.8(7.7) | 3.3(3.5) | 6.1(6.0) |
| | Br | Yellow crystalline solid | 126 | e | 1970 | | | 68.3(67.3) | 7.3(7.5) | 7.5(7.3) | 5.8(5.8) |
| | I | Yellow crystalline solid | 118–120(dec) | e | 1970 | | | 64.7(65.5) | 7.0(7.0) | 11.3(11.3) | 5.6(5.5) |
| $C_5H_{11}$ | Cl | Yellow-brown solid | 67–68(dec) | 315 | 1972 | −23.9 | 126 | 71.1(72.4) | 8.0(8.2) | 3.1(3.2) | 5.9(5.6) |
| | I | Dark oil | – | e | 1975 | | | | | | |
| $C_6H_{13}$ | Cl | Brown solid | 68(dec) | 315 | 1975 | −23.9 | 126 | 72.9(73.3) | 8.5(8.6) | 2.9(3.0) | 5.5(5.2) |
| $C_7H_{15}$ | Cl | Dark oil | – | 315 | 1980 | | | | | | |
| $C_8H_{17}$ | Cl | Dark oil | – | 310 | 1975 | −23.9 | 126 | | | | |

[a]Infrared spectra recorded as nujol mulls. [b]Chemical shifts were measured in deuterochlorofom solution relative to TMP as an external standard. [c]$\nu$(M–X) for all bromide and iodide complexes are assumed to be <200 cm⁻¹.

TABLE X. Rates of Dissociation of 4 x 10⁻⁴ mol l⁻¹ Solutions of [PtL₄] in Benzene at 25 °C.[a]

| L | $k^{obs}$ (s⁻¹) | $k^{obs}$ (s⁻¹) | $k_1^{obs}$ (s⁻¹) | $k_2^{obs}$ (s⁻¹) |
|---|---|---|---|---|
| $PPh_3$ | 1.8(5) x 10⁻³ | 9.5 x 10⁻⁵ | 1.5 x 10⁻³ | 3.5 x 10⁻⁵ |
| $PPh_3$[b] | 1.4 x 10⁻³ | 1.2 x 10⁻⁴ | 1.1 x 10⁻³ | 4.0 x 10⁻⁵ |
| P-⟨ ⟩-CH₃)₃ | 6.2 x 10⁻⁴ | 1.8 x 10⁻⁴ | 3.5 x 10⁻⁴ | 6.7 x 10⁻⁵ |
| $P(C_{10}H_{21})_3$ | e | 8.9 x 10⁻³ | e | 3.7 x 10⁻⁵ |

[a]$k^{obs}$ and $k^{obs}$ evaluated from plots of the type shown in Fig. 1; $k_1^{obs}$ evaluated from equation 4 and $k_2^{obs}$ from equation 6.
[b]In toluene solution. [e]Reaction too fast to be studied by the present method.

29.

TABLE XI. $^{13}$C Chemical Shifts and Coupling Constants for Tertiary Alkyl Phosphine Complexes of Platinum and Palladium.$^a$

| Metal Complex | Chemical Shifts (ppm) | | | | | | | | | | | | | | | | Coupling Constants (Hz) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ | $C_8$ | $C_9$ | $C_{10}$ | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{14}$ | $C_{15}$ | $C_{16}$ | $J_{PC_1}$ | $J_{PC_2}$ | $J_{PC_3}$ | $J_{PC_4}$ | $J_{PC_5}$ |
| [PtCl$_3$(PtBu$^n_3$)]$_2^b$ | –24.5 | –26.6 | –24.6 | –14.1 | | | | | | | | | | | | | 32 | <5 | 15 | – | – |
| [PtCl$_2$(PtBu$^n_3$)]$_2^b$ | –22.8 | –26.2 | –24.6 | –14.2 | | | | | | | | | | | | | 39 | <5 | 15 | 39 | 20 |
| trans-[PtCl$_2${P(Octyl$^n_3$)}$_2$] | –21.6 | –31.9 | –31.3 | –29.2 | –24.1 | | –22.7 | | | | | | | | | | 25.4 | <5 | 11.2 | – | – |
| cis-[PtCl$_2${P(Octyl$^n_3$)}$_2$] | –24.6 | –31.9 | –31.1 | –29.2 | –24.6 | –14.1 | –22.7 | | | | | | | | | | 16.8 | <5 | 6.7 | 26.8 | Not observed |
| trans-[PtCl$_2$(P(C$_{13}$H$_{27}$)$_3$)]$_2$ | –21.7 | –32.0 | –31.3 | –29.7 | –29.7 | –14.1 | –29.7 | –29.4 | –29.4 | –24.1 | –24.1 | –22.7 | –14.1 | | | | 27.2 | <5 | –18 | | |
| Red wax containing | –21.6 | –31.9 | –31.1 | | | | | | | | –24.1 | –22.7 | –14.1 | | | | c | c | c | | |
| Pt(C$_{10}$H$_{21}$)$_2$ from reaction 12 | (broad) | (broad) | (broad) | | | | | | | (broad) | | | | | | | | | | | |
| Dark brown product containing | Not observed | Not observed | Not observed | | –29.7 | | | | | –29.4 | | | Not observed | –22.7 | –14.1 | | c | | | | |
| Pt(C$_{18}$H$_{37}$)$_2$ from reaction 12 | | | | | | | | | | | | | | | | | | | | | |

$^a$ All chemical shifts were measured in CDCl$_3$ solution relative to TMS which was added as an internal standard.  $^b$ From reference 21.  $^c$ Impossible to calculate.

were purified by pumping *in vacuo* at room temperature for 24 hours. The high aryls with seven or more carbon atoms in the alkyl side chain were also rather tarry oils which were purified in the same way. Good microanalytical results (Tables VIII and IX) were obtained for all members of the series except the oily higher members of the aryl series. Of the compounds reported in Table IX only the butyl and octyl members have been described previously and the latter was not obtained in a pure state [31].

The infrared spectra obtained here were consistent with those of the lower homologues reported previously. Thus the C=O stretching frequencies in the present complexes lay in the range 1940–1955 cm$^{-1}$ (trialkyl) and 1963–1980 cm$^{-1}$ (triaryl) and the Rh–Cl stretching frequencies in the range 300–310 cm$^{-1}$ (trialkyl) and 310–317 cm$^{-1}$ (triaryl) (*cf.* *trans*-[Rh(PMe$_3$)$_2$Cl(CO)], $\nu_{C=O}$ = 1954, $\nu_{Rh–Cl}$ = 302 [32] and *trans*-[Rh{P(C$_6$H$_4$Me-p)$_3$}Cl(CO)], $\nu_{C=O}$ = 1960, $\nu_{Rh–Cl}$ = 308 cm$^{-1}$) [33]. The $^{31}$P nmr spectra show a doublet with a chemical shift of about –13 ppm (trialkyl) and about –24 ppm (triaryl) and $^{103}$Rh–$^{31}$P coupling constants of about 116 Hz (trialkyl) and 126 Hz (triaryl) consistent with previous literature reports [18, 34, 35].

Appendix

For reaction 5, the rate of consumption of PtL$_3$ is given by:

$$\frac{-d[PtL_3]}{dt} = k_2[PtL_3] - k_{-2}[PtL_2][L] \qquad (13)$$

Let $C'_0$, $C'_e$ and $C'$ be the concentrations of [PtL$_3$] initially, at equilibrium and at time t respectively. Since the concentrations of [PtL$_2$] and L at t = 0 are zero and $C'_0$ respectively (L is formed in equivalent amount to [PtL$_3$] in reaction 2), it follows that the concentrations of [PtL$_2$] and L at equilibrium are ($C'_0 - C'_e$) and ($2C'_0 - C'_e$) respectively. At

equilibrium, $-d[PtL_3]/dt = 0$, whence from equation 13,,

$$k_2 C'_e = k_{-2}(C'_o - C'_e)(2C'_o - C'_e) \qquad (14)$$

from which

$$k_{-2} = \frac{k_2 C_e}{(C'_o - C'_e)(2C'_o - C'_e)} \qquad (15)$$

Rewriting equation 13 and substituting for $k_{-2}$ from equation 15 gives

$$\frac{-dC'}{dt} = \left\{ k_2 \left[ C' - \frac{C'_e((C'_o - C')(2C'_o - C'_e)}{(C'_o - C'_e)(2C'_o - C'_e)} \right] \right\} \qquad (16)$$

For convenience, let $B = C'_e/\{(C'_o - C'_e)(2C'_o - C'_e)\}$. $B$ will always have a positive value.

$$\therefore \frac{dC'}{dt} = -k_2\{C' - B(2C'^2_o - 3C'C'_o + C'^2)\} \qquad (17)$$

$$\therefore \frac{dC'}{dt} = Bk_2\{C'^2 - \frac{C'}{B}(1 + 3C'_oB) + 2C'^2_o\} \qquad (18)$$

$$\therefore \int \frac{dC'}{C'^2 - \frac{C'}{B}(1 + 3C'_oB) + 2C'^2_o} = Bk_2 t + \text{constant} \qquad (19)$$

$$\therefore \int \frac{dC'}{\left\{C' - \frac{(1 + 3BC'_o)}{2B}\right\}^2 - \left\{\frac{(1 + 6BC'_o + B^2C'^2_o)}{4B^2}\right\}} =$$

$$= Bk_2 t + \text{constant} \qquad (20)$$

Integration of equation 20 yields:

$$\left\{ \frac{1}{\frac{1}{B}\sqrt{(B^2C^2_o + 6BC'_o + 1)}} \right\} \times$$

$$\times \ln \left\{ \frac{\frac{1}{2B}\sqrt{(1 + 6BC'_o + B^2C'^2_o)} + C' - \frac{1}{2B}(1 + 3BC'_o)}{\frac{1}{2B}\sqrt{(1 + 6BC'_o + B^2C'^2_o)} - C' - \frac{1}{2B}(1 + 3BC'_o)} \right\}$$

$$\qquad (21)$$

$$= Bk_2 t + \text{constant}$$

Minor rearrangement of eqn. 21 yields eqn. 6.

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# PREPARATION AND PROPERTIES OF TERTIARY

# PHOSPHINES WITH EXTREME SOLUBILITY IN

# NON-POLAR SOLVENTS

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## ABSTRACT

The preparation and properties of two series of new tertiary phosphines, $P(C_nH_{2n+1})_3$, where n=10-19, $\underline{1}$, and $P(C_6H_4-C_mH_{2m+1}-p)_3$, where m=3-9, $\underline{2}$, are described. These phosphines have been used to prepare a range of transition metal complexes that are extremely soluble in non-polar hydrocarbon solvents. A number of examples are described in which these complexes act as more active and selective catalysts than their more conventional analogues.

## INTRODUCTION

The present paper describes the preparation, characterisation and transition metal complexes of a series of tertiary phosphines that are extremely soluble in non-polar, especially hydrocarbon solvents. The reasons for wishing to prepare such phosphines are many:

1. A major goal confronting all organometallic chemists concerned with catalysis is the activation of alkanes. If homogeneous catalysts are to be used in this role they must be freely soluble in the alkane, since if any other solvent were added to promote miscibility between alkane and catalyst that second solvent would inevitably be more active than the alkane.

2. Homogeneous catalysts are now widely used in industry. As energy becomes ever more expensive, it is necessary to continually improve the catalysts available. Since solvent-catalyst interactions are very important in most homogeneously catalysed systems, it seemed constructive to prepare metal complex catalysts that would be extremely soluble in the hydrocarbon feedstocks that provide the basis of the petrochemicals industry.

3. Metal complexes with high solubilities in non-polar media are of value in the solvent extraction of metals, as stationary phases in gas chromatography, as additives in organic materials such as plastics and paints for prevention of algae growth (eg on ships' hulls) or as catalysts to promote the natural weathering of chemical agents.

4. Long chain phosphines could be used to prepare Langmuir-Blodgett films[1], microemulsions[2,3] and vesicles[4], all of which could be used to coordinate transition metals on their surfaces.

## PREPARATION OF THE PHOSPHINES

We have prepared two series of tertiary phosphines, $\underset{\sim}{1}$[5] and $\underset{\sim}{2}$[6]. Both

$$P(C_nH_{2n+1})_3$$

n=10-19

$\underset{\sim}{1}$

$$P(\text{—}\!\!\left\langle\bigcirc\right\rangle\!\!\text{—}C_mH_{2m+1})_3$$

m=3-9

$\underset{\sim}{2}$

33.
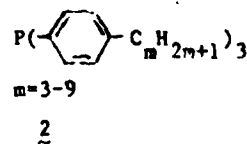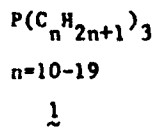
the fully aliphatic and the aromatic series were prepared because the two
series have significantly different electronic effects on coordinated metal
ions, so that for some situations 1 are more valuable than 2, whereas in
other situations the reverse is true. The trialkylphosphines, 1, were
prepared by treating the Grignard reagent of the n-alkyl bromide with
phosphorus trichloride in tetrahydrofuran. . They were purified by very
careful recrystallisation from a mixture of chloroform and ethanol. They
were extremely soluble in hydrocarbon solvents such as dichloromethane,
chloroform, carbon tetrachloride and 1,2-dichloroethane and moderately
soluble in tetrahydrofuran, benzene and other aromatic solvents as well as in
hot alcohols such as methanol and ethanol and warm acetone. 1 were however
insoluble in cold alcohols and acetone. These solubility properties are, of
course, very similar to those of their precursors and of any side products of
their preparation, which leads to any important general conclusion. When
synthesising compounds with extreme solubility properties it is essential to
achieve maximum purity at every stage including the initial reactants. It is
vital not to delay purification because the problems do not increase
linearly, they increase exponentially.

On exposure to the air the tertiary phosphines, 1, were very readily
oxidised to a complex mixture of phosphorus(III) and phosphorus(V) products
of the type $P(OR)_{3-n}R_n$ and $OP(OR)_{3-n}R_n$ where n = 0-3. However treatment with
a slight excess of 6% hydrogen peroxide resulted in smooth oxidation to the
phosphine oxides $OPR_3$, which were stable in air and rather more crystalline
than the corresponding phosphines, although their solubility properties were
essentially the same as those of the phosphines. In direct contrast to
phosphine oxides $OPR_3$ with n-alkyl chains that contain 8 or less carbon
atoms, the present phosphine oxides with 10-19 carbon atoms in their alkyl
chains were not deliquescent at all. The mass spectra of both the tertiary
phosphines, 1, and their corresponding trialkylphosphine oxides all show
strong parent ion peaks[5].

34.

The second series of tertiary phosphines, 2, were prepared in a similar manner to the first series by treating the Grignard reagent of the corresponding p-alkylbromobenzene with phosphorus trichloride in tetrahydrofuran[6]. However in order to use this route it was essential to devise a preparative route for the p-alkylbromobenzene; since purification must be accomplished at all stages it was essential to devise a route that yields the para-isomer in as pure a form as possible since separation of the ortho-, meta- and para-isomers will not be easy. There are many literature routes that yield a mixture of isomers, but only one was available that yielded the pure para-isomer and yields were poor. Accordingly the three stage synthesis of p-alkylbromobenzenes shown in Scheme 1 was developed. It gave the pure para-isomer in 46-60 per cent overall yield. p-Propylbromobenzene can be prepared following Scheme 1,

## Scheme 1
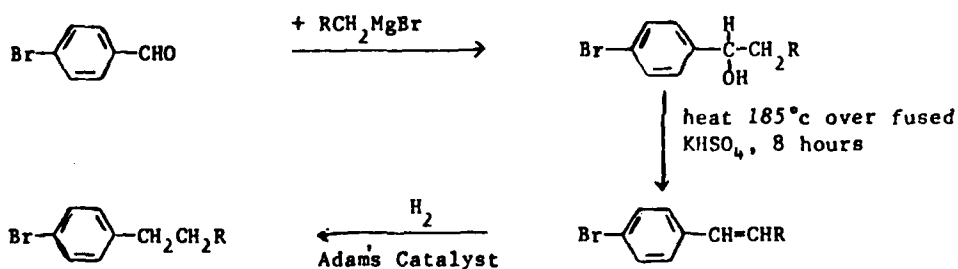


but it is more easily prepared by the reaction of alkyl bromide with the mono-Grignard reagent of p-dibromobenzene, followed by hydrogenation of the resulting p-propenylbromobenzene.

All the tris(p-alkylaryl)phosphines were extremely soluble in hydrocarbon solvents such as hexane and chlorinated hydrocarbons such as dichloromethane, chloroform and carbon tetrachloride, and moderately soluble in tetrahydrofuran, diethyl ether and aromatic solvents such as benzene and

toluene. The lower members of the series were soluble in ethanol but this decreased as the alkyl chain length increased. All $\underset{\sim}{2}$ were sensitive to oxygen both as solids or oils and in solution. This is in contrast to triphenylphosphine itself which is fairly resistant to oxidation both as a solid and in solution. Unlike $\underset{\sim}{1}$, which yield a complex mixture of products on oxidation in air, $\underset{\sim}{2}$ only give a single product, the phosphine oxide $OP(C_6H_4R-\underline{p})_3$. The sensitivity to air oxidation increased as the alkyl chain on the phenyl ring increased in length. Oxidation with 6% hydrogen peroxide gave a convenient preparative route to the phosphine oxides $OP(C_6H_4R-\underline{p})_3$ which had similar solubility characteristics to the parent phosphines, $\underset{\sim}{2}$.

The mass spectra of $\underset{\sim}{2}$ show a strong parent ion peak, whereas the mass spectra of $OP(C_6H_4R-\underline{p})_3$ have M-H as the most intense peak[7]. There are many examples of situations in which minor modifications to triphenylphosphine causes major changes in properties. Ease of oxidation has already been mentioned. The mass spectra of $\underset{\sim}{2}$ provide another example since the most intense ions in the mass spectra of $\underset{\sim}{2}$ are those of $P(C_6H_4R-\underline{p})_3^+$. By contrast the most intense ion in the mass spectrum of triphenylphosphine is $\underset{\sim}{3}$.
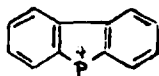


$\underset{\sim}{3}$

PREPARATION OF TERTIARY PHOSPHINE – TRANSITION

METAL COMPLEXES

A number of transition metal complexes of the two series of tertiary phosphines, $\underset{\sim}{1}$ and $\underset{\sim}{2}$, have been prepared and characterised[8]. Since the complexes displayed essentially the same extreme solubility characteristics as the parent phosphines, the preparative routes used were selected on the basis of those which gave the cleanest reactions with either volatile or otherwise easily separated side products, and a minimum of isomers. The

complexes prepared are shown in reactions 1-8[8, 9]. The rhodium(I)-iodo complex shown in reaction 8 can only be prepared in the presence of excess phosphine; in the absence of excess phosphine it dimerises reversibly as in reaction 9.

$$[Pt(cod)Cl_2] + 2PR_3 \xrightarrow[\text{cod=1,5-cyclooctadiene}]{R=\text{alkyl,aryl}} \underline{cis}\text{-}[Pt(PR_3)_2Cl_2] + cod \qquad (1)$$

$$[Pd(cod)Cl_2] + 2PR_3 \xrightarrow{R=\text{alkyl,aryl}} \underline{trans}\text{-}[Pd(PR_3)_2Cl_2] + cod \qquad (2)$$

$$[Pt(PR_3)_2Cl_2] + 2N_2H_4 \xrightarrow[R=\text{alkyl}]{EtOH,CHCl_3} \underline{trans}\text{-}[Pt(PR_3)_2HCl] + NH_4Cl + \uparrow N_2 + NH_3 \quad (3)$$

$$2[Pt(cod)Cl_2] + 2NaOH \xrightarrow{MeOH,H_2O} [PtCl(C_8H_{12}OCH_3)]_2 + 2NaCl$$
$$\downarrow 4PR_3, R=\text{alkyl}$$
$$2 \ \underline{trans}\text{-}[Pt(PR_3)_2HCl] + 2C_8H_{12}OCH_3 \qquad (4)$$

$$[Pt(cod)_2] + 4PR_3 \xrightarrow[R=\text{alkyl, aryl}]{hexane} [Pt(PR_3)_4] + 2cod \qquad (5)$$

$$[Rh_2Cl_2(CO)_4] + 4PR_3 \xrightarrow[R=\text{alkyl, aryl}]{CHCl_3} 2 \ \underline{trans}\text{-}[Rh(PR_3)_2Cl(CO)] + 4CO \qquad (6)$$

$$\underline{trans}\text{-}\left[Rh(PR_3)_2Cl(CO)\right] + NaBr \xrightarrow[R=alkyl, \ aryl]{acetone} \underline{trans}\text{-}\left[Rh(PR_3)_2Br(CO)\right] + NaCl \quad (7)$$

$$\underline{trans}\text{-}\left[Rh(PR_3)_2Cl(CO)\right] + NaI \xrightarrow[R=alkyl, \ aryl]{acetone \ + \ excess \ PR_3} \underline{trans}\text{-}\left[Rh(PR_3)_2I(CO)\right] + NaCl \quad (8)$$



$$2\left[Rh(PR_3)_2I(CO)\right] \underset{+2PR_3}{\overset{-2PR_3}{\rightleftharpoons}} \begin{bmatrix} OC & I & PR_3 \\ & Rh \quad Rh & \\ R_3P & I & CO \end{bmatrix} \underset{-2PR_3, \ +2CO}{\overset{+2PR_3, \ -2CO}{\rightleftharpoons}} \left[Rh(PR_3)_2I\right]_2 \quad (9)$$

The very different solubility properties of these complexes prepared in reactions 1-9 as compared to their triphenylphosphine or triethylphosphine analogues gives rise to differences in their chemical properties. These have been investigated in some detail. Here we summarise the results referring the interested reader to the appropriate literature reference.

The complexes $\left[M(PR_3)_2Cl_2\right]$, M = Pd, Pt, in association with tin(II) chloride provide more selective, more active catalysts for the selective hydrogenation of polyolefins to monoolefins when long alkyl chain aliphatic and aromatic tertiary phosphines are present than their $PEt_3$ and $PPh_3$ analogues. In particular the platinum(II) complexes of 1 and 2 are particularly active in the absence of any added solvent, ie, when the hydrogenation is effected in pure polyolefin [10],[11].

The introduction of long alkyl chains into the para-position of tri-phenylphosphine reduces the ability of $\left[Rh(PR_3)_2Cl(CO)\right]$ complexes to isomerise olefins and enhances their ability to promote the formation of n-aldehydes during hydroformylation; both effects are highly constructive from the viewpoint of the petrochemicals industry[12]. This demonstrates an enhanced selectivity that may have military advantages.

The presence of the para-alkyl groups in $\underset{\sim}{2}$ alters the relative concentrations of the rhodium(I) complexes formed when $\left[Rh(PR_3)_2X(CO)\right]$, $PR_3 = \underset{\sim}{2}$, X = Cl, Br and I, undergoes oxidative-addition with alkyl halides. This has enabled us to gain a greater insight into the mechanism of the rhodium(I) - catalysed carbonylation of methanol which is a commercially very important reaction[9],[13]. Oxidative-addition of alkyl halides is potentially a reaction that could be exploited in the degradation of mustard.

## CONCLUSIONS

Two new series of tertiary phosphines, $\underset{\sim}{1}$ and $\underset{\sim}{2}$ have been prepared and characterised. These phosphines not only form strong complexes with transition metals, but lead to complexes which are extremely soluble in non-polar solvents. This extreme solubility gives rise to enhanced activity specificity and selectivity of these complexes when used as catalysts in a number of reactions.

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## ACKNOWLEDGEMENT

# THE PREPARATION OF *cis*- AND *trans*-[RhI(CO)(PAr₃)₂] (Ar = ARYL) AND THEIR READY DISSOCIATION IN SOLUTION

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(Received April 6th, 1983)

## Summary

Attempts to prepare [RhX(CO)(PAr₃)₂] complexes have shown that when X = I these complexes are far less stable than the well-known [RhCl(CO)(PPh₃)₂]. The bromo complexes [RhBr(CO)(PAr₃)₂] (Ar = C₆H₅, $p$-EtC₆H₄) can be prepared by simple halide exchange from their respective chloro complexes. However a similar attempt to prepare the iodo complexes was frustrated by dissociative equilibria; in the absence of oxygen dimers were formed, whereas in the presence of oxygen polymeric oxygen complexes were formed. The ease of dissociation of phosphine can be attributed to the greater steric crowding in the iodo complexes than in the chloro and bromo complexes. The complex [RhI(CO)(PPh₃)₂] could only be obtained in the presence of excess PPh₃, which inhibits the dissociation. The identification of this monomer was further complicated by the previously unnoticed presence of both *cis* and *trans* isomers in the solid state.

## Introduction

Investigation into the oxidative-addition of methyl iodide to *trans*-[RhCl(CO)(PAr₃)₂] (I) where Ar = $p$-alkylaryl), has been found to be more complex [1] than previously indicated in the literature [2]. Attempts to determine the mechanism, which involves halide catalysis, were complicated by the possibility of halide exchange with the rhodium complex I which may lead to the more reactive species [RhX(CO)(PAr₃)₂] (II, X = I). It was considered appropriate therefore, to prepare and characterise complexes of type II where Ar = aryl and X = Br or I in order to study their oxidative-addition with alkyl bromides or iodides respectively, which would obviate any possibility of halide exchange.

## Experimental

The *trans*-[RhCl(CO)(PAr₃)₂] (Ar = Ph, $p$-EtC₆H₄ and $p$-PrC₆H₄) and [RhX(CO)(PPh₃)]₂ complexes were prepared by literature methods [3–5].

*Preparation of trans-[RhBr(CO)( P(p-EtC$_6$H$_4$)$_3$)$_2$]*

To *trans*-[RhCl(CO)(P( *p*-EtC$_6$H$_4$)$_3$)$_2$] (0.1 g, 1.2 × 10$^{-4}$ mol) was added sodium bromide (0.17 g, 1.7 × 10$^{-3}$ mol) in acetone (100 ml). After stirring for 2½ h at room temperature, the excess sodium bromide together with the sodium chloride formed in the reaction was filtered off. The solvent was evaporated under reduced pressure and the yellow residue washed with ethanol. This was filtered and dried, yield 0.06 g, 56%, $\nu$(CO) 1967 cm$^{-1}$ (Nujol mull), TLC (acetone) gave one spot, $R_f$ 0.83 (cf. *trans*-[RhCl(CO)(P( *p*-EtC$_6$H$_4$)$_3$)$_2$], $R_f$ 0.68 under identical conditions). Recrystallisation of the product from benzene/ethanol, gave the product, m.p. 164°C. Found: C, 65.0; H, 6.0. C$_{49}$H$_{54}$BrOP$_2$Rh calcd.: C, 65.3; H, 5.9%.

*Preparation of trans-[RhBr(CO)(PPh$_3$)$_2$]*

*trans*-[RhBr(CO)(PPh$_3$)$_2$] was prepared by the same method as *trans*-[RhBr(CO)(P( *p*-EtC$_6$H$_4$)$_3$)$_2$], yield 65%, m.p. 173°C, $\nu$(CO) (Nujol mull) 1969 cm$^{-1}$ (as literature [12b]) TLC (acetone) gave one spot, $R_f$ 0.83.

*Attempted preparation of [RhBr(CO)( P(p-PrC$_6$H$_4$)$_3$)$_2$]*

To *trans*-[RhCl(CO)(P( *p*-PrC$_6$H$_4$)$_3$)$_2$] (0.12 g, 1.27 × 10$^{-4}$ mol) in acetone (30 ml) was added sodium bromide (0.2 g, 1.9 × 10$^{-3}$ mol) and the solution stirred for 2½ h at room temperature. The excess sodium halides were filtered off under reduced pressure leaving a yellow solid which was recrystallised from a benzene/ethanol mixture and the orange precipitate filtered and dried, yield 0.06 g, 77%, m.p. 63°C. IR (Nujol mull) indicated no $\nu$(CO) but absorbances typical of tris( *p*-propylphenyl)phosphine were present. Found: C, 56.8; H, 6.1. [C$_{27}$H$_{33}$BrO$_2$PRh], calcd.: C, 56.6; H, 5.8%. TLC (acetone) gave $R_f$ 0.58.

*Reaction of trans-[RhCl(CO)(PPh$_3$)$_2$] with potassium iodide in the presence of triphenylphosphine and air to give trans-[RhI(CO)(PPh$_3$)$_2$]*

*trans*-[RhCl(CO)(PPh$_3$)$_2$] (0.12 g, 1.7 × 10$^{-4}$ mol), triphenylphosphine (0.3 g, 1.2 × 10$^{-3}$ mol) and potassium iodide (0.4 g, 2.4 × 10$^{-3}$ mol) were mixed together in acetone (50 ml). The mixture was stirred at room temperature for 25 h and left at room temperature for a further 3 days. A yellow solid was filtered off and dried. The complex was recrystallised from ethanol/benzene in the presence of some triphenyl-phosphine and washed with ethanol, yield 0.1 g, 75%; m.p. 153-155°C (dec.); $\nu$(CO) (Nujol) 1985 cm$^{-1}$; $\nu$(CO) (CHCl$_3$) 1980 (vs) and 2025 cm$^{-1}$(w). Found C, 56.9; H, 3.8. C$_{37}$H$_{30}$IOP$_2$Rh calcd.: C, 56.9; H, 3.8%. $^{31}$P NMR in CDCl$_3$ gave $\delta$ 27.3 ppm (d), $J$(Rh-P) 123.05 Hz due to *trans*-[RhI(CO)(PPh$_3$)$_2$] and, if air is not rigorously excluded $\delta$ 30.97 ppm (d), $J$(Rh-P) 83.98 Hz due to *trans*-[RhI(CO)(O$_2$)(PPh$_3$)$_2$] together with a very weak signal at $\delta$ 29.04 ppm (d), $J$(Rh-P) 123.0 Hz.

To the filtrate was added water causing triphenylphosphine to precipitate (yield 0.28 g, 93%). The product was identified by IR spectroscopy and melting point.

*Preparation of cis-[RhI(CO)(PPh$_3$)$_2$]*

*cis*-[RhI(CO)(PPh$_3$)$_2$] was prepared in air by an identical method to that used to prepare *trans*-[RhI(CO)(PPh$_3$)$_2$], but here the preparation was carried out at 0°C. The product *cis*-[RhI(CO)(PPh$_3$)$_2$], gave $\nu$(CO) 1969 cm$^{-1}$ (Nujol mull) and $\nu$(CO) 1980 (s) and 2025 cm$^{-1}$ (w) (CHCl$_3$). When dissolved in CDCl$_3$ $^{31}$P NMR gave $\delta$ 27.3 ppm (d), $J$(Rh-P) 123.05 Hz due to *trans*-[RhI(CO)(PPh$_3$)$_2$] and if air is not

vigorously excluded, $\delta$ 30.97 ppm (d), $J$(Rh–P) 83.98 Hz due to *trans*-[RhI(CO)(O$_2$)(PPh$_3$)$_2$]. IR spectroscopy showed the *cis* isomer converted to the *trans* isomer when stored in the solid state at room temperature (25°C) for 1 month.

*Reaction of trans-[RhCl(CO)(PPh$_3$)$_2$] with potassium iodide under carbon monoxide in the absence of added triphenylphosphine*

*trans*-[RhCl(CO)(PPh$_3$)$_2$] (0.13 g, 1.9 × 10$^{-4}$ mol) was dissolved in acetone (40 ml). After 20 minutes at room temperature, under carbon monoxide, potassium iodide was added (0.6 g, 3.6 × 10$^{-3}$ mol). The solution was stirred for 17 h at room temperature, after which time yellow crystals had precipitated. These were filtered under carbon monoxide, washed with water and dried in vacuo, yield 0.14 g, 94%. IR spectroscopy and microanalysis confirmed that the product was *trans*-[RhI(CO)(PPh$_3$)$_2$].

*Reaction of trans-[RhCl(CO)(PPh$_3$)$_2$] with potassium iodide in air in the absence of free triphenylphosphine*

To *trans*-[RhCl(CO)(PPh$_3$)$_2$] (0.19 g, 2.7 × 10$^{-4}$ mol) was added potassium iodide (0.6 g, 3.6 × 10$^{-3}$ mol) in acetone (100 ml). After 24 h the colour of the solution had changed to brown. The potassium iodide and potassium chloride were filtered off. The reaction mixture was then evaporated to dryness, dissolved in benzene and again filtered. On evaporation of the filtrate under reduced pressure a brown oil remained. IR spectroscopy showed no absorbances assignable to $\nu$(CO) or $\nu$(M–Cl) but gave absorbances corresponding to triphenylphosphine oxide and water. The brown oil crystallized on cooling in liquid nitrogen under petroleum ether (b.p. 40–60°C). This was filtered off and dried, yield 0.09 g, 59.0%. Found: C, 37.2; H, 3.57. C$_{18}$H$_{15}$IO$_3$PRh · 2H$_2$O calcd.: C, 37.5; H, 3.3%. [RhCl(O$_2$)(OPPh$_3$)$_{0.67}$], has previously been reported [6] as the product of photoinduced oxidation of *trans*-[RhCl(CO)(PPh$_3$)$_2$].

*Decarbonylation of trans-[RhI(CO)(PPh$_3$)$_2$]*

*trans*-[RhI(CO)(PPh$_3$)$_2$] (0.05 g, 6.4 × 10$^{-4}$ mol) was partially dissolved in degassed acetone (12 ml), after stirring for 45 h under nitrogen the solution remained yellow. On evaporating the acetone under reduced pressure at 50°C, the solution started to darken. After complete evaporation to dryness a brown solid remained. The product was dissolved in degassed dichloromethane, and again evaporated to dryness. This was repeated several times to effect complete decarbonylation. The product was isolated from degassed petroleum ether (b.p. 40–60°C). The product was filtered off and dried, yield 0.04 g, 83%. It was identified as [Rh$_2$I$_2$(PPh$_3$)$_4$] by mixed melting point and IR spectroscopy.

*Reaction of trans-[RhCl(CO)(P(p-EtC$_6$H$_4$)$_3$)$_2$] with potassium iodide*

To *trans*-[RhCl(CO)(P(p-EtC$_6$H$_4$)$_3$)$_2$] (0.16 g, 1.9 × 10$^{-4}$ mol) was added potassium iodide (0.4 g, 2.4 × 10$^{-3}$ mol) in acetone (80 ml) and the mixture stirred for 3 h. The potassium halides were filtered off and the acetone evaporated under reduced pressure. The product was re-dissolved in chloroform, and the remaining halide salts were removed by filtration. After a further evaporation to dryness and washing with ethanol, the product was collected and dried, yield 0.1 g, 89%. TLC (20% chloroform/80% ethanol) gave one spot $R_f$ 0.81, $\nu$(CO) (Nujol) 1976 (s) and 2020 cm$^{-1}$(w). Found: C, 49.05; H, 5.29. C$_{25}$H$_{27}$IOPRh calcd.: C, 49.6; H, 4.5%.

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### Reaction of [Rh₂Cl₂{P(p-EtC₆H₄)₃}₄] with lithium iodide

$[Rh_2Cl_2\{P(p\text{-}EtC_6H_4)_3\}_4]$ (0.4 g, $2.4 \times 10^{-4}$ mol) was stirred with lithium iodide (2.0 g, $1.5 \times 10^{-2}$ mol) in ethanol (30 ml) for 3 h at reflux under nitrogen. The ethanol was evaporated off until only a brown solid was left. Water (50 ml) was added and the brown solid extracted in petroleum ether (b.p. 60–80°C). Evaporation of the petroleum ether left a brown solid which was filtered off under nitrogen. This was washed with water and dried in a drying pistol, yield 0.41 g, 90.7%. The product was washed with petroleum ether (b.p. 40–60°C) and dried. Found: C, 60.4; H, 5.7. $C_{48}H_{54}IP_2Rh \cdot 2H_2O$ calcd.: C, 59.8; H, 6.0%.

### Reaction of [Rh₂I₂(PPh₃)₄] with carbon monoxide [7]

$[Rh_2I_2(PPh_3)_4]$ (0.04 g, $2.7 \times 10^{-5}$ mol) was dissolved in acetone (50 ml) and carbon monoxide was passed through the solution for 2 h. The solution turned yellow and on addition of water gave a yellow precipitate which was filtered off and dried, yield 0.03 g, 72%, $\nu$(CO) (Nujol) 1985 cm$^{-1}$. The IR spectrum was identical to that of $trans$-[RhI(CO)(PPh₃)₂].

### Attempted preparation of [RhI(CO){P(p-EtC₆H₄)₃}₂] from the reaction of carbon monoxide with [Rh₂I₂{P(p-EtC₆H₄)₃}₄] · 2H₂O

$[Rh_2I_2\{P(p\text{-}EtC_6H_4)_3\}_4]\cdot 2H_2O$ (0.16 g, $8.4 \times 10^{-5}$ mol) was dissolved in degassed acetone (80 ml), through which carbon monoxide was passed. After 4 h degassed water was added causing a brown product to precipitate which was filtered off and dried. IR spectroscopy confirmed the presence of some $[Rh_2I_2(CO)_2\{P(p\text{-}EtC_6H_4)_3\}_2]$, but following dissolution in degassed ethanol and evaporation to dryness, the brown product was shown by IR spectroscopy to have no $\nu$(CO) and be identical to the starting material, yield 0.12 g, 75%.

### Preparation of [RhI(PPh₃)₃] [7]

To triphenylphosphine (6.0 g, $2.3 \times 10^{-2}$ mol) in hot ethanol (200 ml) was added $RhCl_3 \cdot 3H_2O$ (1.0 g, $3.8 \times 10^{-3}$ mol) in ethanol (60 ml) and the mixture brought to the boil. When lightening of the colour occurred and orange crystals deposited (5–10 min), a solution of LiI (4.0 g, $2.9 \times 10^{-2}$ mol) in hot ethanol (80 ml) was added and the solution stirred under reflux for 3–4 h and brown crystals collected from the warm solution. These were filtered off and dried, yield 3.85 g, 99.7%. The solid was recrystallised from ethanol/benzene containing some triphenylphosphine. Found: C, 67.2; H, 4.9. $C_{54}H_{45}IP_3Rh$ calcd.: C, 67.8; H, 4.7%.

### Preparation of [Rh₂I₂(PPh₃)₄]

To [RhI(PPh₃)₃] (1.0 g, $9.8 \times 10^{-4}$ mol) under nitrogen was added degassed isobutyl methyl ketone and the mixture refluxed for 2 h; addition of lithium iodide (1.0 g, $7.5 \times 10^{-3}$ mol) and stirring under reflux for another hour gave darkening of the solution. The solution was cooled and then filtered under nitrogen. The red precipitate was dried in vacuo and was recrystallised twice from dichloromethane/petroleum ether (b.p. 40–60°C) under nitrogen, yield 0.7 g, 95%. Found: C, 57.3; H, 4.0. $C_{36}H_{30}IP_2Rh$ calcd.: C, 57.3, H, 4.0%.

### Spectroscopic and TLC measurements

Infrared spectra were recorded on a Perkin–Elmer 577 spectrophotometer. Solids

were run as Nujol mulls using potassium bromide plates for the range 4000-400 cm$^{-1}$ and cesium iodide plates 400-200 cm$^{-1}$. Solution infrared spectra were run in potassium bromide cells. $^{31}$P NMR spectra were recorded on a JEOL PS/PFT Fourier-transform NMR spectrometer with phosphoric acid external reference. TLC was performed using Merck plastic sheets precoated with Silica Gel 60 $F_{254}$.

## Results and discussion

The chloro complexes, trans-[RhCl(CO)(PAr$_3$)$_2$], where Ar = Ph and p-EtC$_6$H$_4$ were prepared by the reaction of the phosphine with [Rh$_2$Cl$_2$(CO)$_4$] [3] and by carbonylation of [RhCl(PAr$_3$)$_3$] by aqueous formaldehyde [4]. Metathesis of these complexes with sodium bromide in acetone solution in the presence of air gave the bromo-derivatives trans-[RhBr(CO)(PAr$_3$)$_2$], where Ar = Ph and p-EtC$_6$H$_4$, in good yield at room temperature. They were readily purified by recrystallisation from benzene/ethanol mixtures.

Attempts to prepare trans-[RhI(CO)(PPh$_3$)$_2$] by the same method yielded a brown solid which did not show a carbonyl absorption in the infrared region. trans-[RhI(CO)(PPh$_3$)$_2$] could only be isolated without decomposition by metathesis and recrystallisation in the presence of excess triphenylphosphine under an atmosphere of either air or nitrogen. The lack of stability of trans-[RhI(CO)(PPh$_3$)$_2$] in solution has previously been noted in the literature [8] and recently attempts to prepare II (X = Br and I) have failed to give any pure products [9]. We have now established that the decomposition is the result of a series of dissociative equilibria which are absent in the chloro complex and only present in the bromo complex when more bulky arylphosphines are coordinated to the rhodium. If the absence of air, decomposition is via the dissociative equilibria shown in Scheme 1. Thus, when
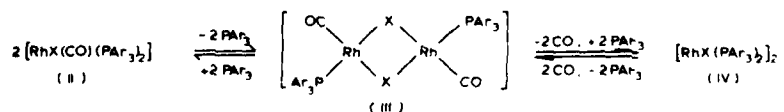


SCHEME 1

II is dissolved in acetone, phosphine is released to give an equilibrium amount of [Rh$_2$X$_2$(CO)$_2$(PAr$_3$)$_2$] (III). Decarbonylation by repeated evaporation of the solvent to dryness under vacuum yields [Rh$_2$X$_2$(PAr$_3$)$_4$] (IV, X = I, Ar = Ph). The product was identified by comparison with an authentic sample prepared from [RhI(PPh$_3$)$_3$] [7]. The reverse of the above reactions was also shown to occur, II being obtained from [Rh$_2$I$_2$(PPh$_3$)$_4$] (IV) and carbon monoxide. Treatment of IV (X = I, Ar = p-EtC$_6$H$_4$) with carbon monoxide yielded III (X = I, Ar = p-EtC$_6$H$_4$) and phosphine. The positions of the equilibria shown in Scheme 1 are strongly dependent on both the phosphine and the halide. Thus when Ar = p-EtC$_6$H$_4$, the equilibria lie in favour of structure IV so that attempts to prepare [RhI(CO)(P(p-EtC$_6$H$_4$)$_3$)$_2$] by treatment of I (Ar = p-EtC$_6$H$_4$) with KI yielded III (X = I, Ar = p-EtC$_6$H$_4$), only traces of II (X = I, Ar = p-EtC$_6$H$_4$) being obtained in solution at 0°C and in the presence of a very large excess of the phosphine. When X = Cl and Br, and Ar = Ph and p-EtC$_6$H$_4$, the equilibria shown in Scheme 1 lie in favour of structure II.

trans-[RhI(CO)(PPh$_3$)]$_2$ has $\nu$(CO) 1980 cm$^{-1}$ (CHCl$_3$ solution). This is the

major isomer formed in solution by the dissociation of [RhI(CO)(PPh$_3$)$_2$], although IR spectroscopy (Table 1) shows that cis-[RhI(CO)(PPh$_3$)]$_2$ ($\nu$(CO) 2025 cm$^{-1}$ in CHCl$_3$ solution) is also present. IR spectroscopy show III (X = I, Ar = p-EtC$_6$H$_4$) to exist as both cis and trans isomers. cis-[RhI(CO)(P( p-EtC$_6$H$_4$)$_3$)]$_2$ has $\nu$(CO) 2020 cm$^{-1}$ (Nujol mull); trans-[RhI(CO)(P( p-EtC$_6$H$_4$)$_3$)]$_2$ has $\nu$(CO) 1980 cm$^{-1}$ (Nujol mull).

$^{31}$P NMR has shown the existence of [RhIO$_2$(CO)(PPh$_3$)$_2$] in solution at 20°C, when both cis- and trans-[RhI(CO)(PPh$_3$)$_2$] are dissolved in CDCl$_3$ under an atmosphere of air. Although the presence of [RhIO$_2$(CO)(PPh$_3$)$_2$] can only arise from the dissociative equilibria shown in Scheme 2, the presence of Rh–P spin–spin coupling indicates that phosphine ligand dissociation is slow on the $^{31}$P NMR time scale at 20°C.

Attempts to prepare trans-[RhI(CO)(PPh$_3$)$_2$] by metathesis from trans-[RhCl(CO)(PPh$_3$)$_2$] in the absence of free phosphine, in air and light, yielded a brown oil which crystallised on freezing in liquid nitrogen. Microanalysis and infrared spectra were consistent with the formula [RhI(O$_2$)(OPPh$_3$)·2H$_2$O]$_x$. The

TABLE 1

INFRARED STRETCHING FREQUENCIES OF [RhX(CO)(PAr$_3$)$_2$] (II) AND [Rh$_2$X$_2$(CO)$_2$(PAr$_3$)$_2$] (III)

| Complex | X | Ar | $\nu$(CO) (cm$^{-1}$) Nujol mull [a] | $\nu$(CO) (cm$^{-1}$) solution [a,b] |
|---|---|---|---|---|
| II | Cl | Ph | 1965 | 1980 |
| | Br | Ph | 1969 | 1980 |
| | I | Ph | 1969 [c] | |
| | | | 1985 | 1980(s) [d], 2025(w) [f] |
| | Cl | ⬡—Et | 1963 | 1976 |
| | Br | ⬡—Et | 1967 | 1980 |
| | I | ⬡—Et | 1985 | 1980 [d], 2032 [f] |
| III | Cl | Ph | 1980(s) [e], 2023(w) [f], 2090(w) [g] | 1980 [e,h], 2023 [f,h] |
| | I | Ph | 1974 [e] | 1980 [e] |
| | I | ⬡—Et | 1976 [e], 2020 [f] | |

[a] trans Isomers except where stated. [b] Chloroform except where otherwise indicated. [c] cis Isomer. [d] Absorption due to both monomeric II and trans-dimeric III (footnote e) dimer formation.

[e] Absorption due to [structure]    [f] Absorption due to [structure]
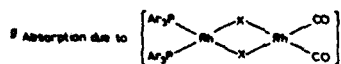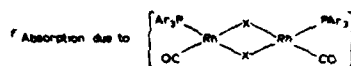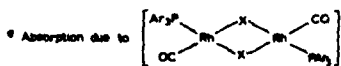
[g] Absorption due to [structure]    [h] Solvent benzene.

photoproduct $[RhCl(O_2)(OPPh_3)_{0.67}]_x$ has previously been isolated [6] from UV irradiation of *trans*-[RhCl(CO)(PPh_3)_2]. In the presence of phosphine, *trans*-[RhI(CO)(PPh_3)_2] is not photo-oxidised, indicating that this reaction proceeds along a dissociative mechanism (Scheme 2). The added phosphine was isolated at the end

$$[RhI(CO)(PPh_3)_2] \xrightleftharpoons[k_{-1}, +PPh_3]{k_1, -PPh_3} \text{ solvated } Rh + O_2 \xrightarrow{k_2} \text{ oxidised products}$$
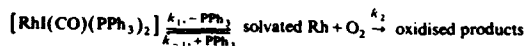
**SCHEME 2**

of the reaction, and this also had not been oxidised. The sensitivity to oxygen of *trans*-[RhX(CO)(PAr_3)_2] is dependent on both phosphine and halide. The complexes with X = Cl are more stable to oxidation than those with X = Br or I. When X = Br, the ease of oxidation is dependent on the phosphine in the order: Ar = $p$-PrC_6H_4 > $p$-EtC_6H_4 ~ Ph. Attempts to prepare II (X = Br, Ar = $p$-PrC_6H_4) by metathesis from the chloride yielded an oil showing no carbonyl absorption in the infrared spectrum. In this case the product was found to crystallise from benzene/ethanol and gave microanalysis and IR spectra consistent with the formula [RhBr(O_2)P($p$-PrC_6H_4)_3)]_x. The decarbonylation may occur via a photo-oxidation to carbon dioxide [6] or via loss of carbon monoxide from an oxidised rhodium(III) species such as V. Decarbonylations are known to occur easily from six-coordinate rhodium(III) complexes [10].

Identification of [RhI(CO)(PPh_3)_2] was complicated by the existence of two isomers in the solid state. Similar isomerism of [RhCl(CO)(PPh_3)_2] has previously been reported in the literature [11]. Both the thermodynamically more stable *trans*-isomer, Ia, and a less stable *cis*-isomer, Ib, can be obtained in pure form and may be distinguished by their infrared absorptions in the carbonyl region, where the *trans*-isomer absorbs at 1965 cm$^{-1}$ and the *cis*-isomer at 1978 cm$^{-1}$ (both in Nujol



(V)        (IIa)        (IIb)
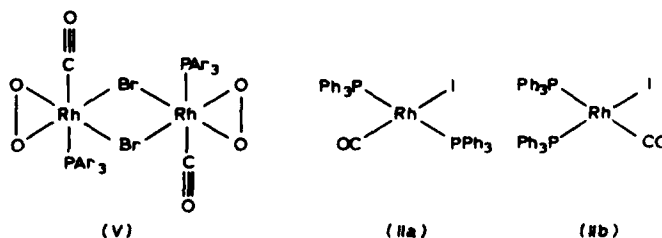
mulls). The two isomers of [RhI(CO)(PPh_3)_2] have been separately reported in the literature previously but not recognised as isomers; IIa was reported as having $\nu$(CO) at 1985 cm$^{-1}$ (Nujol mull) [12] and IIb was reported [2] as having $\nu$(CO) at 1968 cm$^{-1}$, in chloroform solution $\nu$(CO) has been reported as being at 1981 cm$^{-1}$ [13]. Halide exchange of *trans*-[RhCl(CO)(PPh_3)_2] at room temperature was found to give isomer IIa, which has a carbonyl absorption at 1985 cm$^{-1}$ (Nujol mull), whilst an otherwise identical reaction carried out at 0°C yielded IIb which has a carbonyl absorption at 1969 cm$^{-1}$ (Nujol mull). Over a period of one month at room temperature in the solid state, the thermodynamically less stable *cis* isomer, IIb, converts to IIa; at room temperature in chloroform solution this occurs within the time required for dissolution.

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The dissociative equilibria discussed in this paper complicate the study of the oxidative addition of alkyl halides to II, where X = I and Br, when bulky aryl phosphines are coordinated to the rhodium.

### Acknowledgements

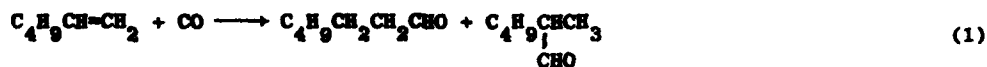### References

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## Chapter 4

## The Influence of Extreme Solubility and Long Alkyl Chains
## on the Catalysts Properties of Tertiary Phosphine Complexes
## of Rhodium(I), Palladium(II) and Platinum(II)


It was of considerable interest to determine whether the presence of the long alkyl chains on the tertiary phosphines modified in any way the catalytic properties of their transition metal complexes. In particular it was hoped that the steric bulk of the resulting phosphines might enhance the selectivity of their complexes. This was examined first by looking at the ratio of normal to branched aldehyde formed when 1-hexene was hydroformylated in the presence of $\left[RhCl(CO)(PR_3)_2\right]$. This reaction (reaction 1) is of considerable interest since the normal aldehyde

$$C_4H_9CH=CH_2 + CO \longrightarrow C_4H_9CH_2CH_2CHO + C_4H_9\underset{\underset{CHO}{|}}{C}HCH_3 \tag{1}$$

is valuable whereas the branched aldehyde is of little commercial value. As reference 1 shows we found that the replacement of $PPh_3$ by $P(C_6H_4C_4H_9-p)_3$ enhanced the ratio of normal to branched aldehyde by a factor of 1.7 without significant loss of yield.

A second catalytic system that has been investigated in some detail is the selective hydrogenation of the di- and tri-olefins methyl linoleate and methyl linolenate to the corresponding mono-olefins. This reaction is of considerable commercial interest since the resulting mono-olefins are important components of margarine. It is commercially essential that the hydrogenation does not proceed all the way to the alkane, since the latter is not digestible. Accordingly the selective hydrogenation of poly-olefins to mono-olefins provided a commercially useful situation in which to examine the influence of long alkyl chain tertiary phosphines on the selectivity of a reaction as well as investigating whether the use of such phosphines would enable the solvent to be dispensed with by allowing the natural polyolefin to act as its own solvent. The results, described in references 2 and 3 show that the palladium(II) and platinum(II) complexes $\left[MCl_2(PR_3)_2\right]$, M = Pd,Pt, in association with tin(II) chloride are effective

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catalysts for the selective hydrogenation of poly-olefins to mono-olefins. The activity of the platinum(II) tertiary aryl phosphine catalysts is enhanced by replacing the para-hydrogen by an alkyl group, an enhancement which is greater when that alkyl group is n-butyl than when it is an ethyl group.

When the poly-olefin was used as its own solvent, the activity of the platinum(II) complexes is greatly enhanced. Not only is this observation of considerable commercial interest, when coupled with exactly the reverse observation in the case of the palladium(II) case, it provides a greater understanding of the intimate mechanisms of these reactions, in particular the role of the solvent, than has hitherto been available. This is discussed at the end of reference 3.

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Short Communication

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Complexes of Long Alkyl Chain Tertiary Phosphines
Part 2 [1]. Hydroformylation of 1-Hexene in the Presence of [RhCl(CO)L₂]

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(Received November 4, 1980)

The hydroformylation of olefins to yield either aldehydes or alcohols is a commercially important reaction [2 - 4]. Commercial interest focuses on the ratio of linear to branched products formed, with the emphasis on maximising the proportion of linear product [5 - 6]. We have recently described the synthesis of two series of tertiary phosphines, $P(n\text{-}C_mH_{2m+1})_3$ where $m = 10 - 19$ and $(n\text{-}C_lH_{2l+1}\text{-}\bigcirc\text{-})_3P$ where $l = 3 - 9$, together with some of their complexes of rhodium(I) [7 - 9]. These phosphines have rather different solubility properties from those previously available; in particular, they are extremely soluble in hydrocarbon solvents.

It was of interest to examine the rhodium(I) complexes of these phosphines, [RhCl(CO)L₂] where L = phosphine, to determine the effect of having long alkyl chains on the ratio of linear to branched aldehydes produced by the hydroformylation of 1-hexene.

*Trans*-[RhCl(CO)L₂] were prepared as described previously [1]. 1-Hexene was redistilled before use. Hydrogenations were performed in a 250 ml glass-lined, stainless steel autoclave built by Baskerville and Lindsey. A solution of 1-hexene (42 ml) and *trans*-[RhCl(CO)L₂] $(4.5 \times 10^{-4}$ mol) in benzene (50 ml) was heated to 80 °C and stirred under an initial atmosphere of carbon monoxide, which was then replaced by a 1:1 atmosphere of carbon monoxide and hydrogen at an initial pressure of either 80 or 100 atmospheres (see Table 1). Stirring at 80 °C was continued for 4 h before the reaction mixture was analysed. Frequent control experiments without catalyst were carried out to confirm that no residual active catalyst had been deposited on the walls of the autoclave. In these control experiments no hydroformylation, isomerisation or hydrogenation of 1-hexene took place.

The reaction mixtures were analysed using a Pye 104 gas chromatograph fitted with a 3 mm bore glass capillary column containing OV17 as the sta-

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TABLE 1

Hydroformylation of 1-hexene at 80 °C in benzene solution in the presence of trans-[RhCl(CO)L$_2$]

| L | Initial pressure (atm) 1:1 CO:H$_2$ | Stirring speed (rpm) | Product analysis | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Total yield of aldehyde | heptanal (%) | 2-methyl-hexanal (%) | 2-ethyl-pentanal (%) | Ratio of linear: branched aldehyde | 1-hexene (%) | cis-2-hexene (%) | trans-2-hexene (%) | Ratio of trans cis 2-hexene | Ratio of 1-hexene: 2-hexene | hexane (%) |
| PPh$_3$ | 100 | 1000 | 44 | 26.2 | 14.5 | 3.3 | 1.5 | 0 | 13.9 | 42.7 | 3.1 | — | 0 |
| P(O-C$_6$H$_5$)$_3$ | 100 | 1000 | 44 | 27.1 | 13.8 | 3.1 | 1.6 | trace | 14.2 | 38.1 | 2.7 | very small | 3.7 |
| P(O-C$_4$H$_9$)$_3$ | 100 | 1000 | 39 | 27.9 | 11.1 | trace | 2.5 | 34.3 | 7.9 | 18.8 | 2.4 | 1.3 | 0 |
| P(O-C$_5$H$_{11}$)$_3$ | 100 | 1000 | 18 | 11.5 | 4.5 | 0 | 2.6 | 78.6 | 1.5 | 3.9 | 2.6 | 14.6 | trace |
| (n-C$_4$H$_9$)$_3$P | 100 | 1000 | 49 | 19.7 | 21.2 | 3.1 | 0.7 | trace | 11.2 | 39.8 | 3.6 | very small | trace |
| (n-C$_5$H$_5$)$_3$P | 80 | 500 | 17 | 8.6 | 6.6 | 1.8 | 1.0 | trace | 21.4 | 60.6 | 2.8 | very small | 1.0 |
| (n-C$_8$H$_{17}$)$_3$P | 80 | 500 | 6 | 4.1 | 1.8 | 0 | 2.3 | 81.7 | 2.8 | 9.5 | 3.4 | 6.6 | 0 |
| (n-C$_6$H$_{53}$)$_3$P | 80 | 500 | ~0 | trace | trace | 0 | — | 94.0 | 0.5 | 4.5 | 9.0 | 18.8 | 0 |

tionary phase. The injection block and flame ionisation detector were held at 100 °C and the oven temperature programmed for a six minute hold at 25 °C followed by an increase of 12 °C/min up to 100 °C. This programme enabled 1-hexene, cis-2-hexene, trans-2-hexene, hexane, benzene, 2-ethyl-pentanal, 2-methylhexanal and heptanal to be separated.

The object of the present work was to examine the influence of having a long alkyl chain as part of the tertiary phosphine on the linear to branched selectivity of [RhCl(CO)L$_2$]-catalysed hydroformylations. In order to inves-tigate this, hydroformylations were not taken to completion but were ana-lysed after four hours. In this way it was possible to examine the propensity of the catalyst for promoting 1-hexene isomerisation. This is an important parameter in the hydroformylation since the hydroformylation of internal olefins inevitably leads to branched aldehydes. It is apparent from Table 1 that the trialkylphosphines tend to promote olefin isomerisation more than do the triarylphosphines, and that within the trialkylphosphines the order of increasing olefin isomerisation is (n-C$_{16}$H$_{33}$)$_3$P < (n-C$_8$H$_{17}$)$_3$P < (n-C$_4$H$_9$)$_3$P, whilst within the triarylphosphines, (p-RC$_6$H$_4$)$_3$P, the order of increasing olefin isomerisation is R = n-C$_5$H$_{11}$ < n-C$_4$H$_9$ < n-C$_2$H$_5$ < H. Both series show a systematic decrease in olefin isomerisation with an increase in alkyl group chain length. It is tempting to ascribe this to the increasing steric demands of the longer alkyl chains inhibiting coordination by the more sterically demanding 2-hexene. However, it is possible that other factors, including both electronic and solvation effects, are equally important. In all cases trans-2-hexene was found to be present in greater amount than cis-2-hexene. This could be due to many factors including the fact that cis-2-hexene is hydroformylated more rapidly than the trans-isomer [9] and therefore is consumed faster.

Carbon monoxide was introduced into the catalyst solution before the addition of hydrogen to minimise hydrogenation as well as isomerisation of the olefin. A small amount of hexane was formed when tris(para-ethylphenyl)-phosphine was used, although none was formed in the presence of triphenyl-phosphine. Trivial amounts of hexane were formed in the presence of other phosphines.

The yield of aldehyde (see Table 1) depends upon the phosphine present in the order (n-C$_4$H$_9$)$_3$P > PPh$_3$ ~ P(C$_6$H$_4$Et-p)$_3$ > P(C$_6$H$_4$Bu-p)$_3$ >> P(C$_6$H$_4$C$_5$H$_{11}$-p)$_3$, and (n-C$_4$H$_9$)$_3$P >> (n-C$_8$H$_{17}$)$_3$P >> (n-C$_{16}$H$_{33}$)$_3$P. Since the electron donor properties of phosphorus in P(C$_6$H$_4$Bu-p)$_3$ and P(C$_6$H$_4$C$_5$H$_{11}$-p)$_3$ are expected to be very similar (the phosphorus atoms have identical [31]P n.m.r. chemical shifts) [8], and the electron donor prop-erties of the three trialkylphosphines are also expected to be similar to each other, the dependence of the yields of aldehydes on the alkyl group chain length is ascribed to a combination of steric and solvation effects. The greater yield of aldehydes obtained in the presence of trans-[RhCl(CO)-(PBu$_3$)$_2$] as compared with trans-[RhCl(CO)(PPh$_3$)$_2$] is noteworthy, since the addition of PBu$_3$ to [RhH(CO)(PPh$_3$)$_3$] gives a catalyst of lower activity than the addition of PPh$_3$ [10].

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A decrease in aldehyde yield is paralleled by an increase in the proportion of linear:branched aldehyde. Thus, under the present conditions, in which we did not attempt to optimise the ratio of linear:branched aldehyde by adding excess phosphine, for example, the proportion of linear:branched aldehyde increases in the order $PPh_3 < P(C_6H_4Et\text{-}p)_3 < P(C_6H_4Bu\text{-}p)_3 < P(C_6H_4C_5H_{11}\text{-}p)_3$, and $(n\text{-}C_4H_9)_3P < (n\text{-}C_8H_{17})_3P$. The optimum phosphine from the present study is thus $P(C_6H_4Bu\text{-}p)_3$ which gives a reasonable compromise between yield and ratio of linear:branched product. Decreasing the pressure of hydrogen/carbon monoxide from 100 to 80 atm and decreasing the stirring rate from 1000 to 500 rpm results in a decrease in the yield of aldehyde, but an increase in the ratio of linear:branched product. This is expected since, under these conditions, the hydroformylation is more difficult, and so the sterically less demanding 1-hexene is hydroformylated more readily than the sterically more demanding 2-hexenes. The same effect has been observed in the presence of $[RhH(CO)(PPh_3)_3]$ and excess triphenylphosphine [11]. It is noteworthy that under less vigorous hydroformylation conditions olefin isomerisation still proceeds and so becomes the dominant reaction (see Table 1 under $L = (n\text{-}C_4H_9)_3P$).

In conclusion, the present work demonstrates that the ratio of linear:branched aldehydes formed by the hydroformylation of 1-hexene in the presence of trans-$[RhCl(CO)L_2]$ is enhanced by the presence of para-alkyl substituents on the phenyl groups of triphenylphosphine. The optimum compromise between the rate of hydroformylation and the ratio of linear:branched aldehyde is obtained when n-butyl substituents are present.

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COMPLEXES OF LONG ALKYL CHAIN TERTIARY PHOSPHINES
PART 5. HOMOGENEOUS CATALYTIC HYDROGENATION OF
METHYL LINOLEATE AND METHYL LINOLENATE USING THE
COMPLEXES [MCl$_2$(PR$_3$)$_2$], M = Pd, Pt; R = n-ALKYL,
p-n-ALKYLPHENYL, IN THE PRESENCE OF TIN(II) CHLORIDE

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(Received September 18, 1982)

Summary

The complexes of a number of trialkyl- and triarylphosphines bearing long alkyl chains, [MCl$_2$(PR$_3$)$_2$], M = Pd, Pt; R = n-alkyl, p-n-alkylphenyl, have been shown to catalyse selectively the reduction of methyl linoleate and methyl linolenate in the presence of tin(II) chloride in benzene–methanol solution. The activity of the resulting catalysts was found to be dependent on both the nature of the metal and the phosphine ligand. Inclusion of a p-n-alkyl substituent on the phenyl ring of the phosphine increased the catalytic activity for the platinum(II) compounds but gave a corresponding decrease for the palladium(II) analogues. The complexes cis-[PtCl$_2$(PR$_3$)$_2$], R = n-alkyl were poor catalysts in contrast to their active palladium(II) analogues. All palladium(II) catalysts slowly decomposed to form a catalytically inactive black precipitate.

Introduction

We have recently reported the preparation and properties of a series of trialkyl- and triarylphosphines bearing long alkyl chains, PR$_3$ (R = n-alkyl, p-n-alkylphenyl) [1, 2] and their Group VIII metal complexes [2 - 4], which have unusual solubility properties and, in particular, are extremely soluble in non-polar hydrocarbon solvents. As solvents play an important part in the intimate mechanisms of many homogeneously catalysed reactions, it was of interest to examine the catalytic ability of the transition metal complexes of these new phosphines, and to observe how changes in phosphine structure within a particular series of complexes modify the overall catalysis. Previously [5] we have shown that when 1-hexene is hydroformylated in the

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presence of *trans*-[RhCl(CO)(PR$_3$)$_2$], R = *p*-n-alkylphenyl, the linear to branched aldehyde ratio increased as the *p*-n-alkyl group was varied in the order H < C$_2$H$_5$ < n-C$_4$H$_9$ < n-C$_5$H$_{11}$, and when R = n-alkyl it again increased as the n-alkyl chain increased in length. In the present paper we examine the ability of platinum(II) and palladium(II) complexes to promote the selective hydrogenation of polyenes to monoenes.

Complexes of the type [MCl$_2$(PR$_3$)$_2$], M = Pd, Pt; R = aryl, in the presence of tin(II) chloride are known to be selective homogeneous catalysts for the reduction of polyenes to monoenes [6, 7] and in particular for the selective hydrogenation of the soybean methyl esters, methyl linoleate (methyl *cis*-9,*cis*-12-octadecadienoate) [8 - 11] and methyl linolenate (methyl *cis*-9,*cis*-12,*cis*-15-octadecatrienoate) [12]. These catalysts were shown:

(a) to cause reduction of all but one double bond, except in short chain alkenes where terminal double bonds may be hydrogenated;

(b) to isomerise *cis*-double bonds to the *trans*-configuration;

(c) to bring about migration of double bonds along the carbon chain until conjugation occurs;

(d) under certain conditions not to effect hydrogenation but cause isomerisation to a conjugated system.

A solvent consisting of a 3:2 mixture of benzene and methanol was generally used, but recognition of the fact that not only could methanol compete with alkene for coordination to the metal but could also act as the source of hydrogen for reduction has led other workers to search for an alternative solvent with limited success [7].

Our aim therefore was to study an extensive series of long alkyl chain tertiary phosphine complexes of palladium(II) and platinum(II) as homogeneous catalysts for the selective reduction of methyl linoleate and methyl linolenate; first to observe, in the presence of a solvent, the effects on catalytic activity of varying the phosphine ligands whose steric demands are difficult to predict, and secondly [13] to determine the effect on catalytic activity of these highly soluble compounds when they are dissolved directly in the substrate without addition of extra solvent.

### Experimental

Methyl linoleate and technical grade methyl linolenate were obtained from Fluorochem Ltd. and freeze-degassed before use. The compounds [MCl$_2$(PR$_3$)$_2$], M = Pd, Pt; R = n-alkyl, *p*-n-alkylphenyl were prepared as described previously [3]. The monomeric compound *trans*-[PdCl$_2$ {P(n-C$_{16}$H$_{29}$)$_3$}$_2$] was prepared in 87% yield by the addition of two equivalents of tertiary phosphine to one equivalent of [PdCl$_2$(COD)] in chloroform, under nitrogen, and stirring for 1.5 h. After removal of solvent and drying under vacuum, careful recrystallisation of the crude product from a mixture of ethanol and chloroform (3:2) yielded a brown amorphous powder.

(Found: C, 69.9; H, 12.3; P, 5.6; Cl, 4.4. $C_{84}H_{174}P_2Cl_2Pd$ requires C, 70.9; H, 12.3; P, 4.4; Cl, 5.0).

*Hydrogenations*

Each reduction was carried out identically using a 250 ml stainless steel autoclave (Baskerville and Lindsay) fitted with a mechanical stirrer, electric thermostatted heater and sampling tube. At the beginning of each run the vessel was charged with substrate (14 mmol), metal complex (0.65 mmol) and tin(II) chloride dihydrate (1.29 g, 5.7 mmol) dissolved in a mixture of degassed benzene (30 ml) and methanol (20 ml). The autoclave was flushed twice with hydrogen and pressurised to 4.05 MN m$^{-2}$, which was maintained throughout the course of the reaction. The heater, stirrer and a stopwatch were then started simultaneously ($t = 0$). A constant stirring speed of 500 rpm was used, while the heater required 40 min to indicate a temperature of 90 °C within the vessel. Care was taken to ensure that the heating rate to 90 °C was the same for each run, and once this temperature was reached was kept constant. After exactly 3 h the stirrer was switched off and a sample withdrawn immediately for analysis by gas chromatography. The autoclave vessel was cleaned thoroughly at regular intervals, by using a concentrated solution of triphenylphosphine in toluene and heating at 90 °C under a pressure of 4.05 MN m$^{-2}$ of hydrogen with stirring for 4 h. Control experiments without catalyst were also carried out periodically and the distribution of products after hydrogenation found to be identical with that of the starting material.

Analysis by gas chromatography was carried out using a Pye-Unicam 204 Chromatograph equipped with a temperature programme controller and a flame ionization detector. A glass column (9 ft × 1/4 in) packed with poly-(diethylene glycol succinate) on diatomite (mesh size 60 - 80) was used for the separation of all products at 195 °C. Peak areas were determined using a planimeter. Typical separations of products for runs involving methyl linoleate and methyl linolenate are shown in Figs. 1 and 2 respectively. It is apparent from Fig. 2 that the non-conjugated triene and the *cis,trans*-conjugated diene have similar retention times and cannot be resolved.

**Results and discussion**

The complexes [MCl$_2$(PR$_3$)$_2$], M = Pd, Pt; R = n-alkyl, *p*-n-alkylphenyl were found to catalyse selectively the reduction of methyl linoleate and methyl linolenate in the presence of tin(II) chloride and a 3:2 mixture of benzene and methanol under the described conditions. Hydrogenations were carried out using a technique similar to that previously reported [6, 8, 9, 11]; in order to investigate the effect of changing the phosphine ligands, the conditions were chosen such that partially hydrogenated esters were obtained.
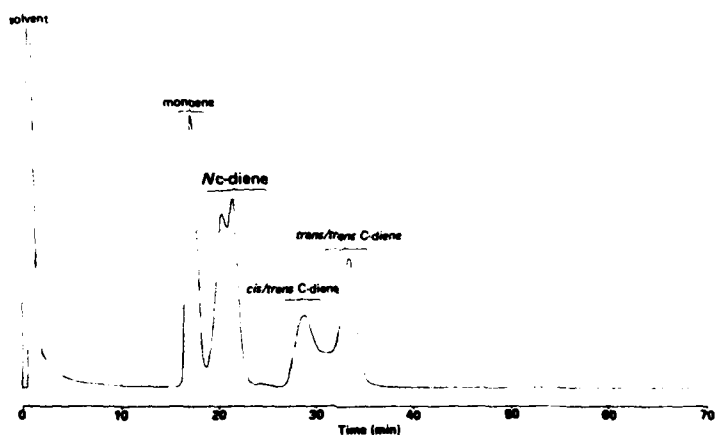
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Fig. 1. Gas chromatograph trace of methyl linoleate after 3 h with *trans*-[PdCl$_2${P(n-C$_4$H$_9$)$_3$}$_2$].
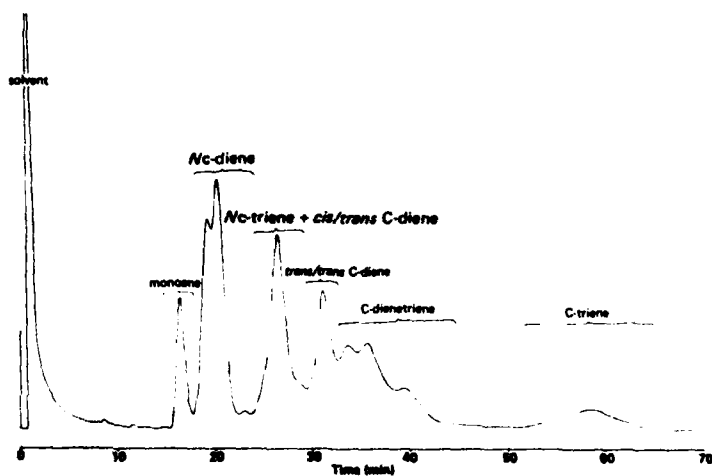


Fig. 2. Gas chromatograph trace of methyl linolenate after 3 h with *trans*-[PdCl$_2${P(n-C$_4$H$_9$)$_3$}$_2$].

## Hydrogenation of methyl linoleate

At the end of 3 h, the products of the hydrogenation of methyl linoleate consisted of a mixture of components arising from the isomerization and reduction of the original non-conjugated diene (Table 1). Each

TABLE 1

Hydrogenation of methyl linoleate in the presence of [MCl₂(PR₃)₂] and tin(II) chloride[a]

| Catalyst precursor | Ppt[b] | Stearate | Monoene | Nc-Diene[c] | C-Diene cis/trans | trans/trans |
|---|---|---|---|---|---|---|
| Control[d] | — | — | — | 97.2 | 2.8 | 31.2 |
| cis-[PtCl₂(PPh₃)₂] | — | — | 13.0 | 35.1 | 20.7 | 27.6 |
| cis-[PtCl₂[P(p-C₆H₅—C₆H₄)₃]₂] | — | — | 18.2 | 34.9 | 19.3 | 25.1 |
| cis-[PtCl₂[P(p-n-C₄H₉—C₆H₄)₃]₂] | — | — | 23.7 | 34.5 | 16.7 | 23.4 |
| cis-[PtCl₂[P(p-n-C₆H₁₃—C₆H₄)₃]₂] | — | — | 15.1 | 40.7 | 20.8 | 11.0 |
| cis-[PtCl₂[P(n-C₄H₉)₃]₂] | — | — | 2.9 | 64.2 | 21.9 | 5.4 |
| cis-[PtCl₂[P(n-C₁₆H₃₃)₃]₂] | — | — | 1.2 | 82.2 | 11.1 | 20.7 |
| trans-[PdCl₂(PPh₃)₂] | + | — | 20.2 | 43.5 | 15.6 | 22.4 |
| trans-[PdCl₂[P(p-C₆H₅—C₆H₄)₃]₂] | + | — | 14.0 | 48.1 | 15.5 | 21.0 |
| trans-[PdCl₂[P(p-n-C₄H₉—C₆H₄)₃]₂] | + | — | 9.9 | 51.8 | 17.3 | 22.6 |
| trans-[PdCl₂[P(n-C₄H₉)₃]₂] | + | — | 24.6 | 37.4 | 15.4 | 22.5 |
| trans-[PdCl₂[P(n-C₁₆H₃₃)₃]₂] | + | — | 9.8 | 54.0 | 13.7 | |

[a] 46 mmol complex per mol substrate, 5.7 mmol tin(II) chloride dihydrate, 30 ml benzene, 20 ml methanol, 90 °C, 3 h and 4.05 MN m⁻² hydrogen pressure; all results listed as %.
[b] +, signifies a black precipitate is present at the end of the hydrogenation.
[c] Nc, non-conjugated; C, conjugated.
[d] The control was treated in exactly the same way as all other samples, except for the absence of any catalyst precursor.

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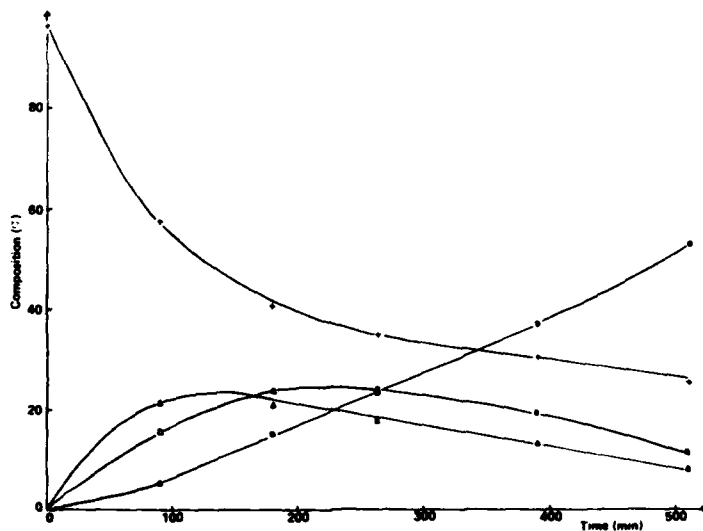


Fig. 3. Plot of the percentage composition as a function of time during the hydrogenation of methyl linoleate in the presence of cis-[PtCl₂{P(p-n-C₉H₁₉—C₆H₄)₃}₂] (46 mmol per mol substrate); O, monoene; +, non-conjugated diene; □, trans-trans conjugated diene; △, cis-trans conjugated diene.

catalytic precursor maintained the selectivity of the reaction and no fully saturated material (methyl stearate) was obtained.

In order to observe how the components of the reaction medium changed as a function of time, the reduction using one of the most active precursors cis-[PtCl₂{P(p-n-C₉H₁₉—C₆H₄)₃}₂] was monitored over an 8½ h period (Fig. 3). It is apparent that the non-conjugated diene is first iso-merised to a mixture of cis,trans- and trans,trans-conjugated dienes, the former being produced faster. These are then hydrogenated subsequently to the monoene stage only, and again the cis,trans-conjugated diene is hydro-genated more rapidly than the trans,trans-isomer. This is in keeping with previous proposals that conjugation preceeds hydrogenation [7]. The overall mechanism is not fully known, but the initial steps are believed to arise according to eqn. 1 [11]. The SnCl₃⁻ ligand plays an important role in these complexes. It is a good $\pi$-acceptor and only a modest $\sigma$-donor [14] and

$$[MCl_2(PR_3)_2] \xrightleftharpoons{+ SnCl_2} [MCl(SnCl_3)(PR_3)_2] \xrightleftharpoons[+ HCl]{+ H_2} [MH(SnCl_3)(PR_3)_2] \quad (1)$$

promotes five-coordination, allowing the olefin to enter the metal coordina-tion sphere. In addition, it is also a good leaving group, which consequently promotes coordinative unsaturation at the metal centre [15].

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Inspection of the data in Table 1 shows that variations in the nature of both the metal and the phosphine ligand have a pronounced effect on the catalytic activity. It has been noted previously [16] that palladium(II) complexes of this type are generally more active than their platinum(II) analogues. The same was found here (Table 1) when the phosphine was $PPh_3$, $P(n-C_4H_9)_3$ or $P(n-C_{14}H_{29})_3$. However, in the platinum(II) series, the activity of the catalysts was enhanced when an n-alkyl group replaced a *para*-hydrogen atom in the phenyl ring of the tertiary phosphine ligand, whereas the converse was true for palladium(II). As a result, when the phosphine was $P(p-R-C_6H_4)_3$ with $R = C_2H_5$ or $n-C_4H_9$ the platinum(II) complexes were more active than those of the corresponding palladium(II) species. From Table 1, the order of decreasing activity for *cis*-[$PtCl_2(PR_3)_2$] is:

$$R = p-n-C_4H_9-C_6H_4 > p-C_2H_5-C_6H_4 > p-n-C_9H_{19}-C_6H_4 > Ph \gg n-C_4H_9 >$$

$$n-C_{14}H_{29} \qquad \qquad (i)$$
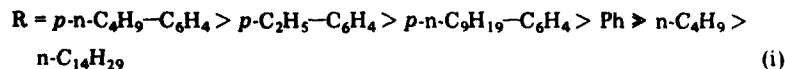
In contrast, the palladium(II) series showed a marked decrease in activity on introducing a *para*-alkyl substituent, such that the order of decreasing efficiency for *trans*-[$PdCl_2(PR_3)_2$] becomes:

$$R = n-C_4H_9 > Ph > p-C_2H_5-C_6H_4 > p-n-C_4H_9-C_6H_4 \sim n-C_{14}H_{29} \qquad (ii)$$
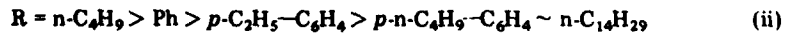
During each hydrogenation involving palladium(II) compounds, varying amounts of a black precipitate were formed from the decomposition of the catalyst. Such decomposition is generally observed when palladium(II) complexes are used [9]. We tested the activity of this black precipitate and, as reported previously [9], we found it to be catalytically inactive. Accordingly, wherever a black precipitate was formed the observed hydrogenation and isomerisation were assumed to arise prior to decomposition. The amount of decomposition product increased as the *p*-n-alkyl chain lengthened, and it seems likely, therefore, that the decreasing catalytic activity originates from the diminishing stabilities of the complex and/or catalytic intermediates.

In the case of the platinum(II) systems where increased ability to hydrogenate accompanies phenyl ring substitution, a greater electron density at phosphorus, and hence at the metal making the centre a good nucleophile, might account for the observed trends. If this is the case then it would be expected that the tri(n-alkyl)phosphines would increase activity still further owing to their greater basicities [15]. As can be seen, this is not the case. *Cis*-[$PtCl_2\{P(n-C_4H_9)_3\}_2$] yielded a poor catalyst, in agreement with previous observations [7, 11, 16], and *cis*-[$PtCl_2\{P(n-C_{14}H_{29})_3\}_2$] was even less effective. The overall trend for the complexes *cis*-[$PtCl_2L_2$] to enhance reduction of methyl linoleate followed the order:

$$L = P(n-alkyl)_3 \ll PPh_3 < P(p-n-alkyl-C_6H_4)_3 \qquad (iii)$$
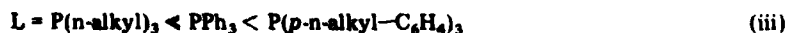
This is very similar to the observation that substitution of a phenyl ring by a methyl group in triphenylphosphine increased the activity of these compounds according to the sequence [7]:

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$$L \approx P(n\text{-}C_4H_9)_3 \sim PMe_3 \ll PPh_3 < PMePh_2 < PMe_2Ph \qquad \text{(iv)}$$

These orders do not follow sequences of basicities relating to electronic effects or cone angle size [17], and we would suggest that the observed activities arise from a combination of both electronic and steric constraints as previously proposed to explain the effects of hydroformylations using the complexes cis-[PtCl$_2$(CO)(PR$_3$)] [15]. However, solvation effects may be important and indeed may be dominant in determining the steric requirements of the long alkyl chain phosphines. It has been suggested previously [7] that sequence (iv) indicates that the phenyl ring plays some part in the reaction. However, the complexes trans-[PdCl$_2$[P(n-alkyl)$_3$]$_2$] yielded efficient hydrogenation catalysts and furthermore, trans-[PdCl$_2$[P(n-C$_4$H$_9$)$_3$]$_2$] provided the greatest activity of all. It seems therefore contrary to previous suggestions [7] that the presence of an aryl group attached to the phosphine ligand is not necessary for catalytic activity.

### Hydrogenation of methy linolenate

We extended our studies using a similar series of palladium(II) and platinum(II) tertiary phosphine complexes to include the hydrogenation of the non-conjugated triene methyl linolenate under identical conditions. The technical grade substrate contained 77.7% non-conjugated triene, 20.9% non-conjugated diene and 1.4% monoene. For each run, a complex mixture of products was obtained after 3 h arising from the extensive isomerisation and reduction of the substrate, and no methyl stearate formation was observed (Table 2).

In order to observe the change in distribution of the products of the hydrogenation with time, the reduction using two of the most active catalytic precursors was sampled periodically over 8½ h (Figs. 4 and 5). When cis-[PtCl$_2$[P(p-C$_2$H$_5$—C$_6$H$_4$)$_3$]$_2$] was used in the presence of tin(II) chloride (Fig. 4) it is evident that the non-conjugated triene was first isomerised to a mixture of a triene with two double bonds conjugated, and then to a fully conjugated triene as previously found when other tertiary phosphines were present [12]. When trans-[PdCl$_2$[P(n-C$_4$H$_9$)$_3$]$_2$] was used to catalyse the same reaction at a slightly greater catalyst:alkene ratio, the isomerisation was much slower; this was found to be the case for all palladium(II) complexes (Table 2). Furthermore, the palladium(II) species slowly decomposed to a catalytically inactive black precipitate, total decomposition being complete within 475 min. Although the rate of isomerisation of the triene was slower with palladium(II), the initial rate of formation of monoene was faster than with the platinum(II) compound. This would suggest that the former is more efficient for catalysing the reduction of the diene to monoene, which parallels the results obtained for the hydrogenation of methyl linoleate in which [PdCl$_2$[P(n-C$_4$H$_9$)$_3$]$_2$] yielded the most active catalyst.

The relative activities of the tertiary phosphine complexes with changing ligand (Table 2) show trends similar to those found for the hydrogenation of methyl linoleate such that the order of decreasing efficiency for

TABLE 2

Hydrogenation of *methyl linolenate* in the presence of [MCl$_2$(PR$_3$)] and tin(II) chloride[a]

| Catalyst Precursor | Ppt[b] | Stearate | Monoene | Nc-Diene[c] | trans/trans | Nc-Triene + cis/trans | C-Dienetriene | C-Triene |
|---|---|---|---|---|---|---|---|---|
| Control[d] | — | — | 1.4 | 20.9 | — | 77.7 | — | 10.0 |
| cis-[PtCl$_2$(PPh$_3$)] | — | — | 3.3 | 21.4 | 16.5 | 11.0 | 37.8 | 10.3 |
| cis-[PtCl$_3$(P(p-C$_6$H$_5$-C$_6$H$_4$)$_3$)] | — | — | 5.9 | 27.1 | 16.7 | 9.0 | 31.0 | 6.8 |
| cis-[PtCl$_3$(P(p-n-C$_4$H$_9$-C$_6$H$_4$)$_3$)] | — | — | 6.1 | 26.6 | 16.0 | 10.1 | 35.4 | 3.6 |
| cis-[PtCl$_3$(P(n-C$_4$H$_{17}$)$_3$)] | — | — | 2.5 | 22.7 | 9.4 | 24.2 | 37.6 | 4.7 |
| trans-[PdCl$_2$(PPh$_3$)] | + | — | 4.2 | 25.9 | 10.8 | 30.2 | 24.2 | 4.1 |
| trans-[PdCl$_3$(P(p-C$_6$H$_5$-C$_6$H$_4$)$_3$)$_2$] | + | — | 4.0 | 25.6 | 10.7 | 32.1 | 23.5 | 3.0 |
| trans-[PdCl$_3$(P(p-n-C$_4$H$_9$-C$_6$H$_4$)$_3$)$_2$] | + | — | 2.0 | 21.0 | 5.1 | 49.2 | 19.7 | 3.0 |
| trans-[PdCl$_3$(P(n-C$_4$H$_9$)$_3$)$_2$] | + | — | 7.2 | 28.1 | 13.0 | 21.4 | 24.8 | 5.5 |
| trans-[PdCl$_3$(P(n-C$_4$H$_{17}$)$_3$)$_2$] | + | — | 3.6 | 22.5 | 9.8 | 30.2 | 28.2 | 5.7 |

[a]46 mmol complex per mole of substrate, 5.7 mmol tin(II) chloride dihydrate, 30 ml benzene, 20 ml methanol, 90 °C, 3 h, 4.05 MN m$^{-2}$ hydrogen; all results listed as %.

[b]+ signifies a black precipitate is present at the end of the hydrogenation.

[c]Nc, non-conjugated, C, conjugated; trans/trans, cis/trans, conjugated diene. C-Dienetriene, triene with two double bonds conjugated.

[d]The control was treated in exactly the same way as all other samples, except for the absence of any catalyst precursor.
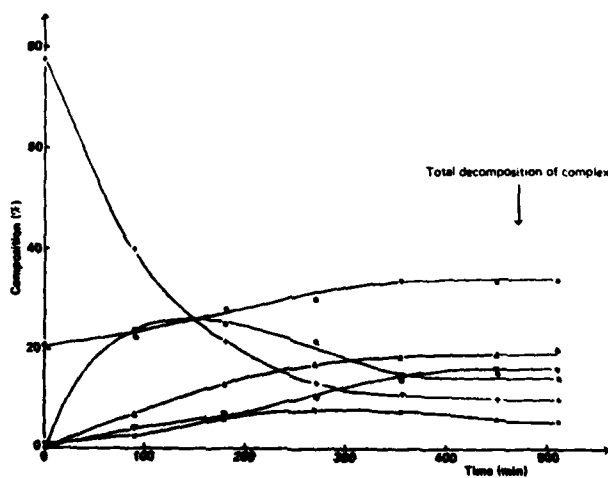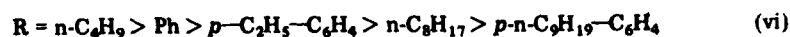
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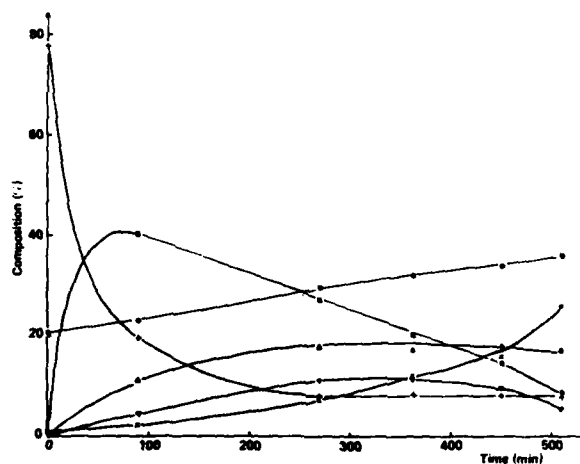


Fig. 4. Plot of the percentage composition as a function of time during the hydrogenation of methyl linolenate in the presence of $cis$-[$PtCl_2${$P(p$-$C_2H_5$—$C_6H_4)_3$}$_2$] (35 mmol per mol substrate); O, diene; ×, monoene; △, $trans$-$trans$ conjugated diene; □, triene with two double bonds conjugated; +, triene; ▽, conjugated triene.



Total decomposition of complex

Fig. 5. Plot of the percentage composition as a function of time during the hydrogenation of methyl linolenate in the presence of $trans$-[$PdCl_2${$P(n$-$C_4H_9)_3$}$_2$] (46 mmol per mol substrate); O, diene; △, $trans$-$trans$ conjugated diene; ▽, monoene; □, triene with two double bonds conjugated; +, triene; ×, conjugated triene.

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cis-[PtCl$_2$(PR$_3$)$_2$] is:

$$R = p\text{-}C_2H_5\text{---}C_6H_4 > p\text{-n-}C_9H_{19}\text{---}C_6H_4 > Ph > n\text{-}C_8H_{17} \qquad \text{(v)}$$

and for trans-[PdCl$_2$(PR$_3$)$_2$] is:

$$R = n\text{-}C_4H_9 > Ph > p\text{---}C_2H_5\text{---}C_6H_4 > n\text{-}C_8H_{17} > p\text{-n-}C_9H_{19}\text{---}C_6H_4 \qquad \text{(vi)}$$

Thus, introduction of a p-n-alkyl substituent on the phenyl rings of the tertiary phosphine increased the activity for platinum(II) but decreased it for palladium(II). It is interesting to note that cis-[PtCl$_2$\{P(n-C$_9$H$_{17}$)$_3$\}$_2$] gave a reasonably efficient catalyst, at least as active as the palladium(II) analogue, while trans-[PdCl$_2$\{P(n-C$_4$H$_9$)$_3$\}$_2$] again yielded one of the most active compounds.

In conclusion, it would appear that a relationship between catalyst activity and ligand properties for both platinum(II) and palladium(II) is not a simple one, and that there may be inherent differences in the mechanism depending on the metal. The catalytic efficiency may well depend on a number of contributing factors, not least of all the nature of the solvent. Indeed the hydrogenation of methyl linoleate is known to proceed nearly six times faster in the non-coordinating solvent dichloromethane than in a methanol–benzene mixture [11]. Other factors include:

(a) the relative basicity of the ligands affecting the M—H bond strength;

(b) steric effects of the phosphine ligands which may be shown by the difference in activity using the complexes cis-[PtCl$_2$\{P(p-n-C$_4$H$_9$—C$_6$H$_4$)$_3$\}$_2$] and cis-[PtCl$_2$\{P(p-n-C$_9$H$_{19}$—C$_6$H$_4$)$_3$\}$_2$] as well as trans-[PdCl$_2$\{P(n-C$_4$H$_9$)$_3$\}$_2$] and trans-[PdCl$_2$\{P(n-C$_{14}$H$_{29}$)$_3$\}$_2$] in the methyl linoleate study. The decrease in each case presumably originates from steric hindrance caused by the alkyl chain about the metal centre. This, however, is not so great as to inhibit completely interaction with the olefin substrate.

(c) The ability of the phosphine complex to coordinate reversibly to any solvent present. These features may be of differing importance for palladium(II) and platinum(II), this point being highlighted by cis-[PtCl$_2$\{P-(n-C$_4$H$_9$)$_3$\}$_2$] and trans-[PdCl$_2$\{P(n-C$_4$H$_9$)$_3$\}$_2$] which show the two extremes of catalytic activity. Since solvent plays a profound part in these catalytic systems [6, 7, 18] and may even furnish the source of hydrogen necessary for reduction [9, 11], predicting the relative activity of such compounds will prove difficult until the nature of the complex–solvent interaction can be established.

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# COMPLEXES OF LONG ALKYL CHAIN TERTIARY PHOSPHINES PART 6*. HOMOGENEOUS CATALYTIC HYDROGENATION OF METHYL LINOLEATE IN THE ABSENCE OF SOLVENT USING THE COMPLEXES [MCl₂)PR₃)₂], M = Pd, Pt; R = n-ALKYL, p-n-ALKYLPHENYL, IN THE PRESENCE OF TIN(II) CHLORIDE

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(Received December 14, 1982)

## Summary

The complexes [MCl₂(PR₃)₂], M = Pd, Pt; R = n-alkyl, p-n-alkylphenyl, in the presence of tin(II) chloride, have been used to catalyse selectively the hydrogenation of methyl linoleate in the absence of solvent. A precipitate remained at the end of each run, the nature of which depended on the solubility of the catalyst. The activity of the platinum(II) species was greatly increased in the absence of solvent; conversely, the palladium(II) compounds required the presence of a solvent such as methanol in order to function efficiently as catalysts. In only two cases was any decomposition of palladium(II) complexes observed and was found to be much less than in previous experiments. In the light of the results obtained with and without added solvent, the role of methanol and the nature of the rate-limiting step, which was found to be different for platinum(II) and palladium(II), are discussed.

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## Introduction

In the preceding paper [1] we reported the hydrogenation of methyl linoleate (methyl cis-9,cis-12-octadecadienoate) and methyl linolenate (methyl cis-9, cis-12, cis-15-octadecatrienoate) using the long alkyl chain containing tertiary phosphine complexes of platinum(II) and palladium(II) in the presence of tin(II) chloride and a 3:2 mixture of benzene and methanol. The results indicated that the variation in catalytic activity, not only between the two different metals but also on changing the phosphine ligand, was not a simple function of electronic and steric effects. The importance of the solvent in selective homogeneous catalytic hydrogenations was

noted in the reduction of polyenes using $[RhCl(PPh_3)_3]$, in which changing the solvent altered not only the rate of hydrogenation but also the selectivity [2]. Furthermore, the presence of a solvent such as methanol is sometimes necessary for reduction to occur [3]. The nature of the solvent was observed to affect the rate of hydrogenation of 1,5-cyclooctadiene using cis-$[PtCl_2$-$(PPh_3)_2]$ and tin(II) chloride such that the observed rate decreased according to the following sequence [4 - 6]:

$$CH_3CO_2H \sim CH_3CO_2H-CH_2Cl_2 > CH_3CO_2H-C_6H_6 > CH_2Cl_2 >$$
$$CH_3CO_2H-(CH_3)_2CO > CH_3OH-C_6H_6$$
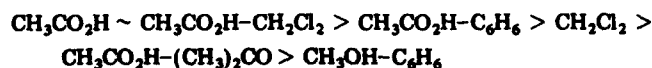
Methanol has been shown to coordinate to palladium(II) [7] and platinum(II) [8] and indeed was used as the source of hydrogen for the selective reduction of soybean methyl esters with $[MCl_2(PR_3)_2]$, M = Pd [9, 10], Pt [11] in the presence of tin(II) chloride via formation of a metal hydride intermediate (eqn. 1).

$$-\overset{|}{\underset{|}{M}}-Cl + CH_3OH \rightarrow -\overset{|}{\underset{|}{M}}-H + HCHO + HCl \tag{1}$$
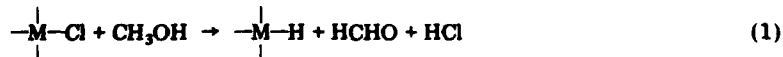
This reaction is to be expected since platinum(II)–chloro complexes are known to form hydride complexes with alcohols [12].

The tertiary phosphine complexes containing long alkyl chains, $[MCl_2$-$(PR_3)_2]$, M = Pd, Pt; R = n-alkyl, p-n-alkylphenyl, prepared in our laboratory [13], were found to be appreciably soluble in the substrate, methyl linoleate. Thus it was of interest to observe how effective these complexes were in selectively catalysing the hydrogenation of methyl linoleate in the absence of added solvent. Furthermore, their relative catalytic activities have already been determined in a benzene–methanol solvent system [1], and therefore it may be possible to learn more about the role of the methanol in these catalytic reactions.

### Experimental

The nature of the polyenes, preparation of the complexes and gas chromatographic analyses were as previously described [1, 13].

#### Hydrogenations

The reductions were carried out as before [1] using a 250 ml stainless steel autoclave (Baskerville and Lindsay) fitted with a glass liner, mechanical stirrer and electric thermostatted heater. At the beginning of each run the liner was charged with methyl linoleate (10 g, 34 mmol), metal complex (0.33 mmol) and tin(II) chloride dihydrate (0.64 g, 2.8 mmol). The autoclave was flushed twice with hydrogen and pressurised to 4.05 MN $m^{-2}$. A constant pressure and stirring speed (500 rpm) was maintained for 3 h, while
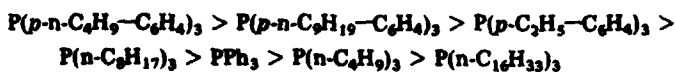
the heater required 40 min to attain a steady temperature of 90 °C. At the end of each run a sample was withdrawn for analysis by gas chromatography. The glass liner was cleaned thoroughly in chromic acid before each new experiment, and control runs carried out as previously described [1].

## Results and discussion

The hydrogenation of methyl linoleate in the presence of $[MCl_2(PR_3)_2]$, M = Pd, Pt; R = n-alkyl, p-n-alkylphenyl and tin(II) chloride without solvent was carried out using a very low catalyst to polyene ratio (10 mmol per mol substrate) compared to the previous runs performed in the presence of added solvent, where a ratio of 46 mmol per mol polyene was used [1]. This was done in order to achieve conditions which gave partially hydrogenated esters.

For each catalytic run, a mixture was obtained resulting from the isomerisation and reduction of methyl linoleate (Table 1). In only one instance using the most active precursor, cis-$[PtCl_2\{p$-n-$C_4H_9-C_6H_4)_3\}_2]$ was any saturated material observed; however, this constituted less than 1% of the total products. At the end of each run a precipitate always remained. Sometimes this contained only excess tin(II) chloride, shown to be catalytically inactive for hydrogenation under these conditions [5]. When the phosphine was $PPh_3$, $P(p$-$C_2H_5-C_6H_4)_3$ or $P(n$-$C_4H_9)_3$ a metal(II) complex was also present in the precipitate. However, the observation of some hydrogenation in the presence of both the platinum(II) and palladium(II) complexes of these phosphines suggests that during the reaction at 90 °C some of these compounds dissolve, at least partially. Only in the cases of palladium(II) with $P(p$-n-$C_9H_{19}-C_6H_4)_3$ and $P(n$-$C_8H_{17})_3$ were any decomposition products observed, and in both instances it was far less than in the presence of benzene–methanol solvent [1]. The infrared spectra of the insoluble complexes remaining after hydrogenation were similar to their spectra before; in particular, no bands attributable to $\nu(M-H)$ were detected.

The data obtained without added solvent in the presence of the platinum(II) complexes and tin(II) chloride followed trends similar to the reduction in benzene–methanol solvent, activity decreasing in the order of phosphine ligands:

$P(p$-n-$C_4H_9-C_6H_4)_3 > P(p$-n-$C_9H_{19}-C_6H_4)_3 > P(p$-$C_2H_5-C_6H_4)_3 >$

$P(n$-$C_8H_{17})_3 > PPh_3 > P(n$-$C_4H_9)_3 > P(n$-$C_{16}H_{33})_3$

The difference in the position of $P(p$-$C_2H_5-C_6H_4)_3$ in the presence of added solvent was presumably due to its limited solubility in the pure substrate. However, the most striking feature of the results was that although the catalyst:polyene ratio was about one-fifth of that used previously in benzene–methanol, the activity of the catalysts was greatly increased. Although this applied to both trialkyl- and triarylphosphine complexes, it was particularly noteworthy for the former which were almost totally inactive when solvent

**TABLE 1**

Hydrogenation of methyl linoleate in the presence of [MCl$_2$(PR$_3$)$_2$] and tin(II) chloride[a]

| Catalyst precursor | Ppt | Stearate | Monoene | Nc-diene[b] | C-diene[b] cis/trans | trans/trans |
|---|---|---|---|---|---|---|
| Control | — | — | — | 97.2% | 2.8% | |
| cis-[PtCl$_2$(PPh$_3$)$_2$] | d | — | 12.5% | 40.9% | 23.5% | 23.3% |
| cis-[PtCl$_2${P(p-C$_2$H$_5$—C$_6$H$_4$)$_3$}$_2$] | d | — | 42.0% | 25.4% | 12.8% | 19.8% |
| cis-[PtCl$_2${P(p-C$_6$H$_5$—C$_6$H$_4$)$_3$}$_2$] | c | 0.8% | 76.6% | 21.4% | 0.4% | 0.8% |
| cis-[PtCl$_2${P(p-C$_6$H$_{10}$—C$_6$H$_4$)$_3$}$_2$] | c | — | 64.0% | 24.0% | 4.8% | 7.2% |
| cis-[PtCl$_2${P(n-C$_4$H$_9$)$_3$}$_2$] | d | — | 9.0% | 55.4% | 28.3% | 12.3% |
| cis-[PtCl$_2${P(n-C$_8$H$_{17}$)$_3$}$_2$] | c | — | 14.5% | 46.9% | 22.1% | 16.0% |
| cis-[PtCl$_2${Pt(n-C$_{14}$H$_{29}$)$_3$}$_2$] | c | — | 6.6% | 58.1% | 22.9% | 12.4% |
| trans-[PdCl$_2$(PPh$_3$)$_2$] | d | — | 1.4% | 89.0% | 6.1% | 3.5% |
| trans-[PdCl$_2${P(p-C$_2$H$_5$—C$_6$H$_4$)$_3$}$_2$] | d | — | 2.8% | 65.2% | 17.1% | 15.4% |
| trans-[PdCl$_2${P(p-C$_6$H$_{10}$—C$_6$H$_4$)$_3$}$_2$] | ce | — | 18.0% | 47.7% | 15.7% | 18.6% |
| trans-[PdCl$_2${P(n-C$_4$H$_9$)$_3$}$_2$] | d | — | 3.1% | 80.3% | 9.5% | 7.1% |
| trans-[PtCl$_2${Pt(n-C$_8$H$_{17}$)$_2$}$_2$] | ce | — | 2.8% | 78.2% | 10.2% | 8.8% |

[a]10 mmol complex per mol substrate, 2.8 mmol tin(II) chloride dihydrate, 90 °C, 3 h and 4.05 MN m$^{-2}$ hydrogen.
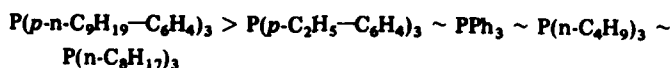[b]Nc, non-conjugated; C, conjugated.
[c]Tin(II) chloride present after hydrogenation.
[d]Tin(II) chloride and metal complex present after hydrogenation.
[e]Decomposition observed.
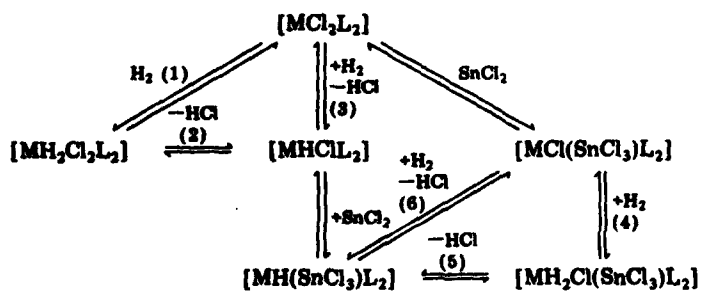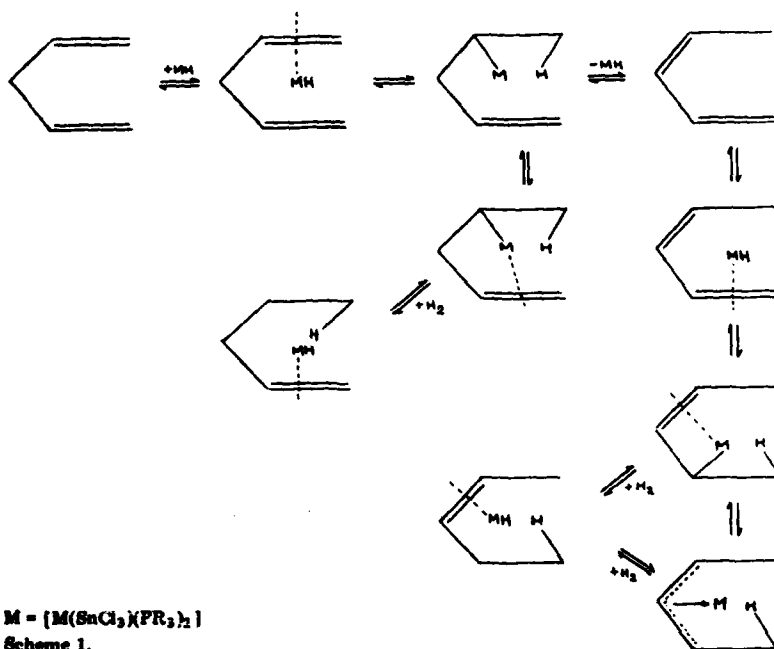
was present. In contrast, the palladium(II) species were almost completely inactive in the absence of benzene–methanol, although $trans$-[PdCl$_2$ $\{$P($p$-n-C$_9$H$_{19}$–C$_6$H$_4$)$_3$$\}_2$], which showed only modest activity, was an exception. This may well have resulted from its greater solubility in the substrate compared to the others. However, this complex was far less active than its platinum(II) analogue and showed only a slight tendency to decompose. Particularly noticeable was the decreased catalytic efficiency of $trans$-[PdCl$_2$-$\{$P(n-C$_4$H$_9$)$_3$$\}_2$], which gave the most active catalyst in benzene–methanol. It might be argued that this was due to its lower solubility in the neat substrate; however, neither $cis$-[PtCl$_2$(PPh$_3$)$_2$] nor $cis$-[PtCl$_2$ $\{$P($p$-C$_2$H$_5$–C$_6$H$_4$)$_3$$\}_2$] dissolved completely but both were catalytically active. The activity of the palladium(II) complexes decreased according to the order of phosphine ligand:

$$P(p\text{-}n\text{-}C_9H_{19}\text{–}C_6H_4)_3 > P(p\text{-}C_2H_5\text{–}C_6H_4)_3 \sim PPh_3 \sim P(n\text{-}C_4H_9)_3 \sim$$
$$P(n\text{-}C_8H_{17})_3$$

The results obtained from the hydrogenations in the presence and absence of solvent suggest that there are differences in the detailed mechanisms for palladium(II) and platinum(II). Thus: (a) palladium(II) complexes were generally inactive in the absence of benzene–methanol, whereas platinum(II) species were more active in the absence of solvent. (b) Much less decomposition of palladium(II) complexes occurred in the absence of added solvent. This supports the earlier suggestion [14] that an unstable intermediate complex involving methanol is necessary for activity, since the instability of the palladium(II) complexes, $trans$-[PdCl$_2$(PR$_3$)$_2$], relative to their platinum(II) analogues is not thermal.

The differences may be accounted for by consideration of the proposed mechanism (Scheme 1) [5, 6, 10, 11, 15, 16]. This involves three stages; formation of a metal hydride, production of a metal alkene and interaction of the hydride and alkene ligands. Generation of the metal hydride can either involve hydrogen gas or methanol as the hydride source. Hydrogen gas can react with [MCl$_2$L$_2$] to form [MHClL$_2$] either by oxidative addition (Scheme 2, steps 1 and 4) followed by reductive elimination of HCl (steps 2 and 5), or alternatively by heterolytic fission of H$_2$ (steps 3 and 6) [17]. Oxidative addition is known to be much easier for platinum(II) than palladium(II) [18]. Heterolytic fission of H$_2$ is more likely in the case of palladium(II). This would be promoted by the presence of a polar solvent such as methanol. In addition to hydrogen gas, methanol can act as the hydride source through eqn. 1, and indeed both platinum(II) and palladium(II) complexes have been found to be nearly as active in the reduction of soybean esters in methanol under nitrogen as under hydrogen [6, 9, 11]. The relative importance of methanol and gaseous hydrogen as the source of hydride depends not only on the metal and the ligands but also on the reaction conditions. For example, when $cis$-[PtCl$_2$(AsPh$_3$)$_2$] was used for the isomerisation of 1,5-hexadiene in

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M = [M(SnCl$_3$)(PR$_3$)$_2$]
Scheme 1.



Scheme 2.

methanol–benzene under one atmosphere of deuterium gas, then no deuterium was incorporated in the product [19]. However when greater pressures of hydrogen were used, it was suggested that the solvent was an insignificant source of hydride [5]. Certainly, there was only one source of hydrogen in our experiments without solvent, and the observation that some reduction

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and isomerisation occurred in the palladium(II) systems without solvent suggests that at least some palladium(II) hydride complexes were formed from hydrogen gas.

Metal alkene complex formation involves a substitution reaction. Substitution reactions at platinum(II) are slow, whereas they occur more rapidly at palladium(II) [18]. A coordinating solvent such as methanol will compete with the alkene for a coordination site on the metal [7, 8]. This would account for the reduced activity of platinum(II) complexes in the presence of coordinating solvents found in the present work as well as previously [4, 5]. The differences in the activities of the palladium(II) and platinum(II) complexes in the presence and absence of added methanol observed in the present work are entirely consistent with the mechanism in Scheme 1 if metal hydride complex formation, which is known to be slower for palladium(II) than platinum(II), is rate-limiting in the presence of palladium(II) complexes. If on the other hand metal alkene complex formation, which will be slower for platinum(II) than palladium(II), is the rate-limiting step in the presence of platinum(II) then the greater rates observed with the platinum(II) complexes in the absence of methanol, which competes with the alkene for coordination, are explained. Increasing the rate of the alkene substitution step by increasing the alkene concentration to neat substrate will not affect the overall rate for palladium(II), whereas in the case of platinum(II), where alkene substitution is rate determining, increasing the concentration of alkene will significantly enhance the rate as observed. Further support for the conclusion that it is platinum(II) alkene rather than platinum(II) hydride complex formation that is rate-limiting, is provided by the observation that cis-[PtCl$_2$(PPh$_3$)$_2$] and trans-[PtHCl(PPh$_3$)$_2$] are equally active polyene hydrogenation catalysts [5, 11]. The present conclusions are consistent with, and extend, the previous conclusion that the rate-limiting step is the formation of a metal–alkene–hydride intermediate [16].

## Acknowledgements

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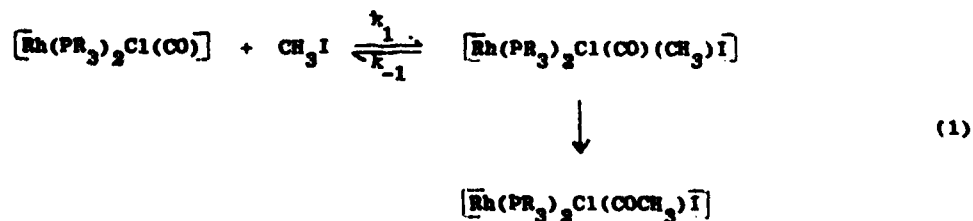19 R. W. Adams, G. E. Batley and J. C. Bailar, *J. Am. Chem. Soc.*, *90* (1968) 6051.

## Chapter 5

### The Influence of Long Alkyl Chains on the ability

### of Tertiary Phosphine Complexes of Platinum(O) and

### Rhodium(I) to Undergo Oxidation-Addition

As already mentioned in the Introduction (Chapter 1) a major goal for the
present work was the activation of alkanes.  A key step in this is the oxidative-
addition of C-H bonds to transition metal complexes (this is discussed further in
Chapter 7).  In the present chapter we describe studies on the influence of
long alkyl chain tertiary phosphines on the ability of firstly platinum(O) and secondly
rhodium(I) complexes to promote oxidative-addition.  These two systems were
chosen because they yield platinum(II) and rhodium(III) alkyl complexes, both of
which are known to have an extensive chemistry[1,2].

The ease of oxidative-addition of methyl iodide to $[Pt(PR_3)_2]$ and $[Pt(PR_3)_3]$
complexes was investigated in detail as described in reference 3.  It was found,
as expected, that trialkylphosphines promote oxidative-addition more readily than
triarylphosphines; within both series an increase in alkyl chain length decreases
the rate of oxidative-addition probably due to very specific and subtle solvation
effects.  The ease of oxidative-addition of $[Pt(PR_3)_2]$ was greater than of
$[Pt(PR_3)_3]$.

The ease of oxidative-addition at rhodium(I) has been investigated in
considerable detail as described in references 4-6.  This was not originally
intended.  The original aim was to take a simple well characterised rhodium(I)
system and examine the effect of long alkyl chains in the tertiary phosphine ligands
to see whether their effect was the same as that observed in the case of platinum(O).
The system chosen for study was that shown in reaction 1 which had been reported

$$[Rh(PR_3)_2Cl(CO)] + CH_3I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Rh(PR_3)_2Cl(CO)(CH_3)I]$$

$$\downarrow$$

$$[Rh(PR_3)_2Cl(COCH_3)I] \qquad (1)$$

in the literature in 1969[7]. This system appeared to follow pseudo-first order kinetics. It soon became apparent that the system was not as simple as it first appeared to be. In particular only with triphenylphosphine could be kinetics be mistaken for pseudo first order in the presence of excess methyl iodide. Accordingly a full non-linear kinetic analysis was carried out. This is described in references 4 and 5. This suggested that the literature mechanism was a considerable oversimplification. However the reaction chosen (reaction 1) is unnecessarily complicated in that two different halides, chloride and iodide, are present. It would be much easier to interpret the results if only one halide were present in the reaction. Since alkyl iodides undergo oxidative-addition much more readily than alkyl chlorides or bromides the ideal system would be that between methyl iodide and $[Rh(PR_3)_2I(CO)]$. Investigation of this showed that $[Rh(PR_3)_2I(CO)]$ is more difficult to prepare and *less* stable than its chloro-analogue. This system and the corresponding bromo-system $[Rh(PR_3)_2Br(CO)]$ are described in more detail in Chapter 3 reference 3.

A detailed study of the oxidative-addition of methyl iodide to $[Rh(PR_3)_2X(CO)]$ and $[Rh(PR_3)X(CO)]_2$ where X = Cl and I, methyl bromide to $[Rh(PEt_2Ph)_2Br(CO)]$ and n-propyl bromide to $[Rh\{P(C_6H_4Et-p)_3\}_2Br(CO)]$ showed:

(i)     The addition of alkyl bromides is very slow.

(ii)    The ease of oxidative-addition to the iodo-complexes is dimer > monomer (i.e. $[Rh(PR_3)I(CO)]_2$ > $[Rh(PR_3)_2I(CO)]$).

(iii)   The ease of oxidative-addition to the chloro-complexes appears to be very similar for the monomeric and dimeric complexes.

(iv)    Iodo-rhodium(I) complexes undergo oxidative-addition more readily than the corresponding chloro-complexes.

(v)     The introduction of alkyl substituents in the para-position of coordinated triphenylphosphine enhances oxidative-addition at rhodium(I); n-butyl substituents are more effective than ethyl substituents.

(vi)    Trialkylphosphines are more effective than triarylphosphines at promoting oxidative-addition at rhodium(I); alkyl chains longer than n-butyl are

marginally less effective than _n_-butyl itself.

The results of this work strongly suggested that it would be constructive to examine the possibility of oxidative-addition of the C-Cl bond of mustard to rhodium(I) as a potential means of deactivating mustard. This is reported in detail in Chapter 6.

(vii) The oxidative-addition of methyl iodide to trans-$\overline{[}$RhI(CO)(PPh$_3$)$_2$$]$ in air gives $\underset{\sim}{I}$ as shown in equation 2. This rhodium(III) complex and

$$2 \text{ trans-}\overline{[}\text{RhI(CO)(PPh}_3\text{)}_2] + 2\text{MeI} \xrightarrow{\text{O}_2}$$



$$+ 2\text{CO} \qquad (2)$$
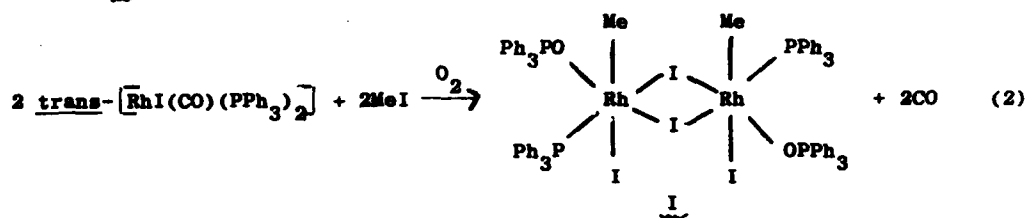
$\overline{[}$RhI(O$_2$)(OPPh$_3$).2H$_2\overline{\text{O}}]$ reported earlier[6] demonstrates the ability of rhodium complexes to coordinate phosphine oxides.

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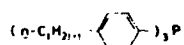# Phosphine Complexes [1]

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Received October 21, 1980

*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$_6$H$_4$Et-p)$_3$ < P(C$_6$H$_4$Me-p)$_3$ < P(n-C$_{16}$H$_{33}$)$_3$ < P(n-C$_8$H$_{17}$)$_3$. 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-C$_m$H$_{2m+1}$)$_3$ where m = 10 to 19 and

$$(n\text{-}C_l H_{2l+1}\ \langle\ \rangle\ )_3 P$$

where l = 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). Accord-

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ingly we investigated the oxidative addition of methyl iodide to [PtL$_n$] where L = tertiary phosphine and n = 3 or 4 (reaction 1). We have

$$PtL_n + CH_3I \rightarrow [PtL_2(CH_3)I] + (n - 2) \qquad (1)$$
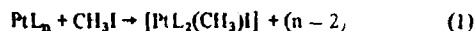
previously reported on the ability of the present phosphines to promote oxidative addition at rhodium(I) [5].

## Experimental

The tertiary phosphines and their platinum(0) complexes were prepared as described previously [2–4]. Solutions of PtL$_n$ (4 × 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 2.303log(A$_\infty$ - A$_t$) against time, where A$_\infty$ and A$_t$ were the absorbances at infinite time and time

**TABLE 1.** Kinetic Data for the Oxidative Addition of Methyl Iodide to $[PtL_n]$ at $25.0 \pm 0.1$ °C.

| $[PtL_n]$ | Wavelength studied (nm) | $k_1$ ($s^{-1} \times 10^3$) | $k_2$ ($s^{-1} \times 10^3$) |
|---|---|---|---|
| $[Pt\{P( \langle \rangle\ CH_3)_3\}_4]$ | 358 | 2.3 | 9.1 |
| $[Pt\{P( \langle \rangle\ C_2H_5)_3\}_4]$ | 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

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

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

$[PtL_3] + CH_3I$

$[PtL_2] + CH_3I$
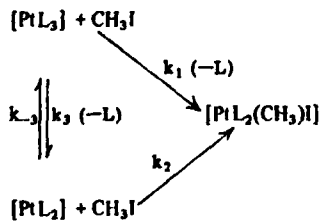
*Scheme*

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 corres-

pond 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

$$[A] = [A_o]e^{-k_1 t} \qquad (7)$$

$$[B] = [B_o]e^{-k_2 t} \qquad (8)$$

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

$$[C] = [C_\infty] - [A_o]e^{-k_1 t} - [B_o]e^{-k_2 t} \qquad (11)$$

and

$$\log([C_\infty] - [C]) = \log([A_o]e^{-k_1 t} + [B_o]e^{-k_2 t}) \qquad (12)$$

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,

$$\log[A] = \log([C_\infty] - [C]) = \log[A_o] - \frac{k_1 t}{2.303} \qquad (13)$$

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

$$L = P(\langle \rangle\text{-}C_2H_5)_3 < P(\langle \rangle\text{-}CH_3)_3 < P(n\text{-}C_{16}H_{33})_3 <$$
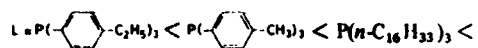
$P(n\text{-}C_8H_{17})_3$. The order triarylphosphine < trialkylphosphine reflects an increase in the basicity of the tertiary phosphine ligand which promotes nucleophilic attack by platinum on the carbon atom of methyl iodide. Within the trialkyl- and triarylphosphine series an increase in alkyl chain 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.

## Acknowledgements

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# The Preparation, Characterization, and Properties of Highly Soluble Transition-Metal Complexes of Long-Chain Tertiary Phosphines

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*Two series of phosphines, I ($PR_3R$ = n-$C_{10}H_{21}$ – n-$C_{18}$-$H_{39}$) and II ($P(\quad R')_3$ $R'$ = $C_2H_5$ – n-$C_9H_{19}$), which form very soluble complexes, have been prepared, characterized, and used to prepare cis-[$PtL_2Cl_2$], trans-[$PdL_2$-$Cl_2$], trans-[$PtL_2'HCl$], [$PtL_4$], and trans-[$RhL_2Cl(CO)$] where L = I and II and L' = I only. The problems of isolating and purifying the complexes are discussed. The influence of the two series of phosphines on (1) selective hydrogenation catalysts of the type [$PtL_2Cl_2$] or [$PdL_2$-$Cl_2$] in association with $SnCl_2$ for polyunsaturated olefins and (2) the oxidative addition of methyl iodide to trans-[$RhL_2Cl(CO)$] is reported. The mechanism of the latter reaction in the presence of triarylphosphines is more complex than suggested previously.*
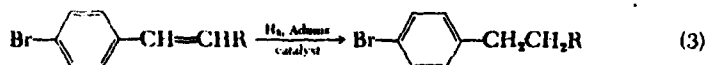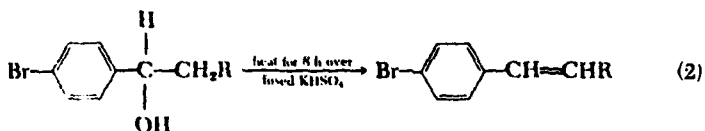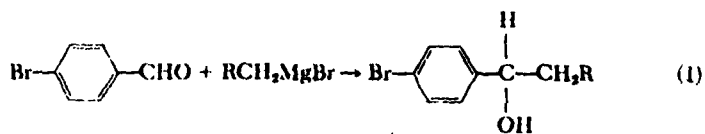
Phosphine complexes have been used widely as homogeneous catalysts, and in many of their reactions the solvent plays a very important part. Accordingly we decided to prepare phosphine complexes with rather different solubility properties to those previously available. In particular two series of tertiary phosphine complexes were prepared that would confer extreme solubility in hydrocarbon solvents such as alkanes. Part of the rationalization for doing this was the view that if alkanes were ever going to be activated using homo-

geneous catalysts, the activation would have to be effected in the presence of solvents that were chemically more inert than the alkanes themselves. No such solvents are, of course, available and if homogeneous catalysts are to be used then those catalysts must dissolve freely in the alkanes themselves.

Two series of tertiary phosphine ligands that are very soluble in hydrocarbon solvents were prepared. The first series, $P(n-C_mH_{2m+1})_3$, where $m$ = 10 to 19, were prepared by treating the Grignard reagent of the $n$-alkyl bromide with phosphorus trichloride in tetrahydrofuran (THF) ($1$). They were purified by recrystallization from a mixture of chloroform and ethanol. The lower members of the series were waxy materials, $C_{10}$–$C_{12}$ being soft waxes and $C_{13}$–$C_{15}$ being hard waxes, while the higher members of the series were crystalline. All were fairly low melting—the melting points increasing steadily from 37°–40°C for $P(n-C_{10}H_{21})_3$ to 60°–62°C for $P(n-C_{19}H_{39})_3$. They were extremely soluble in hydrocarbon solvents such as hexane and chlorinated solvents such as dichloromethane, chloroform, carbon tetrachloride, and 1,2-dichloroethane and moderately soluble in THF, benzene, and other aromatic solvents, hot alcohols such as methanol and ethanol, and warm acetone. They were, however, insoluble in cold methanol, ethanol, and acetone. On exposure to air they were oxidized readily to a complex mixture of products of the type $P(OR)_{3-n}R_n$ ($n$ = 0, 1, or 2) and $P(O)(OR)_{3-n}R_n$ ($n$ = 0, 1, 2, or 3). However treatment with a slight excess of hydrogen peroxide (6% w/v) resulted in a smooth oxidation to the trialkylphosphine oxides which were stable in air and more crystalline than the corresponding tertiary phosphines. These phosphine oxides had very similar solubility characteristics to the parent trialkylphosphines. In contrast to trialkylphosphine oxides below $PO(n-C_8H_{17})_3$, the long-chain trialkylphosphine oxides were not deliquescent.

The second series of phosphines prepared were a series of tris($p$-alkylaryl)phosphines with alkyl groups ranging from $n$-C$_3$H$_7$ to $n$-C$_9$H$_{19}$. They were prepared by treating the Grignard reagent of the corresponding $p$-alkylbromobenzene with phosphorus trichloride in THF ($2$). However in order to use these routes it was necessary to devise a preparative route for synthesizing $p$-alkylbromobenzenes. Many of the methods for preparing alkylbromobenzenes yield a mixture of isomers. Since these are liquids with similar boiling points, their separation is difficult. A three-stage synthesis was adopted eventually (see Reactions 1, 2, and 3) which gave the pure para isomer in overall yields of 46 to 60%. The compound $p$-propylbromobenzene also can be prepared in this way but it is prepared more easily by reacting allylbromide with the mono-Grignard reagent of $p$-dibromobenzene followed by hydrogenating the resulting $p$-propenylbromobenzene to yield the desired product.

83.

$$Br-\langle C_6H_4 \rangle-CHO + RCH_2MgBr \rightarrow Br-\langle C_6H_4 \rangle-\underset{OH}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_2R \qquad (1)$$

$$Br-\langle C_6H_4 \rangle-\underset{OH}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_2R \xrightarrow[\text{fused KHSO}_4]{\text{heat for 8 h over}} Br-\langle C_6H_4 \rangle-CH=CHR \qquad (2)$$

$$Br-\langle C_6H_4 \rangle-CH=CHR \xrightarrow[\text{catalyst}]{H_2, \text{ Adams}} Br-\langle C_6H_4 \rangle-CH_2CH_2R \qquad (3)$$

After completing this work our attention was drawn to the synthetic procedure of Manassen and Dror (3) based on reacting bromobenzene with an acyl chloride in the presence of aluminum trichloride. This then is followed by a Wolff–Kischner reduction of the acyl group to an alkyl group using alkaline hydrazine. Although these authors do not give overall yields, the acylation step (4) gives only 30% of the desired product together with 25% of $C_6H_5COR$. Thus our procedure gives much higher overall yields with only minor quantities of side products to be separated off in the final vacuum distillation.

The tris($p$-alkylaryl)phosphine with a propyl group was a crystalline solid, whereas the $n$-butyl to $n$-octyl derivatives were viscous oils. The $n$-nonyl derivative was a viscous, waxy solid. The solids were purified by recrystallization from ethanol and the oils by vacuum distillation. All of the tris($p$-alkylaryl)phosphines were extremely soluble in hydrocarbon solvents such as hexane and chlorinated solvents such as dichloromethane, chloroform, and carbon tetrachloride, and moderately soluble in THF, diethyl ether, and aromatic solvents such as benzene and toluene. The lower members of the series were soluble in ethanol but this decreased as the alkyl chain length increased. The higher members were insoluble in cold ethanol, methanol, and other polar solvents. P-31 NMR chemical shifts were measured in $CDCl_3$ solution relative to a trimethylphosphate external standard and were found to be as follows: $p$-alkyl = $C_3H_6$, +10.6; $C_3H_7$, +10.5; $C_4H_9$, +10.6; $C_5H_{11}$, +10.6; $C_7H_{15}$, +10.8; $C_8H_{17}$, +10.7, and $C_9H_{19}$ +10.8 ppm. All of the tris($p$-alkylaryl)phosphines were sensitive to oxygen both as solids or oils and in solution. This contrasts with triphenylphosphine which is fairly resistant to oxidation both as a solid and in solution. Unlike the trialkylphosphines which yield a complex mixture of products on oxidation in the air, the tris($p$-alkylaryl)phosphines give a single product, the phosphine oxide. The sensitivity to air oxidation

increased as the alkyl chain on the phenyl ring increased in length. Oxidation with hydrogen peroxide (6% w/v) gave a convenient preparative route to the tris(p-alkylaryl)phosphine oxides.

Five series of transition-metal complexes of the new tertiary phosphines have been prepared: cis-[Pt(PR$_3$)$_2$Cl$_2$], trans-[Pd(PR$_3$)$_2$Cl$_2$], trans-[Pt(PR$_3$')$_2$HCl], [Pt(PR$_3$)$_4$], and trans-[Rh(PR$_3$)$_2$Cl(CO)] where R = n-alkyl or p-alkylaryl and R' = n-alkyl (5). All of the complexes displayed essentially the same solubility characteristics as the parent phosphines. Accordingly the synthetic routes that were used were chosen because they gave the cleanest reactions with largely volatile side products and a minimum of isomers.

## cis-[Pt(PR$_3$)$_2$Cl$_2$]

When [Pt(COD)Cl$_2$] was treated with two equivalents of the tertiary phosphine, cyclooctadiene was displaced and cis-[Pt(PR$_3$)$_2$Cl$_2$] was formed. The displaced cyclooctadiene was removed easily in vacuo. The lower triarylphosphine complexes were recrystallized from a 60:40 mixture of ethanol and chloroform. The higher triarylphosphine complexes could be obtained only as either waxes or viscous oils. These were purified chromatographically on alumina (Brockman activity I, neutral) eluting with a 60:40 mixture of chloroform and methanol. The trialkylphosphine complexes were recrystallized from a mixture of chloroform and ethanol except for the trioctylphosphine complex which was purified chromatographically to yield a yellow wax. The melting points of the trialkylphosphine complexes are interesting (see Figure 1) in that the long-chain alkyl groups clearly disrupt the packing in the crystal structure so that the melting point initially decreases sharply until the tri-n-octylphosphine is reached after which a slight rise occurs, presumably due to increasing molecular weight. The initial sharp drop in Figure 1 has been observed previously for platinum(II) complexes with n in the 2–4 range as well as for palladium(II) complexes with n in the 2–5 range (6, 7). On heating the cis isomers decompose but they do not either isomerize or give any metallation. When [Pt(MeCN)$_2$Cl$_2$] is used as the starting platinum(II) complex, a mixture of cis- and trans-[Pt(PR$_3$)$_2$Cl$_2$] is formed. This mixture is virtually impossible to separate because of the very similar physical characteristics of the two isomers.

## trans-[Pd(PR$_3$)$_2$Cl$_2$]

When [Pd(COD)Cl$_2$] was treated with two equivalents of the tris(p-alkylaryl) phosphines, PAr$_3$, trans-[Pd(PAr$_3$)$_2$Cl$_2$] complexes were formed. Apart from their trans geometry they were very similar to their platinum(II) analogues, although less crystalline so that purifica-
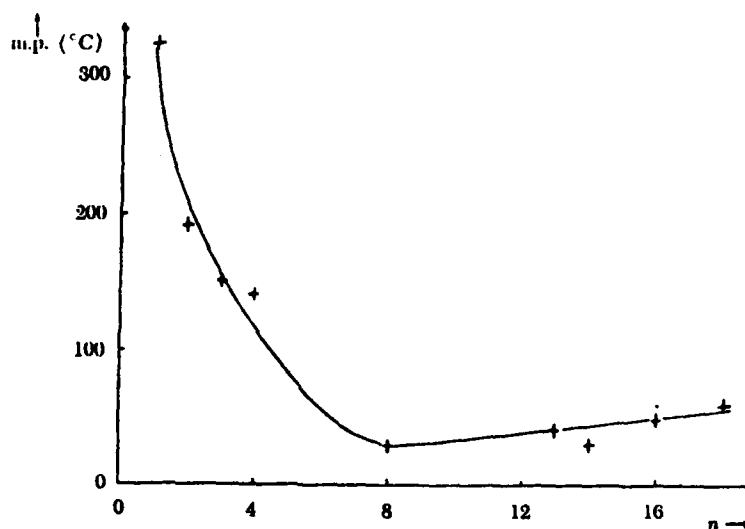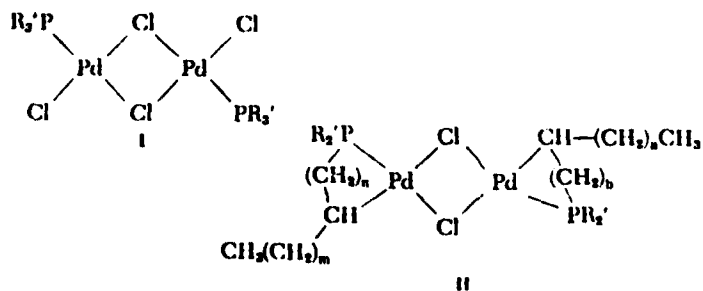
*Figure 1. Melting points of cis-[Pt{P(n-C_mH_{2m+1})_3}_2Cl_2] complexes*

tion depended more on column chromatography. With the trialkyl-phosphines, $PR_3'$, two products were obtained. The first was a yellow material, *trans*-[Pd(PR_3')_2Cl_2], which was very similar to the *trans*-[Pd(PAr_3)_2Cl_2] complexes. However a second, darker product was also present and in an increasing amount as the chain length increased. H-1, C-13, and P-31 NMR analyses and IR spectroscopy combined to suggest that this darker material is a mixture of chloride-bridged, dimeric Species I and II. In spite of repeated attempts it was impossible to separate these species by column chromatography. The metallated species, II, appear to be a complex mixture of products; the five-
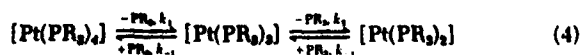
membered ring species ($n = b = 2$) would be expected to predominate. It is surprising, in view of the work of Shaw ($8$, $9$) which has shown platinum(II) to be more susceptible to metallation than palladium(II), that in the present work the reverse is found. In spite of repeated attempts we were unable to thermally induce metallation at platinum(II).

### trans-[Pt(PR$_3$')$_2$HCl]

The cis-[Pt(PR$_3$')$_2$Cl$_2$] compounds, where R' = alkyl, were converted smoothly to trans-[Pt(PR$_3$')$_2$HCl] by treating them with hydrazine hydrate in a mixture of ethanol and chloroform. Chloroform must be added since the complexes are insoluble in pure ethanol. The hydride complexes are cream-colored, low-melting, crystalline solids that closely resemble the physical properties of the parent dichloro complexes.

### [Pt(PR)$_3$]$_4$

When [Pt(COD)$_2$] ($10$) is treated with 4 equiv of tertiary phosphine in a hexane solution under nitrogen, [Pt(PR$_3$)$_4$] is formed. These platinum(0) complexes are yellow, air-sensitive, low-melting, crystalline solids with solubility properties that are very similar to the parent phosphines. When dissolved in solution these complexes reversibly dissociate (see Equation 4). Thus the P-31 NMR spectra in benzene

$$[Pt(PR_3)_4] \underset{+PR_3, k_{-1}}{\overset{-PR_3, k_1}{\rightleftharpoons}} [Pt(PR_3)_3] \underset{+PR_3, k}{\overset{-PR_3, k}{\rightleftharpoons}} [Pt(PR_3)_2] \qquad (4)$$

solution at ambient temperatures show a broad singlet only with no platinum–phosphorus coupling. A spectrophotometric study of the kinetics of phosphine dissociation at 25°C in a $4 \times 10^{-4}$ mol L$^{-1}$ benzene solution showed that the rate of the first step decreased in the following order: P($n$-C$_{18}$H$_{33}$)$_3$ ($k_1$(obs) too large to measure) $\gg$ P(—$\quad$—CH$_3$)$_3$ ($k_1$(obs) = $3.5 \times 10^{-4}$ sec$^{-1}$) > PPh$_3$ ($k_1$(obs) = $1.5 \times 10^{-3}$ sec$^{-1}$). The rates of the second step were more similar, decreasing in the following order: P(—$\quad$—CH$_3$)$_3$ ($k_2$(obs) = $6.7 \times 10^{-3}$ sec$^{-1}$) > P($n$-C$_{18}$H$_{33}$)$_3$ ($k_2$(obs) = $3.7 \times 10^{-3}$ sec$^{-1}$) $\geq$ PPh$_3$ ($k_2$(obs) = $3.5 \times 10^{-3}$ sec$^{-1}$). The significantly faster rate of dissociation of the tetrakis(trialkylphosphine)platinum(0) complex than the triarylphosphine complexes is probably due to the unfavorable build-up of electron density at platinum(0) effected by the more strongly electron-donating trialkylphosphine.

**trans-[ $Rh(PR_3)_2Cl(CO)$ ]**

The *trans*-[Rh(PR$_3$)$_2$Cl(CO)] complexes were prepared by treating [RhCl(CO)$_2$]$_2$ under nitrogen in chloroform solution with 2 equiv of tertiary phosphine per rhodium atom. The only side product was carbon monoxide so that purification by recrystallization from ethanol or ethanol–chloroform was relatively simple. The lower-molecular-weight trialkylphosphine and higher-molecular-weight triarylphosphine complexes were orange, viscous oils; the others were cream-colored, low-melting crystalline solids.

## Olefin Hydrogenation

Bailar and his co-workers have studied using mixtures of [M(PR$_3$)$_2$Cl$_2$] and stannous chloride as catalysts for selectively hydrogenating the polyolefins present in vegetable oils to monoolefins that subsequently may be used as components of margarine (*11*). Selectivity is very important in this hydrogenation because diolefins of the type —CH=CH—CH$_2$—CH=CH— are very susceptible to aerial oxidation at the activated methylene group resulting in the fat becoming rancid, while the fully saturated products, although stable to storage, are very difficult to digest. From previous work it is likely that the solvent plays a very important role in the selectivity of these hydrogenations. Since the present tertiary phosphines convey unusual and somewhat extreme solubility properties, it seemed desirable to examine them as possible catalysts. Accordingly their effectiveness in promoting the selective hydrogenation of two of the common components of vegetable oils, linoleic esters III and linolenic esters IV, was examined using the methyl esters.



|           III           |           IV           |
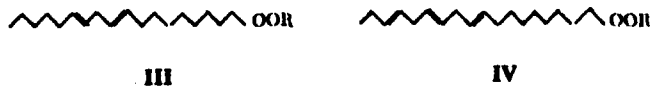
When methyl linoleate was hydrogenated in a 3:2 mixture of benzene and methanol at 90°C under 40 atm of hydrogen pressure in the presence of 0.65 mmol [M(PR$_3$)$_2$Cl$_2$] and 5.7 mmol stannous chloride (*see* Table I), it was apparent that of the platinum(II) complexes, that with P(—⟨⟩—C$_4$H$_9$)$_3$ was the most selective giving 87.2% monoolefin while P(—⟨⟩—C$_3$H$_9$)$_3$ and P(C$_8$H$_{17}$)$_3$ were close behind. P(—⟨⟩—C$_9$H$_{19}$)$_3$ was the most selective (87.8% monoolefin) with palladium(II). All of these complexes were much more specific than the triphenylphosphine complex under comparable conditions. It

Table 1. The Homogeneous Hydrogenation of Methyl Linoleate (4 g) in the Presence of 0.65 mmol [ML₂CL₂] and 5.7 mmol SnCl₂ in a Mixture of Benzene (30 mL) and Methanol (20 mL) at 90°C Under 40 atm of Hydrogen Pressure for 3 h

| M | L | | Products Formed (%) | | | Conjugated Diolefin | |
|---|---|---|---|---|---|---|---|
| | | Methyl Stearate | Mono-olefin | Non-conjugated Diolefin | cis–trans | trans–trans |
| None* | PPh₃ | — | 2.4 | 97.6 | — | — |
| Platinum | | | 41.0 | 24.7 | 8.5 | 25.8 |
| | P(—⬡—Et)₃ | 3.7 | 83.7 | 12.6 | — | — |
| | P(—⬡—Bu)₃ | 2.0 | 87.2 | 10.8 | — | — |
| | P(n-C₄H₉)₃ | — | 11.8 | 52.8 | 16.8 | 18.6 |
| | P(n-C₈H₁₇)₃ | — | 78.2 | 21.8 | — | — |
| | P(n-C₁₆H₃₃)₃ | — | 4.4 | 64.5 | 20.2 | 10.9 |
| Palladium | PPh₃ | — | 29.0 | 39.5 | 11.2 | 20.3 |
| | P(—⬡—Et)₃ | — | 50.2 | 25.0 | 6.9 | 17.9 |
| | P(—⬡—Bu)₃ | — | 17.2 | 40.9 | 13.3 | 28.6 |
| | P(—⬡—C₉H₁₉)₃ | — | 87.8 | 12.2 | — | — |
| | P(n-C₄H₉)₃ | — | 35.3 | 29.3 | 11.0 | 24.4 |
| | P(n-C₈H₁₇)₃ | — | 56.2 | 22.4 | 5.3 | 16.1 |

* Control hydrogenation carried out in the absence of catalyst.

89.

is very obvious from Table I that the selectivity is very dependent on the phosphine used. Thus while $P(C_9H_{19})_3$ gives high selectivity on platinum(II), $P(C_4H_9)_3$ and $P(C_{14}H_{29})_3$ give only 11.8 and 4.4% mono-olefin, respectively. A similar result occurs with palladium(II), with monoolefin yields varying apparently randomly as the R' group in

$P(—\qquad—R')_3$ is varied systematically in the following order: R' = H

(29.0%), $C_2H_3$ (50.2%), $C_4H_9$ (17.2%), and $C_9H_{19}$ (87.8%). Since it is hard to see how variations in either steric or electronic factors or even in both could account for this result on their own, we suggest that the interaction of the solvent with the active catalyst has a profound and subtle effect on the reaction.

When the same catalyst precursors and the same conditions were used to hydrogenate the triolefin methyl linolenate we found (*see* Table II) that platinum(II) complexes were more active under the present conditions than palladium(II) complexes, and that the introduction of a para-ethyl group into triphenylphosphine increased the activity of the platinum(II) catalyst markedly and that of the palladium(II) catalyst slightly. Introducing a para-nonyl group into the palladium(II) system markedly depressed both activity and selectivity, again suggesting that a complex set of factors probably including interaction with the solvent are involved in determining catalytic activity. The greater activity of the platinum(II) over the *palladium(II)* complexes under present conditions well may be a reflection of their greater stability. No signs of decomposition were detected when platinum(II) complexes were used, whereas deposition of metal was apparent when palladium(II) complexes were used.

Since the nature of the solvent plays an important part in these hydrogenations (*11*) and since methanol coordinates to palladium(II) and platinum(II) (*12*) and will therefore compete with the substrate, it was interesting to examine the effectiveness of the present catalysts in the absence of any solvent other than the substrate itself. When comparing the results obtained in the absence of solvent (*see* Table III) with those in Tables I and II, we must emphasize that in the former case the amount of substrate has been increased by a factor of 2.5, the amount of catalyst has been halved, and the amount of hydrogen has remained unaltered. Qualitative observation of the rate of fall of hydrogen pressure in the autoclave suggested that the initial reaction in the absence of solvent was faster than in its presence. Further work is currently in progress to confirm this observation and to modify the autoclave, enabling hydrogenations to be carried out under constant hydrogen pressure rather than merely constant hydrogen volume as is being done presently. This will ensure that hydrogenations can be totally completed.

Table II.  The Homogeneous Hydrogenation of Methyl Linolenate (4 g) in the Presence of 0.65 mmol [$ML_2Cl_2$] and 5.7 mmol $SnCl_3$ in a Mixture of Benzene (30 mL) and Methanol (20 mL) at 90°C Under 40 atm of Hydrogen Pressure for 3 h

| | | | | | Products Formed (%) | | | |
| | | | | Non- | Conjugated Diolefin | | Non- | Con- jugated |
| M | L | Methyl Stearate | Mono- olefin | conjugated Diolefin | cis–trans | trans–trans | conjugated Triolefin | jugated Triolefin |
|---|---|---|---|---|---|---|---|---|
| None[a] | | — | 2.0 | 19.9 | — | — | 78.1 | — |
| Plat- inum | PPh₃ | — | 55.6 | 38.8 | 1.9 | 3.7 | — | — |
| | P(—Et)₃ | 5.4 | 75.0 | 19.6 | — | — | — | — |
| Palla- dium | PPh₃ | — | 21.4 | 61.8 | 4.8 | 12.0 | — | — |
| | P(—Et)₃ | — | 26.6 | 59.3 | 5.3 | 8.8 | — | — |
| | P(—C₆H₁₀)₃ | — | 12.2 | 44.9 | 17.9 | 10.5 | 14.6 | — |

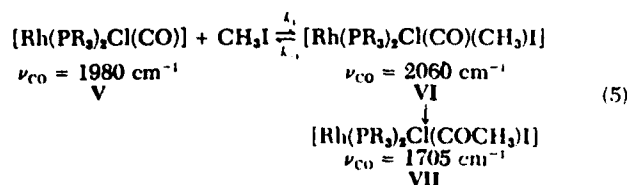[a] Control hydrogenation carried out in the absence of catalyst.

## Experimental

Olefin hydrogenations were performed in a 250-mL stainless steel auto-clave equipped with a glass liner using a stirring speed of 500 rpm. The auto-clave was charged with reactants, assembled, and gas was introduced to the desired initial pressure. All valves remained closed throughout the reaction. A thermostat was provided to enable temperature control. Product analysis was carried out via gas chromatography using a 20% diethylene glycol succinate on Chromasorp P (60–80 mesh) stationary phase in a glass column at 200°C.

The reaction of *trans*-[Rh(PR$_3$)$_2$Cl(CO)] with methyl iodide was studied by monitoring the IR spectra of solutions of the complex (2 × 10$^{-2}$ mol L.$^{-1}$) in methyl iodide (redistilled) in a thermostatted solution IR cell provided with sodium chloride windows. A Perkin–Elmer model 577 spectrometer was used. The data was analyzed using the FACSIMILE computer program (14).

## Oxidative Addition to trans-[Rh(PR₃)₂Cl(CO)]

Since one of the key steps in the activation of alkanes is believed to be oxidative addition, and since this reaction is very important in the mechanism of many homogeneous catalysts, it was interesting to determine the influence of the present series of phosphines on this type of reaction. Therefore we decided to study the oxidative addition of methyl iodide to *trans*-[Rh(PR$_3$)$_2$Cl(CO)] because this reaction has been studied previously (13) with PR$_3$ = PPh$_3$, P(C$_6$H$_4$OMe-$p$)$_3$, P(C$_6$H$_4$F-$p$)$_3$, and AsPh$_3$, and also because it is relatively easy to independently monitor the loss of *trans*-[Rh(PR$_3$)$_2$Cl(CO)], the formation and later decay of [Rh(PR$_3$)$_2$Cl(CO)(CH$_3$)I], and the subsequent formation of [Rh(PR$_3$)$_2$Cl(COCH$_3$)I] by recording the C=O *stretching region* of the IR spectrum as a function of time. The reaction is reported to occur by the following mechanism:

$$[Rh(PR_3)_2Cl(CO)] + CH_3I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Rh(PR_3)_2Cl(CO)(CH_3)I]$$

$$\nu_{CO} = 1980 \text{ cm}^{-1} \qquad\qquad \nu_{CO} = 2060 \text{ cm}^{-1}$$
$$\mathbf{V} \qquad\qquad\qquad \mathbf{VI} \qquad\qquad (5)$$
$$\downarrow$$
$$[Rh(PR_3)_2Cl(COCH_3)I]$$
$$\nu_{CO} = 1705 \text{ cm}^{-1}$$
$$\mathbf{VII}$$

which in the presence of excess methyl iodide can be examined in terms of a model:

$$\mathbf{V} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathbf{VI} \overset{k_2}{\rightarrow} \mathbf{VII} \qquad (6)$$

The FACSIMILE computer program (14) was used to analyze data obtained when solutions of *trans*-[Rh(PR$_3$)$_2$Cl(CO)] (2 × 10$^{-2}$ mol L.$^{-1}$)
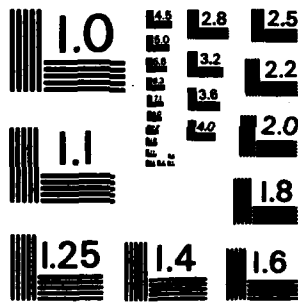
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Table III. The Homogeneous Hydrogenation of Methyl Linolenate in the Presence of 0.33 mmol [ML$_2$Cl$_2$] and 2.9 mmol

| M | L | H$_2$ Pressure (atm) | Methyl Stearate |
|---|---|---|---|
| Methyl Linolenate | | | |
| None[a] | | 40 | — |
| Platinum | P($n$-C$_8$H$_{17}$)$_3$ | 40 | — |
| Palladium | PPh$_3$ | 40 | — |
| Methyl Linolenate + Methyl Linoleate (Mixture 1) | | | |
| None[a] | — | 40 | — |
| Platinum | P(—   —C$_4$H$_9$)$_3$ | 40 | — |
| Palladium | P(—   —C$_9$H$_{19}$)$_3$ | 40 | — |
| Palladium | P(—   —C$_9$H$_{19}$)$_3$ | 20 | — |
| Methyl Linolenate + Methyl Linoleate (Mixture 2) | | | |
| None[a] | — | 40 | — |
| Platinum | PPh$_3$ | 40 | — |

[a] Control hydrogenation carried out in the absence of catalyst.

in methyl iodide were allowed to react at various temperatures. An analysis of the data obtained with P(C$_6$H$_4$Bu-$p$)$_3$ according to Equation 6 gave a rather poor fit to the data (see Figure 2). In particular the rate of formation of [Rh{P(C$_6$H$_4$Bu-$p$)$_3$}$_2$(COCH$_3$)ClI] at times very close to the start is more rapid than expected from Equation 6. However, when a number of alternative models were tried, we found that the following model in which VI is formed but is not an intermediate in the formation of VII gave the best fit. The calculated

$$V \underset{k_4}{\overset{k_3}{\rightleftharpoons}} VI \tag{7}$$
$$\searrow_{k_3}$$
$$VII$$

absorbances obtained when the data is analyzed according to Equation 7 and the observed absorbances are shown in Figure 3. For comparison the sum of the squares of errors (observed absorbance — calculated absorbance) in Figure 2 is 210 whereas in Figure 3 it is 65.

A mechanism that is consistent with the scheme in Equation 7 is given in Scheme I. If $k_4$ were small relative to $k_6$, $k_5$, $k_6$, and $k_7$ then the reaction mechanistically would follow Equation 7. Halide ions

(10 g) and Mixtures of Methyl Linolenate and Methyl Linoleate (10 g)
SnCl₂ in the Absence of Solvent at 90°C for 3 h

*Products Formed (%)*

| Mono-olefin | Non-conjugated Diolefin | Conjugated Diolefin | | Non-conjugated Triolefin | Con-jugated Triolefin |
|---|---|---|---|---|---|
| | | cis–trans | trans–trans | | |
| — | — | — | — | 100 | — |
| 15.8 | 45.4 | 16.5 | 22.3 | — | — |
| 8.8 | 45.0 | 16.3 | 29.9 | — | — |
| 2.0 | 19.9 | — | — | 78.1 | — |
| 36.9 | 32.4 | 7.7 | 23.0 | — | — |
| 47.1 | 33.4 | 5.2 | 14.3 | — | — |
| 3.5 | 20.5 | 11.5 | 18.5 | 30.0 | 16.0 |
| 1.2 | 12.0 | — | — | 86.8 | — |
| 11.6 | 29.4 | 16.9 | 42.1 | — | — |

catalyze the oxidative addition of alkyl halides to rhodium(I) (15) so that $k_3$ undoubtedly will be quite large. However, is there any evidence for the presence of any halide ions to effect the $k_4$ step? There is, although the mechanism by which they are formed is uncertain because both we and others (13) observe that there is an increase in the conductance during the course of the reaction. In addition both we and others (13) observe an initial induction period during which these halide ions may be formed. Both $k_6$ and $k_7$ are believed to be even larger than $k_5$ because previous work with anionic rhodium(I) complexes has shown that the oxidative addition of methyl iodide rather than the combination of methyl and carbonyl ligands is rate determining (16). Thus of the rate constants $k_4$, $k_5$, $k_6$, and $k_7$, $k_5$ is the smallest and it is larger than $k_1$. Although the mechanism in Scheme I (and in Equation 7) gives a significantly better fit for the observed data in the case of tris(p-butylphenyl)phosphine than that in Equation 5 (and in Equation 6), the distinction in the case of triphenylphosphine is less clear-cut (see Table IV). However we favor Scheme I because it readily accounts for both the observed induction period and the increase in conductance during the reaction.

When *trans*-[Rh(PR₃)₂Cl(CO)] complexes in which R was n-C₄H₉ and n-C₁₈H₃₇ were dissolved in methyl iodide, rapid oxidative addition

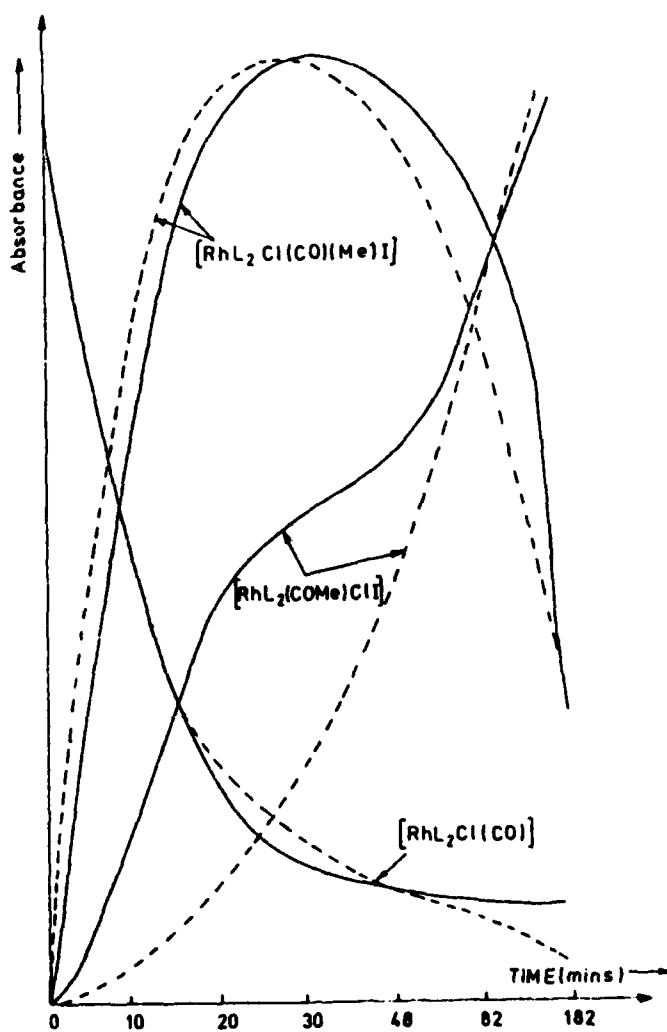Figure 2. *Observed (——) and calculated (---) absorbances for* [Rh{P(—      —Bu)₃}₂Cl(CO)] + *MeI based on the model in Equation 6*
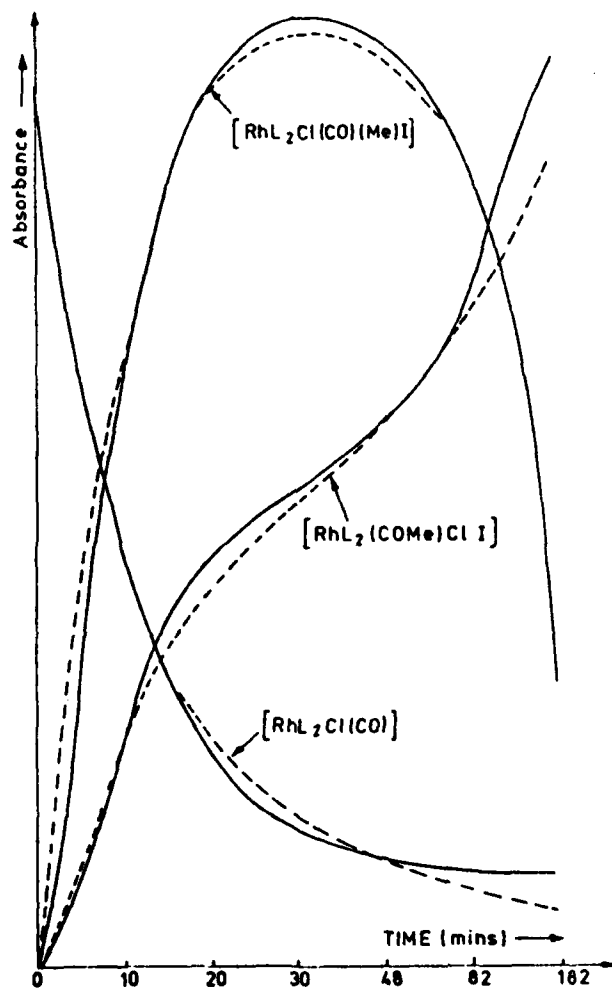
*Figure 3. Observed (——) and calculated (---) absorbances for [Rh{P(  —  —Bu)₃}₂Cl(CO)] + MeI based on the model in Equation 7*

Table IV. Analysis of the Absorbance Data for the Reaction of
trans-[Rh(PR$_3$)$_2$Cl(CO)] with Methyl Iodide According to
Equations 6 and 7

| | | Sum of Squares of Errors | |
|---|---|---|---|
| Phosphine | Temperature (°C) | Equation 6 | Equation 7 |
| P(—    —Bu)$_3$ | 16.5 | 640 | 72 |
| | 28.5 | 690 | 107 |
| | 36.3 | 270 | 65 |
| PPh$_3$ | 20.5 | 1510 | 780 |
| | 26.5 | 1610 | 740 |
| | 33.3 | 1480 | 620 |

of methyl iodide to yield trans-[Rh(PR$_3$)$_2$Cl(CO)(CH$_3$)I] occurred, but
subsequent combination of methyl and carbonyl ligands to form an
acyl complex did not take place. These reactions accordingly followed
simple first-order rate laws.

The observed rate constants are given in Table V. In order to com-
pare rate constants, values at 18°C were determined from plots of ln $k$
vs. $T^{-1}$ (see Table V). It is apparent that the rate of oxidative addition of
methyl iodide to trans-[Rh(PR$_3$)$_2$Cl(CO)] as measured by the values of
$k_1$ at 18°C increases as the phosphine is altered in the following order:

PPh$_3$ < P(—   —Bu)$_3$ < P(n-C$_{18}$H$_{37}$)$_3$ < P(n-C$_4$H$_9$)$_3$ < P(n-C$_8$H$_{17}$)$_3$.

The order PPh$_3$ < P(—   —Bu)$_3$ < P(n-alkyl)$_3$ follows the expected
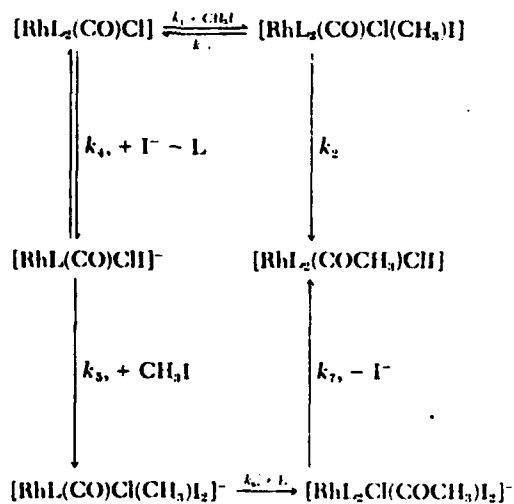order of electron-donating ability. The electron-donor abilities of all

Table V. Rate Constants $k_1$ and $k_2$ Defined According to Equation 7
for the Reaction of 2 × 10$^{-2}$ mol L$^{-1}$ trans-[Rh(PR$_3$)Cl(CO)] with
Methyl Iodide

| PR$_3$ | Temperature (°C) | $k_1$(sec$^{-1}$) | $k_2$(sec$^{-1}$) | $k_1^{18}$(sec$^{-1}$)$^a$ |
|---|---|---|---|---|
| PPh$_3$ | 20.5 | 7.2 × 10$^{-5}$ | 9.9 × 10$^{-5}$ | 5.0 × 10$^{-5}$ |
| | 26.5 | 1.7 × 10$^{-4}$ | 1.3 × 10$^{-4}$ | |
| | 33.3 | 5.2 × 10$^{-4}$ | 2.8 × 10$^{-4}$ | |
| P(—   —Bu)$_3$ | 16.5 | 4.0 × 10$^{-4}$ | 1.4 × 10$^{-4}$ | 4.2 × 10$^{-4}$ |
| | 28.5 | 9.0 × 10$^{-4}$ | 4.1 × 10$^{-4}$ | |
| | 36.3 | 2.4 × 10$^{-3}$ | 6.1 × 10$^{-4}$ | |
| P(n-C$_{18}$H$_{37}$)$_3$ | 10.5 | 5.6 × 10$^{-3}$ | — | 7.8 × 10$^{-3}$ |
| | 19.0 | 7.9 × 10$^{-3}$ | — | |
| P(n-C$_8$H$_{17}$)$_3$ | 18.0 | 1.3 × 10$^{-2}$ | — | 1.3 × 10$^{-2}$ |
| P(n-C$_4$H$_9$)$_3$ | 18.3 | 1.2 × 10$^{-2}$ | — | 1.2 × 10$^{-2}$ |

$^a$ The $k_1$ values at 18°C obtained from plots of ln $k_1$ vs. $T^{-1}$.

three trialkylphosphines are expected to be very similar. The larger steric bulk of $P(n\text{-}C_{18}H_{37})_3$ may be responsible for its significantly lower ability at promoting oxidative addition. However the relative order of the trialkylphosphines suggests that subtle solvation effects are very important. In the previous paragraph we suggested that the $k_3$ values in Table V largely reflect the $k_3$ step of Scheme I which is itself the oxidative addition of methyl iodide to an anionic rhodium(I) complex. Again the rate constants $(k_3)$ in Table V show that $P(-\quad-Bu)_3$ is more effective than triphenylphosphine at promoting this oxidative addition.

### Scheme I

$$[RhL_2(CO)Cl] \xrightleftharpoons[k_{-1}]{k_1 \cdot CH_3I} [RhL_2(CO)Cl(CH_3)I]$$

$k_{4}, + I^- - L$ $\qquad\qquad$ $k_2$

$$[RhL(CO)ClI]^- \qquad\qquad [RhL_2(COCH_3)ClI]$$

$k_{5}, + CH_3I$ $\qquad\qquad$ $k_{7}, - I^-$

$$[RhL(CO)Cl(CH_3)I_2]^- \xrightarrow{k_6 \cdot L} [RhL_2Cl(COCH_3)I_2]^-$$

### Conclusions

Tertiary phosphine groups with long alkyl chains bound directly to phosphorus or substituted at the para position of triphenylphosphine give rise to a range of interesting and potentially useful complexes. In particular these may be used to prepare polyolefin hydrogenation catalysts based on platinum(II) and palladium(II) complexes that are both more active and more selective towards reduction to monoolefins than previous catalysts based on these systems. The platinum(II) complexes are better than the palladium(II) complexes. Additionally the new phosphines are more effective than triphenylphosphine in promoting the oxidative addition of methyl iodide to *trans*-$[Rh(PR_3)_2Cl(CO)]$.

*Acknowledgments*

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# Complexes of Long Alkyl Chain Tertiary Phosphines. 4. Oxidative Addition of Methyl Iodide to *trans*-[RhCl(CO)(PR3)2]

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*Received December 4, 1980*

The kinetics of the oxidative addition of methyl iodide to *trans*-[RhCl(CO)L2] have been determined. When L is a trialkylphosphine, the product of oxidative addition is *trans*-[RhClI(CH3)(CO)L2]; the influence of L on the rate of this reaction is P(n-C8H17)3 ≳ P(n-C4H9)3 > P(n-C10H21)3. When L is a triarylphosphine, two products are formed: *trans*-[RhClI(CH3)(CO)L2] and a rhodium(III)–acyl complex. The formation of two products precludes a simple linear treatment of the kinetic data. A nonlinear treatment was effected with use of the program FACSIMILE. This clearly shows, contrary to earlier reports, that *trans*-[RhClI(CH3)(CO)L2] is not a significant intermediate in the formation of the final acyl product. A mechanism is proposed which involves anionic rhodium species formed by reaction of dissociated phosphine ligands with methyl iodide to yield the corresponding methylphosphonium salts and iodide ions which subsequently coordinate to rhodium(I). Analysis of the data obtained shows that introduction of alkyl substituents in the para position of coordinated triphenylphosphine enhances oxidative addition at rhodium(I). Trialkylphosphines are more effective than triarylphosphines at promoting oxidative addition at rhodium(I); alkyl chains longer than butyl are marginally less effective than butyl itself

## Introduction

We have recently described the syntheses of two series of phosphines P(n-C$_m$H$_{2m+1}$)$_3$ where $m$ = 10–19 and P-(C$_6$H$_4$C$_n$H$_{2n+1}$-*p*)$_3$ where $n$ = 3–9.[2] These phosphines have rather different solubility properties to those previously available; in particular they are extremely soluble in aliphatic hydrocarbon and chlorinated aliphatic hydrocarbon solvents. We have prepared a number of palladium(II), platinum(II), platinum(0), and rhodium(I) complexes of these phosphines.[3] Our reasons for doing this were twofold.

First, phosphine complexes have been widely used as homogeneous catalysts, and in many of their reactions the solvent plays a very important role. Complexes with rather different solvation properties might behave in a different and perhaps more useful way to those already known.

Second, if alkanes are ever going to be activated with use of homogeneous catalysts that activation will have to be effected in solvents that are chemically more inert than the alkanes themselves. No such solvents are, of course, available, and if homogeneous catalysts are to be used, then those catalysts must dissolve freely in the alkanes themselves.

A very important step in many homogeneous catalytic cycles, including alkane activation,[4] is oxidative addition.[5-7] Accordingly it was of interest to determine how effective the new phosphines were at promoting oxidative addition to transition metals. Since the oxidative addition of methyl iodide to *trans*-[RhCl(CO)(PR3)2] appeared to be well understood,[8] it was decided to study this system first. The present paper reports this study and shows that the system is more complex than previously suggested. A preliminary account of this work has been given.[9]

## Experimental Section

*trans*-[RhCl(CO)(PR3)2] was prepared as described previously.[3] Solutions of *trans*-[RhCl(CO)(PR3)2] (2 × 10$^{-2}$ mol L$^{-1}$) in methyl iodide (redistilled) were prepared and their infrared spectra between

2100 and 1650 cm$^{-1}$ monitored as a function of time with use of a Perkin-Elmer Model 577 spectrometer. *Caution!* Methyl iodide is a depressant and should only be handled in well-ventilated areas. Solution infrared cells provided with sodium chloride windows were mounted in a methanol-jacketed cell housing which was maintained at constant temperature by a Techne C100 circulating bath coupled to a Techne 1000 refrigeration unit.

**Data Analysis. (1) PR3 = Triarylphosphine.** The kinetic data obtained when PR3 was a triarylphosphine was initially analyzed as described previously.[8] In this analysis a series of assumptions are made in order to enable a linear analytical method to be used. It soon became apparent that the assumptions that must be made were invalid, and accordingly a nonlinear analysis was undertaken with use of the computer program FACSIMILE.[10] The program uses the initial concentrations, molar absorptivities, rate equations, and guessed values of the rate coefficients to calculate the expected variation with time of the absorbances, $A_t$, of each component. It can vary any chosen parameters (such as molar absorptivities or rate coefficients) and calculates the values of these parameters which make the sum of the squares of the residuals, $\sum w(A_{obsd} - A_{calcd})^2$, for all times and components a minimum. An $F$ test[11] was used to determine whether the fit given by model a is better or worse than that given by model b. If $S_a$ and $S_b$ are the minimum sum of squares of residuals by the two models, then, if $[(S_a - S_b)/n_p]/[S_b/(n_o - n_p)]$ is greater than $F_{n_o, n_p}$ - $n_p$, model b is a better fit than model a at the $\alpha$ level, where $n_o$ is the number of observations and $n_p$ is the number of parameters determined from these.

The molar absorptivity, $\epsilon_I$, of the initial rhodium(I) complex (species I) was known, but those, $\epsilon_{II}$ and $\epsilon_{III}$, of the second and third rhodium complexes (species II and III, respectively) were not immediately available because the reaction proceeds further, albeit slowly, making it difficult to get reliable $\epsilon_{III}$ values. They were calculated as follows. For each species the absorbance due to that species $A_i$ is given by eq 1, where $c_i$ is the concentration of species i and $l$ is the cell length.

$$A_i = \epsilon_i c_i l \quad (1)$$

If $c_o$ is the total concentration of rhodium present, then

$$c_o = c_I + c_{II} + c_{III} \quad (2)$$

and substituting from eq 1 into eq 2 gives

$$\frac{A_I}{\epsilon_I l} + \frac{A_{II}}{\epsilon_{II} l} + \frac{A_{III}}{\epsilon_{III} l} = c_o \quad (3)$$

or

$$\frac{A_I}{\epsilon_I} + \frac{A_{II}}{\epsilon_{II}} + \frac{A_{III}}{\epsilon_{III}} - c_o l = 0 \quad (4)$$

(1) (a) The Royal Military College of Science. (b) The University of Hull.
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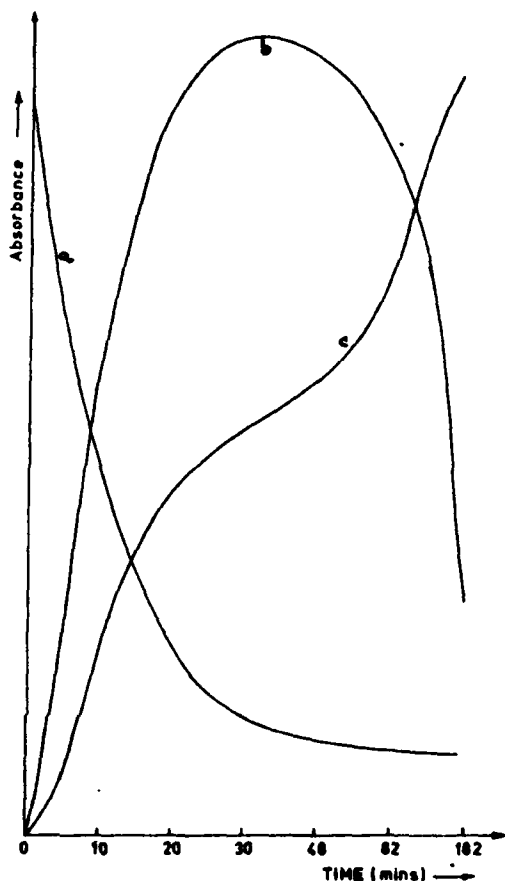(11) Hoel, P. G. "Introduction to Mathematical Statistics", 4th ed.; Wiley: New York, 1971; Chapter 10.

**Figure 1.** Observed absorbances for the reaction of [RhCl(CO){P-$(C_6H_4Bu\text{-}p)_3$}] with methyl iodide at 36.3 °C: (a) 1980 cm$^{-1}$;-(b) 2060 cm$^{-1}$; (c) 1705 cm$^{-1}$. Note the nonlinearity of the time scale.

In order to obtain $\epsilon_{II}$ and $\epsilon_{III}$ from the known value of $\epsilon_I$ together with the sets of values of $A_I$, $A_{II}$, and $A_{III}$ at different times, it is necessary to find the "best fit" values of $\epsilon_{II}$ and $\epsilon_{III}$ such that

$$\sum_{t=0}^{t=\infty}\left(\frac{A_{I,t}}{\epsilon_I} + \frac{A_{II,t}}{\epsilon_{II}} + \frac{A_{III,t}}{\epsilon_{III}} - c_e t\right)^2 = \text{minimum} \quad (5)$$

Condition 5 will be met when eq 6 and 7 are fulfilled. These are two

$$\frac{\partial}{\partial(1/\epsilon_{II})}\left\{\sum_{t=0}^{t=\infty}\left(\frac{A_{I,t}}{\epsilon_I} + \frac{A_{II,t}}{\epsilon_{II}} + \frac{A_{III,t}}{\epsilon_{III}} - c_e t\right)^2\right\} = 0 \quad (6)$$

$$\frac{\partial}{\partial(1/\epsilon_{III})}\left\{\sum_{t=0}^{t=\infty}\left(\frac{A_{I,t}}{\epsilon_I} + \frac{A_{II,t}}{\epsilon_{II}} + \frac{A_{III,t}}{\epsilon_{III}} - c_e t\right)^2\right\} = 0 \quad (7)$$

simultaneous equations which can be solved to give eq 8 and 9. A simple computer program was used to evaluate eq 8 and 9 from sets of absorbance data obtained as a function of time.

$$\epsilon_{II} = [\Sigma A_{II}^2 \Sigma A_{III}^2 - (\Sigma A_{II} A_{III})^2] / [\epsilon_I \{(\Sigma A_{III}^2 \Sigma A_{II} - \Sigma A_{II} A_{III} \Sigma A_{III}) - (1/c_e)(\Sigma A_{II} A_t \Sigma A_{III}^2 - \Sigma A_{II} A_{III} \Sigma A_t A_{III})\}] \quad (8)$$

$$\epsilon_{III} = [\Sigma A_{II}^2 \Sigma A_{III}^2 - (\Sigma A_{II} A_{III})^2] / [\epsilon_I \{(\Sigma A_{II}^2 \Sigma A_{III} - \Sigma A_{II} A_{III} \Sigma A_{II}) - (1/c_e)(\Sigma A_{III} A_t \Sigma A_{II}^2 - \Sigma A_{II} A_{III} \Sigma A_t A_{II})\}] \quad (9)$$

**(2) PR$_3$ = Trialkylphosphine.** First-order rate coefficients for compounds where PR$_3$ was a trialkylphosphine were calculated from the measured absorbance data with use of the usual equation,[12] [ln
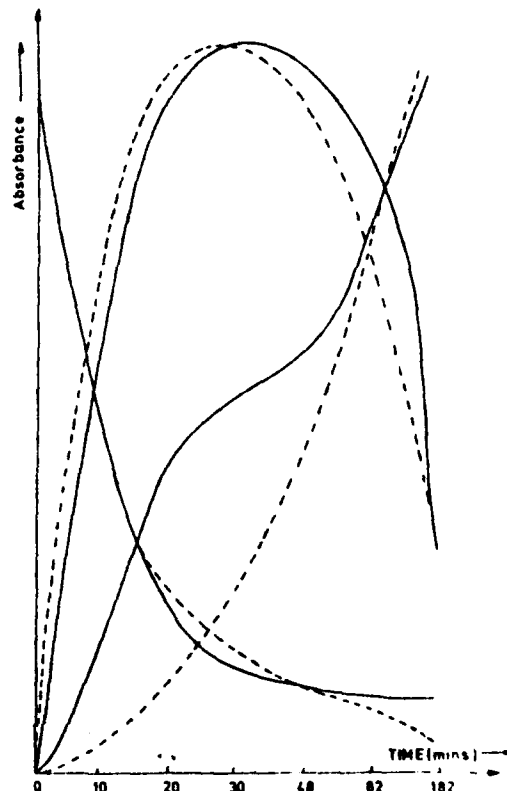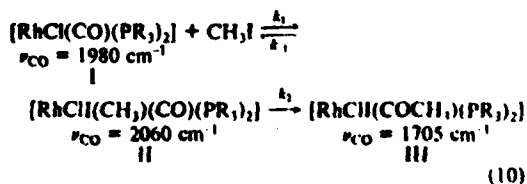


**Figure 2.** Observed (—) and calculated (- - -) absorbances for the reaction of [RhCl(CO)L$_2$], where L = P(C$_6$H$_4$Bu-$p$)$_3$, with methyl iodide at 36.3 °C analyzed in terms of the model in eq 11.

$[(A_\infty - A_0)/(A_t - A_0)] = k_1 t$, and a least-squares computer program.

**Results**

**(1) Triarylphosphines.** When *trans*-[RhCl(CO)(PR$_3$)$_2$], in which PR$_3$ is a triarylphosphine, is dissolved in methyl iodide, the initial infrared spectrum shows an absorption band at 1980 cm$^{-1}$. This band slowly decays in intensity, and a new band at 2060 cm$^{-1}$ due to [RhClI(CH$_3$)(CO)(PR$_3$)$_2$] develops; in time this band also decays with the formation of a third band at 1705 cm$^{-1}$ due to [RhClI(COCH$_3$)(PR$_3$)$_2$]. A typical record of absorbance against time for these three bands is shown in Figure 1. The reactions occurring have been suggested to be initial formation of the rhodium(III)–carbonylmethyl complex followed by combination of the carbonyl and methyl ligands to form the final rhodium(III)–acyl complex (reaction 10).[5] In the presence of methyl iodide this can be examined

$$\text{[RhCl(CO)(PR}_3)_2] + \text{CH}_3\text{I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$
$$\nu_{CO} = 1980 \text{ cm}^{-1}$$
$$\text{I}$$

$$\text{[RhClI(CH}_3)(\text{CO})(\text{PR}_3)_2] \xrightarrow{k_2} \text{[RhClI(COCH}_3)(\text{PR}_3)_2]$$
$$\nu_{CO} = 2060 \text{ cm}^{-1} \qquad\qquad \nu_{CO} = 1705 \text{ cm}^{-1}$$
$$\text{II} \qquad\qquad\qquad\qquad \text{III}$$
$$(10)$$

(12) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961.
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101.

in terms of the model in eq 11. When this was done with use

$$I \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} II \overset{k_2}{\longrightarrow} III \qquad (11)$$

of experimentally determined molar absorptivities, the fit seemed poor. A comparison between the observed absorbances and those calculated when the data for [RhCl(CO)[P-$(C_6H_4Bu-p)_3$]] at 36.3 °C was analyzed is shown in Figure 2. The poor fit in Figure 2 suggested that the model represented by eq 2 was wrong. Accordingly an alternative, chemically reasonable,[12] model represented by eq 12 was investigated. The

$$(12)$$
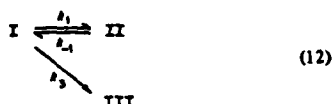
fit to the data for [RhCl(CO)[P(C_6H_4Bu-p)_3]] at 36.3 °C was much improved, particularly the fit to the data at 1705 cm$^{-1}$ in the early stages of the reaction (Figure 3); the sum of the squares of the differences in the observed and calculated absorbances fell from 802 when analyzed according to eq 11 to 341 when analyzed according to eq 12. The same improvement of fit applies at all three temperatures investigated (Table I); it also applies both when the molar absorbances of species II and III are constrained at their experimentally determined values (obtained as described in the Experimental Section) and when they are treated as variables and refined by FACSIMILE as part of the minimization procedure. F tests (see Experimental Section and Table I) also indicated that the model in eq 12 gave a very much better fit than that in eq 11 at the 0.5% level for all the different phosphine complexes. A model that lies intermediate between that of eq 11 and 12 is shown in eq 13. When the data was analyzed according to eq 13

$$(13)$$
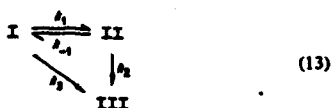
with $k_1 + k_3$ set equal to $k_1$(obsd), the apparent first-order rate constant for the decomposition of I, differences in the observed and calculated absorbances were higher than those from eq 12 but lower than those from eq 11.

Analysis of the data for the other triarylphosphine complexes [RhCl(CO)(PR_3)_2] where R = C_6H_5, p-C_2H_5C_6H_4, and p-C_6H_{13}C_6H_4 according to eq 11-13 showed the same trend as with the data for [RhCl(CO)[P(C_6H_4Bu-p)_3]] with eq 12 giving the best fit (Table I) and eq 11 giving the worst fit.

A mechanism that is consistent with the model in eq 12 is given in Scheme I. If $k_2$ were small relative to $k_4$, $k_5$, $k_6$, and $k_7$, then mechanistically the reaction would follow eq 12. It is known that halide ions catalyze the oxidative addition of alkyl halides to rhodium(I),[14] so that $k_5$ will undoubtedly be quite large. However is there any evidence for the presence of any halide ions to effect the $k_6$ step? There is; both we and previous workers[9] have observed that there is a slight increase in the conductance during the course of the reaction. In addition there is an induction period at the start of the reaction during which these iodide ions may be formed. We initially ascribed both observations to competition between methyl iodide and rhodium(I) for the tertiary phosphine resulting in the formation of some (PR_3N )$^+$[RhClI(CO)(PR_3)]$^-$. However a revic r has point  t that the single step that we have ascrib  is i  .t a composite step involving first dissociation of a r  phin  from the rhodium(I), $k_6$. The free phosphine so f... ...ed then reacts with methyl iodide to form the phosphonium iodide. The iodide then attacks the rhodium(I) to form [RhClI(CO)(PR_3)]$^-$, $k_{6b}$. It is not possible



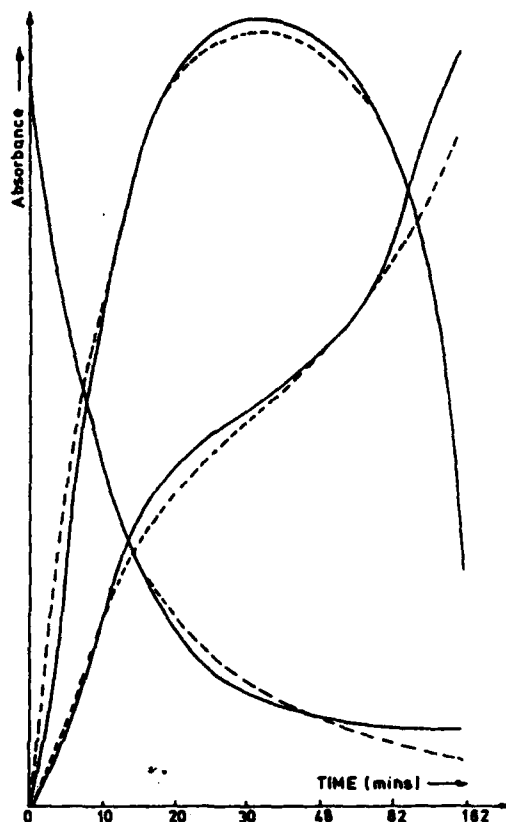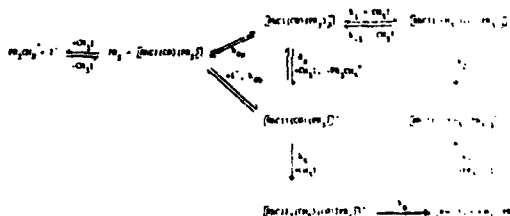Figure 3. Observed (—) and calculated (- - -) absorbances for the reaction of [RhCl(CO)L_2], where L = P(C_6H_4Bu-p)_3, with methyl iodide at 36.3 °C analyzed in terms of the model in eq 12.

Scheme I



experimentally to distinguish between the single step ($k_6$) in which methyl iodide and rhodium(I) are in direct competition for the nucleophilic tertiary phosphine and the double step ($k_{6a}$ + $k_{6b}$) mechanism in which phosphine dissociation from rhodium(I) precedes reaction with methyl iodide. This is because as soon as excess phosphine is added it reacts with the methyl iodide present to form the phosphonium iodide. Both $k_6$ and $k_7$ are believed to be even larger than $k_5$ because previous work with anionic rhodium(I) complexes has shown that oxidative addition of methyl iodide rather than the combination of methyl and carbonyl ligands is rate determining.[15] Thus of the rate constants $k_4$, $k_5$, $k_6$, and $k_7$, it is $k_5$ that is the smallest and this is known to be larger than $k_1$. We believe that the final rhodium(III)-acyl product is not a single species

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Table I.   Analysis of the Data for Oxidative Addition of Methyl Iodide to [RhCl(CO)(PAr₃)₂] according to the Models in Eq 11 and 12

| | C₆H₄Bu-p | | | Ph | | | C₆H₄Et-p, 28.3 °C | | C₆H₄C₈H₁₇-p, 28.3 °C |
| | 16.5 °C | 28.3 °C | 36.3 °C | 20.5 °C | 26.5 °C | 33.3 °C | no added n-Pr₄N⁺ | added n-Pr₄N⁺ (0.006 M) | |
|---|---|---|---|---|---|---|---|---|---|
| **calcd rate const, s⁻¹** | | | | *Analysis according to Eq 12* | | | | | |
| $10^4 k_1$ | 4.57 ± 0.09 | 9.10 ± 0.23 | 21.5 ± 1.20 | 0.72 ± 0.08 | 1.68 ± 0.12 | 5.21 ± 0.45 | 6.51 ± 0.22 | 9.70 ± 0.50 | 5.90 ± 0.11 |
| $10^4 k_{-1}$ | 0.64 ± 0.06 | 3.22 ± 0.16 | 10.30 ± 0.80 | 0.49 ± 0.19 | 1.93 ± 0.29 | 8.83 ± 1.10 | 3.36 ± 0.27 | 4.83 ± 0.49 | 2.06 ± 0.10 |
| $10^4 k_2$ | 0.93 ± 0.05 | 4.11 ± 0.08 | 6.82 ± 0.23 | 0.99 ± 0.06 | 1.31 ± 0.06 | 2.84 ± 0.09 | 6.07 ± 0.11 | 6.30 ± 0.22 | 3.10 ± 0.05 |
| min sum of squares of differences ($S_{12}$) | 282 | 111 | 341 | 781 | 745 | 617 | 93 | 270 | 41.6 |
| **calcd rate const, s⁻¹** | | | | *Analysis according to Eq 11* | | | | | |
| $10^4 k_1$ | 5.24 ± 0.10 | 13.40 ± 0.62 | 33.20 ± 2.60 | 1.51 ± 0.12 | 3.10 ± 0.21 | 9.07 ± 0.94 | 12.20 ± 1.00 | 18.40 ± 2.00 | 9.64 ± 0.58 |
| $10^4 k_{-1}$ | 0.40 ± 0.07 | 3.21 ± 0.38 | 13.00 ± 1.50 | 0.27 ± 0.30 | 1.91 ± 0.43 | 10.60 ± 2.00 | 3.56 ± 1.04 | 8.60 ± 1.80 | 2.79 ± 0.50 |
| $10^4 k_2$ | 0.53 ± 0.04 | 2.32 ± 0.14 | 3.80 ± 0.25 | 1.43 ± 0.32 | 2.29 ± 0.27 | 5.80 ± 0.54 | 7.34 ± 0.56 | 5.64 ± 0.56 | 2.58 ± 0.20 |
| min sum of squares of differences ($S_{11}$) | 386 | 635 | 802 | 1512 | 1606 | 1485 | 832 | 1400 | 552 |
| | | | | *Molar Absorptivities, L mol⁻¹ cm⁻¹* | | | | | |
| $\varepsilon_{II}$ | 466 | 466 | 466 | 717 | 717 | 717 | 683 | 683 | 413 |
| $\varepsilon_{III}$ | 371 | 371 | 371 | 334 | 334 | 334 | 286 | 286 | 335 |
| | | | | *F Test Data* | | | | | |
| no. of observns | 119 | 92 | 94 | 76 | 91 | 92 | 78 | 82 | 87 |
| $[(S_{11}-S_{12})/3] / [S_{12}/(n_0-3)]$ | 14.3 | 140 | 41.1 | 22.7 | 33.9 | 41.7 | 199 | 110 | 343 |
| $F_{3,n_0-3,0.001}$ | 4.46 | 4.45 | 4.55 | 4.64 | 4.56 | 4.55 | 4.63 | 4.61 | 4.59 |

Table II.   Activation Parameters for the Oxidative Addition of Methyl Iodide to trans-[RhCl(CO)(PAr₃)₂]

| PAr₃ | rate const | $\Delta H^{\ddagger}$, kJ mol⁻¹ | $\Delta S^{\ddagger}$, J K⁻¹ mol⁻¹ |
|---|---|---|---|
| PPh₃ | $k_1$ | 113.4 ± 6.8 | 61.7 ± 22.8 |
| | $k_{-1}$ | 166.7 ± 1.0 | 240.0 ± 3.4 |
| | $k_2$ | 59.5 ± 15.2 | -119.6 ± 50.7 |
| P(C₆H₄-Bu-p)₃ | $k_1$ | 54.3 ± 10.9 | -122.0 ± 36.5 |
| | $k_{-1}$ | 101.4 ± 3.3 | 24.6 ± 11.1 |
| | $k_2$ | 74.0 ± 11.4 | -65.9 ± 38.1 |

Table III.   First-Order Rate Constants for the Oxidative Addition of Methyl Iodide to trans-[RhCl(CO)(PR₃)₂] (2 × 10⁻³ mol L⁻¹) Yielding trans-[RhCl(CH₃)(CO)(PR₃)₂] in Methyl Iodide Solution

| PR₃ | temp, °C | $10^3 k_1$, s⁻¹ |
|---|---|---|
| P(n-C₄H₉)₃ | 18.3 | 12.5 ± 0.2 |
| P(n-C₆H₁₃)₃ | 18.0 | 13.8 ± 0.1 |
| P(n-C₁₄H₂₉)₃ | 10.5 | 5.2 ± 0.5 |
| | 19.0 | 7.8 ± 0.1 |

but a mixture of mainly [RhClI(COCH$_3$)(PR$_3$)$_2$] together with a small amount of [RhClI$_2$(COCH$_3$)(PR$_3$)]$^-$ equivalent to the small amount of (PR$_3$Me)$^+$ formed, since the observed carbonyl absorption in the final product is rather broad.

The mechanism in Scheme I envisages the observed slight increase in conductivity arising from the reaction of the dissociated tertiary phosphine ligand with methyl iodide to form the phosphonium iodide. Each iodide ion is thus formed in 1:1 ratio to the tertiary phosphine dissociated. Thus in the present system excess iodide ions are never present. However if excess iodide ions are intentionally added then they will compete with and displace chloride ions from rhodium which should promote oxidative addition at rhodium(I).[16] That this is so was confirmed by studying the reaction of [RhCl-(CO)[P(C$_6$H$_4$Et-*p*)$_3$]] in the presence and absence of added tetra-*n*-propylammonium iodide. It is apparent (see Table I) that addition of excess iodide has more effect on the $k_1$ rate constant than on $k_3$. Again we believe that this is consistent with the scheme put forward because in the absence of intentionally added iodide there are no iodide ions free to take part in the $k_1$ step. When iodide ions are added intentionally, they will compete with chloride and so enhance the $k_1$ rate constant. Since iodide ions are present in the $k_3$ (effectively $k_5$) step whether or not tetra-*n*-propylammonium iodide is added, the effect of adding extra iodide ions on the $k_3$ step is relatively small.

Activation parameters were calculated for the rate constants in Table I evaluated according to the model in reaction 12. These are given in Table II.

**(ii) Trialkylphosphines.** When *trans*-[RhCl(CO)(PR$_3$)] complexes in which R was *n*-C$_4$H$_9$, *n*-C$_8$H$_{17}$, and *n*-C$_{18}$H$_{37}$ were dissolved in methyl iodide, rapid oxidative addition of methyl iodide to yield *trans*-[RhClI(CH$_3$)(CO)(PR$_3$)$_2$] occurred, but subsequent combination of methyl and carbonyl ligands to form an acyl complex did not take place. These reactions accordingly followed simple first-order rate laws. The first-order rate constants are given in Table III.

**Discussion**

First-order rate constants for the oxidative addition of methyl iodide to *trans*-[RhCl(CO)L$_2$], $k_1$, can be seen from Tables I and III to decrease as a function of L in the order L = P(*n*-C$_8$H$_{17}$)$_3$ $\gtrsim$ P(*n*-C$_4$H$_9$)$_3$ > P(*n*-C$_{18}$H$_{37}$)$_3$ > P-(C$_6$H$_4$C$_4$H$_9$-*p*)$_3$ $\gtrsim$ P(C$_6$H$_4$C$_2$H$_5$-*p*)$_3$ > P(C$_6$H$_4$C$_6$H$_{13}$-*p*)$_3$ > P(C$_6$H$_5$)$_3$. The greater ease of oxidative addition at rhodium(I) complexes containing trialkylphosphine ligands compared to those containing triarylphosphine ligands is expected on the basis of previous results and is ascribed to the greater electron density present at the rhodium atom when trialkylphosphine ligands are present. We anticipate that the electron-donating abilities of P(*n*-C$_n$H$_{2n+1}$) as *n* is varied from 4 to 8 to 18 will not vary significantly. Accordingly we ascribe

(16) Shaw, B. L., personal communication.

the decrease in first-order rate constants for the oxidative addition of methyl iodide to bis(trialkylphosphine)chlorocarbonylrhodium(I) complexes as the alkyl chain increases in length beyond eight carbon atoms to steric effects, whereby the phosphine with very long alkyl chains is slightly more sterically demanding, so decreasing the ease of oxidative addition.

The ease of oxidative addition to rhodium(I) complexes containing tris(para-substituted aryl)phosphines varied with the para substituent in the order *n*-C$_4$H$_9$ > C$_2$H$_5$ > *n*-C$_6$H$_{13}$ > H. The order *n*-alkyl > H is expected on electronic grounds. The order C$_2$H$_5$ > *n*-C$_6$H$_{13}$ could be due to the marginally greater steric demands of P(C$_6$H$_4$C$_6$H$_{13}$-*p*)$_3$ than P-(C$_6$H$_4$C$_2$H$_5$-*p*). However the position of the *n*-butyl substituted phosphine is anomalous, and we ascribe its position to subtle and not yet understood solvation factors. In doing this, it should be emphasized that the simplistic steric and electronic arguments we have advanced to explain the order of the remaining ligands may themselves, in reality, be not more than convenient conventional arguments. All the results may be dominated by solvation effects.

The rate of reductive elimination of methyl iodide from *trans*-[RhClI(CH$_3$)(CO)[P(C$_6$H$_4$R-*p*)$_3$]], $k_{-1}$, decreases in the order C$_2$H$_5$ > *n*-C$_4$H$_9$ > *n*-C$_6$H$_{13}$ > H (Table I). The differences between the three alkyl groups are very small. The greater ease of reductive elimination from the complexes containing alkyl substituted phosphines compared to triphenylphosphine is probably a consequence of the greater steric demands of the alkyl substituted phosphines.

Since $k_5$ of Scheme I is the least of $k_4$, $k_5$, $k_6$, and $k_{-}$, the rate constants $k_3$ in Table I correspond to $k_5$ tempered by the equilibrium constant $K_4$ or the equilibrium constants $K_{4a}$ and $K_{4b}$; that is, they reflect the ease of oxidative addition at anionic rhodium(I) complexes containing tris(*p*-alkylaryl)phosphines. $k_3$ increases as a function of the alkyl sustituent in the order C$_2$H$_5$ > *n*-C$_4$H$_9$ > *n*-C$_6$H$_{13}$ > H. The order *n*-alkyl > H is the same as found for oxidative addition to neutral rhodium(I) species, $k_1$. The order within the alkyl groups could reflect the marginally increasing steric demands of the ligands as the alkyl group increases in size.

In conclusion the present work has demonstrated that the mechanism for the oxidative addition of methyl iodide to *trans*-[RhCl(CO)(PR$_3$)$_2$] is more complex than previously reported.[8] The introduction of alkyl substituents in the para position of coordinated triphenylphosphine promotes oxidative addition at rhodium(I). Trialkylphosphines are more effective than triarylphosphines at promoting oxidative addition at rhodium(I); alkyl chains longer than *n*-butyl are marginally less effective than *n*-butyl itself.

Proofs to Dr S G Murray

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## The oxidative addition of 1-haloalkanes to trans — [RhX(CO)(PR$_3$)$_2$] (R = aryl)

F R Hartley*[1a], S G Murray*[1a], D M Potter[1a] and J R Chipperfield[1b].

The oxidative-addition of 1-bromopropane to trans—[RhBr(CO){P(p-EtC$_6$H$_4$)$_3$}$_2$]
has been found to follow pseudo first-order kinetics and give only an acyl

rhodium(III) product. The reaction is not catalysed by added bromide ion

in chloroform solution, indicating that an anionic intermediate such as

[RhBr$_2$(CO){P(p-EtC$_6$H$_4$)$_3$}]$^-$ does not play an important part in this reaction.

The oxidative-addition of iodomethane to trans-[RhI(CO)(PPh$_3$)$_2$] has been

shown to be more complicated than previously indicated. A non-linear treat-

ment of IR absorbance data has clearly shown the importance of the dimer

trans-[Rh($\mu$-I)(CO)(PPh$_3$))$_2$ in this reaction. The reaction is oxygen sensitive,

the oxidation of phosphine to phosphine oxide having an accelerating effect.

The oxidative-addition of iodomethane to trans-[Rh($\mu$-X)(CO)(PPh$_3$)$_2$, X = Cl

and I, is pseudo first-order, the reactivity increasing by replacing

chloride by iodide.

## Introduction

The oxidative-addition of iodomethane to trans-[RhCl(CO)(PR$_3$)$_2$], I, has recently been shown[2] to be more complicated than previously indicated[3]. A mechanism involving the anionic intermediate [RhClI(CO)(PR$_3$)]$^-$ has been proposed[2], although the possibility of halide exchange between iodomethane and I to give trans-[RhI(CO)(PR$_3$)$_2$] complicates this system. Thus it was decided to study systems in which the same halogen was present in both the 1-haloalkane and the rhodium(I) complex trans-[RhX(CO)(PR$_3$)$_2$], II. The systems chosen were 1-bromopropane to trans-[RhBr(CO){P(p-EtC$_6$H$_4$)$_3$}$_2$] as well as iodomethane to trans-[RhI(CO)(PPh$_3$)$_2$]. Unfortunately, during the preparation of II, X = I, R = para-substituted phenyl, the phosphine was found to dissociate readily to give dimeric trans-[Rh(μ-I)(CO)(PR$_3$)]$_2$, III[4]. Although the oxidative-addition of iodomethane to trans-[RhI(CO)(PR$_3$)$_2$], has been reported previously[3,5] the presence of the dimer III, R = Ph, was not noted by these authors. The reactivity of trans-[Rh(μ-Cl)(CO)(PPh$_3$)]$_2$ to both oxidative-addition[6,7] and reductive-elimination[7] has been compared to that of monomeric rhodium(I) species and has been found to be greater. It would be expected, therefore, that the dimer would play an important part in the mechanism of oxidative-addition of iodomethane to trans-[RhI(CO)(PPh$_3$)$_2$]. To further understand the role played by trans-[Rh(μ-I)(CO)(PPh$_3$)]$_2$ in the latter system, the oxidative addition of iodomethane to trans-[Rh(μ-X)(CO)(PPh$_3$)]$_2$, III, X = Cl and I, was also investigated.

## Experimental Section

Trans-[RhX(CO)(PR$_3$)$_2$], II, X = Br and I, R = Ph and p-EtC$_6$H$_4$, were prepared by the literature method[4]. The complexes trans-[Rh(μ-X)(CO)(PR$_3$)]$_2$, III, X = Cl and I, R = Ph, were prepared by a modified literature method[8]

under an atmosphere of nitrogen and in the dark .

Solution of trans-[RhX(CO)(PPh$_3$)$_2$], III, X = Cl and I, trans-[RhI(CO)(PPh$_3$)]$_2$ in iodomethane and trans-[RhBr(CO)(PR$_3$)$_2$], R = Ph and p-EtC$_6$H$_4$ in 1-bromopropane were prepared and their infrared spectra between 2200 and 1600cm$^{-1}$ monitored as a function of time. The iodomethane and 1-bromopropane were redistilled under an atmosphere of nitrogen, freeze degassed twice and stored under nitrogen prior to use. Trans-[RhI(CO)(PPh$_3$)$_2$] was subjected to a high vacuum (0.08mm Hg) to remove any oxygen absorbed onto the surface of the complex and then stored under nitrogen, at 25°C, until addition of the iodomethane. The reaction mixture was then transferred to the IR cell which had been flushed out by nitrogen using a syringe. The rate of reaction between 1-bromopropane and trans-[RhBr(CO){P(p-EtC$_6$H$_4$)$_3$}$_2$] was also measured in chloroform solution in the presence and absence of added tetra-n-propylammonium bromide.

The infrared spectra were monitored by use of a Perkin-Elmer Model 577 spectrometer. Solution infrared cells fitted with potassium bromide windows were mounted in a methanol-jacketed cell housing which was maintained at constant temperature by a Techne C100 circulating bath coupled to a Techne 1000 refrigeration unit.

*Data analysis*

The kinetic data was analysed by a pseudo first-order method and this proved satisfactory for all systems except the oxidative-addition of iodomethane to trans-[RhI(CO)(PPh$_3$)$_2$] where a nonlinear analysis was necessary. This was undertaken with the FACSIMILE computer program[9] which uses the initial concentrations, molar absorptivities, rate equations and estimated values of the rate coefficients to calculate the expected variation with time of the absorbances A$_i$ of each component. It can vary any chosen parameters (such as molar

absorptivities or rate coefficients) and calculates the values of these parameters which make the sum of the squares of the residuals, $\Sigma_{w}(A_{obs} - A_{calc})^2$, for all times and components a minimum. An F test[10] was used to determine whether the fit given by model $a$ is better or worse than that given by model $b$. If $S_a$ and $S_b$ are the minimum sum of squares of the residuals by the two models, then if $[(S_a-S_b)/n_p]/[S_b/(n_o-n_p)]$ is greater than $F_{n_o,n_p-n_o,\alpha}$, model $b$ is a better fit than model $a$ at the $\alpha$ level, where $n_o$ is the number of observations and $n_p$ is the number of parameters determined from these. The molar absorptivities for the carbonyl absorption of the rhodium complexes shown in Scheme 3 could not be calculated by use of simultaneous equations[2] because decarbonylation occurs to give XII. The molar absorptivity due to $\nu_{CO}$ of II in iodomethane was initially obtained by comparison with its molar absorptivity in chloroform. The molar absorptivity of III in iodomethane and the value of $k_E$ had already been measured (see Table 1). Thus by use of these values and an estimation of the molar absorptivities due to the carbonyl absorptions of IX and X by comparison with earlier work[2] enabled computer fitting to be achieved.

Results

*Reaction of trans-[RhBr(CO)(PR$_3$)$_2$], R = Ph and p-EtC$_6$H$_4$ with 1-bromopropane.*

A pseudo first-order plot was obtained for the reaction of trans-[RhBr(CO)(PR$_3$)$_2$] with 1-bromopropane by following the decrease in the IR absorption at 1980cm$^{-1}$ due to $\nu_{CO}$ in II. The IR spectrum showed the only product to be a rhodium acyl complex, whose structure is assigned as [RhBr$_2$(COPr){P(p-EtC$_6$H$_4$)$_3$}$_2$] V by comparison with earlier work[2,3]. IR spectroscopy showed no $\nu_{CO}$ corresponding to IV. Thus the reaction is not complicated by either halide exchange or dimerisation in spite of the fact

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**Table 1:** Observed rate constants for the reaction of 1-haloalkanes with $[RhX(CO)(PR_3)_2]$ and $[Rh(\mu-X)(CO)(PR_3)]_2$

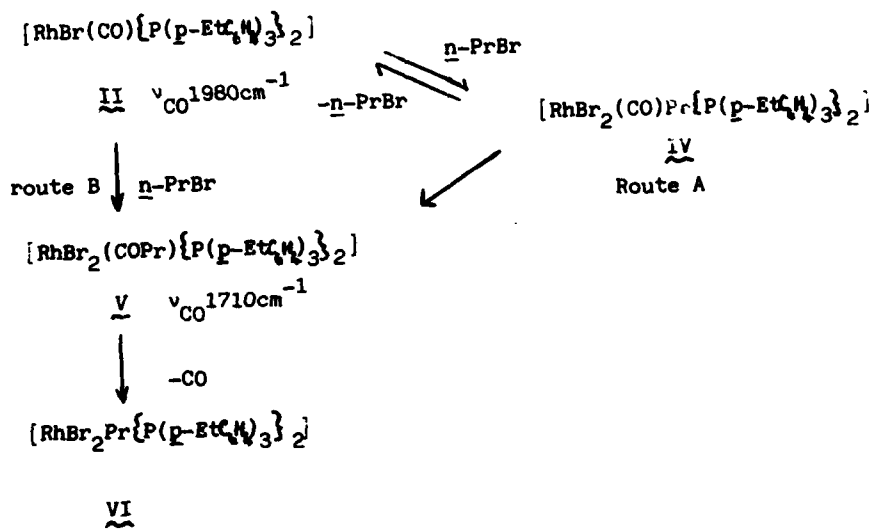| Complex | Halo-alkane | Temp (°C) | Rate constant | $k(s^{-1})$ | $\epsilon(M^{-1}cm^{-1})$ [a] |
|---|---|---|---|---|---|
| $[RhI(CO)(PPh_3)_2]$ | MeI | 20 | $k_A$ [b] | $7.33 \times 10^2$ | $\epsilon_A 1022$ |
|  |  |  | $k_{AA}$ [b] | $8.1 \times 10^{-3}$ | $\epsilon_{AA} 554$ |
|  |  |  | $k_C$ [b] | $6.7 \times 10^7$ | $\epsilon_C 1083$ |
|  |  |  | $k_{-C}$ [b] | $3.12 \times 10^{-4}$ | $\epsilon_D 558$ |
|  |  |  | $k_D$ [b] | $1.0 \times 10^{12}$ | $\epsilon_E 554$ |
|  |  |  | $k_{-D}$ [b] | $1.11 \times 10^{-6}$ |  |
|  |  |  | $k_E$ [b] | $2.4 \times 10^{-3}$ |  |
|  |  |  | $k_p$ | $1.53 \times 10^{-4}$ |  |
| $[Rh(\mu-I)(CO)(PPh_3)]_2$ | MeI | 20 | $k_{obs}$ | $2.4 \times 10^{-3}$ | $\epsilon\ 554$ |
|  |  |  | $k_{obs}$ | $2.2 \times 10^{-3}$ |  |
| $[Rh(\mu-Cl)(CO)(PPh_3)]_2$ | MeI | 20 | $k_{obs}$ | $4.9 \times 10^{-4}$ | $\epsilon\ 553$ |
|  |  |  | $k_{obs}$ | $5.7 \times 10^{-4}$ |  |
| $[RhCl(CO)(PPh_3)_2]$ | MeI | 20 | $k_{obs}$ [c] | $1.17 \times 10^{-4}$ | $\epsilon\ 1340$ |
| $[RhBr(CO)\{P(Et)_2Ph\}_2]$ | MeBr | 25 | $k_{obs}$ [d] | $6.0 \times 10^{-7}$ |  |
| $[RhBr(CO)\{P(p-EtC_6H_4)_3\}_2]$ | n-PrBr | 40 | $k_{obs}$ | $4.25 \times 10^{-5}$ | $\epsilon\ 1200$ |

a. Extinction coefficients are for the rhodium(I) complexes except where otherwise stated.

b. Obtained by analysis according to equations 1-5 using FACSIMILE (ref 9).

c. An approximate first order value

d. From reference 15.

that due to the lower reactivity of the 1-bromoalkane the reaction was followed at 40°C.

Two reaction routes are possible (Scheme 1). There could be either a fast propyl transfer to give an acyl complex, V, from IV, which is in equilibrium with II as shown in route A, or simultaneous addition and transfer as shown in route B. The rhodium(III) complex V was observed to slowly decarbonylate, the expected product being VI. Similar decarbonylations have been reported previously[11]. The reaction was studied in the presence and absence of added tetra-n-propylammonium bromide in chloroform, but two otherwise identical reactions showed no significant difference in rate (Table 2). This indicates that the anionic intermediate $[RhBr_2(CO)\{P(p-EtC_6H_4)_3\}]^-$ does not play an important role in the oxidative-addition of 1-bromopropane to II, X = Br and R = p-EtC$_6$H$_4$. The oxidative-addition of 1-bromopropane to trans-[RhBr(CO)(PPh$_3$)$_2$] occurs at a rate too slow to measure at this temperature. Wilkinson found no reaction occurred between bromoethane and trans-[RhCl(CO)(PPh$_3$)$_2$] at 25°C.[3]

*Reaction of trans-[Rh(μ-X)(CO)(PPh$_3$)]$_2$ with iodomethane.* The oxidative-addition of iodomethane to trans-[Rh(μ-I)(CO)(PPh$_3$)]$_2$ was found to follow a pseudo first-order rate law with iodomethane always present in a large excess. The observed rate constant ($k_{obs}$) was obtained by measurement of the decrease of carbonyl absorption in the IR due to trans-[Rh(μ-I)(CO)(PPh$_3$)]$_2$ ($v_{CO}$ 1980cm$^{-1}$). The reaction products are the rhodium(III) alkyl complex VII and the rhodium-(III) acetyl complex VIII which are in equilibrium. [Rh(μ-Cl)X(CO)(Me)(PMe$_3$)]$_2$, X = Cl, Br and I, equilibrate in an identical manner to give the acyl complex [Rh(μ-Cl)X(COMe)(PMe$_3$)]$_2$.[12] In Scheme 2 the assumption has been made that VII is the initial product although this may not necessarily be the case.
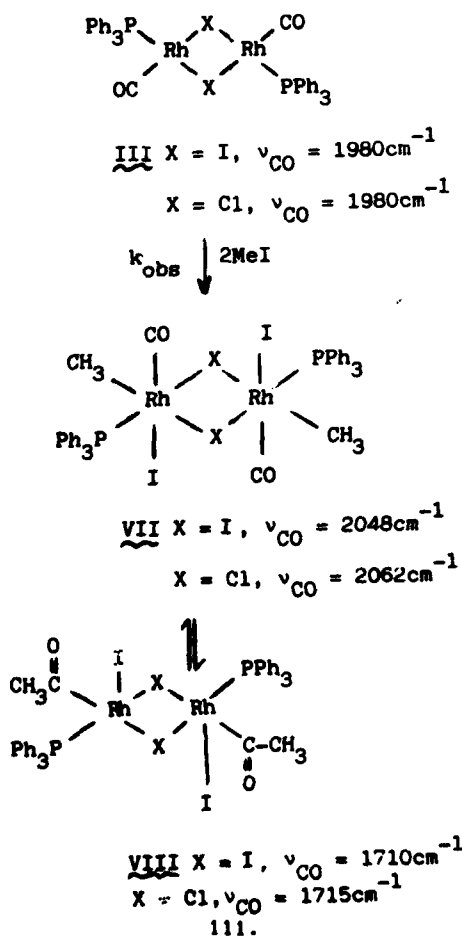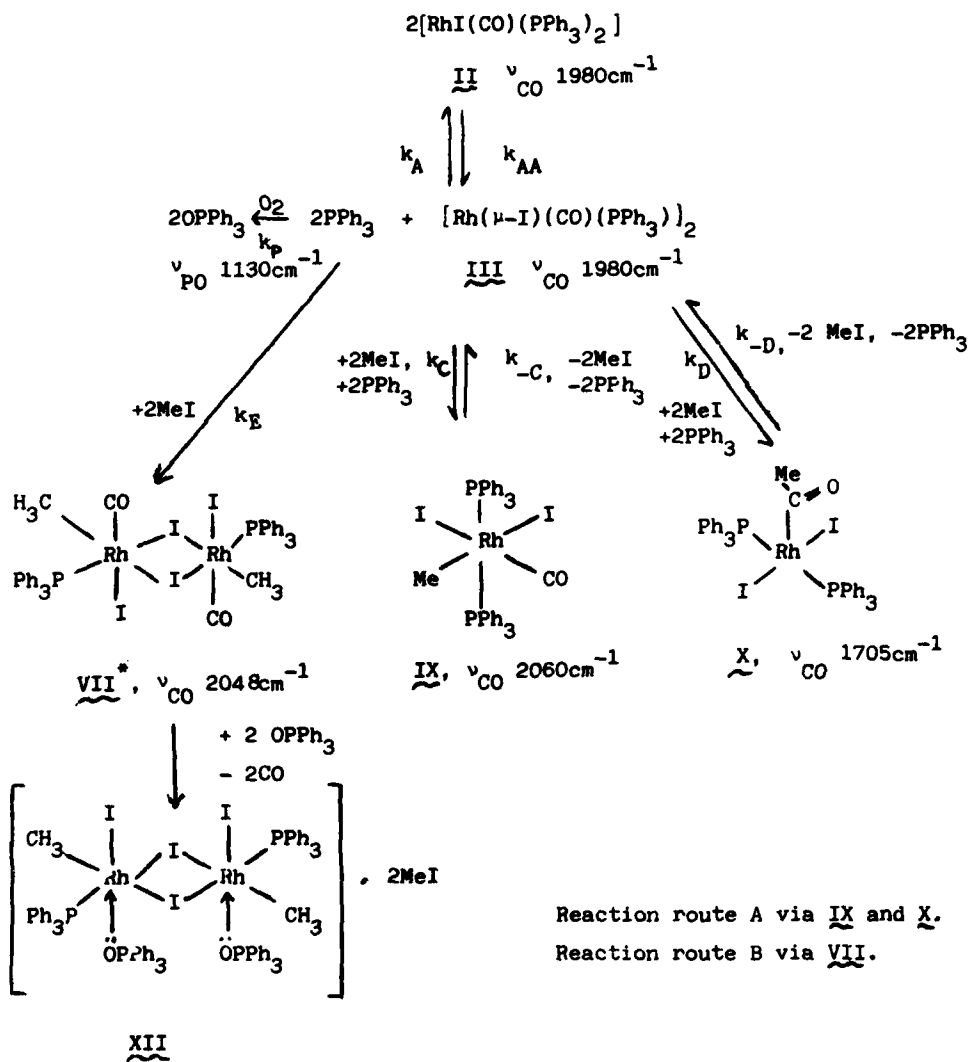
## Scheme 1

$[RhBr(CO)\{P(p\text{-}EtC_6H_4)_3\}_2]$

$\underset{\sim}{II}$  $\nu_{CO}$ 1980cm$^{-1}$

$\xrightleftharpoons[-n\text{-}PrBr]{n\text{-}PrBr}$

$[RhBr_2(CO)Pr\{P(p\text{-}EtC_6H_4)_3\}_2]$

$\underset{\sim}{IV}$

Route A

route B $\downarrow$ n–PrBr

$[RhBr_2(COPr)\{P(p\text{-}EtC_6H_4)_3\}_2]$

$\underset{\sim}{V}$  $\nu_{CO}$ 1710cm$^{-1}$

$\downarrow$ –CO

$[RhBr_2Pr\{P(p\text{-}EtC_6H_4)_3\}_2]$

$\underset{\sim}{VI}$

## Scheme 2



$\underset{\sim}{III}$ X = I, $\nu_{CO}$ = 1980cm$^{-1}$

X = Cl, $\nu_{CO}$ = 1980cm$^{-1}$

$k_{obs}$ $\downarrow$ 2MeI



$\underset{\sim}{VII}$ X = I, $\nu_{CO}$ = 2048cm$^{-1}$

X = Cl, $\nu_{CO}$ = 2062cm$^{-1}$



$\underset{\sim}{VIII}$ X = I, $\nu_{CO}$ = 1710cm$^{-1}$

X = Cl, $\nu_{CO}$ = 1715cm$^{-1}$

111.

Table 2: Observed rate constants for the reaction of 1-bromopropane with
trans-[RhBr(CO){P(p-Et C₆H₄)₃}₂] in the presence and absence of added
bromide ion in chloroform.

| Complex | Temp °C | [Pr$_4$N$^+$Br$^-$] (M) | [n-PrBr] (M) | $k_{obs}$ (s$^{-1}$) |
|---|---|---|---|---|
| trans-[RhBr(CO){P(p-Et C₆H₄)₃}₂] | 40 | 0.0185 | 2.53 | $3.44 \times 10^{-3}$ |
| trans-[RhBr(CO){P(p-Et C₆H₄)₃}₂] | 40 | 0.0 | 2.53 | $3.41 \times 10^{-5}$ |

The molecular structures of VII, X = Cl and I, have been assigned by compari-

son with [Rh($\mu$-Cl)Br(CO)Me(PMe$_2$Ph)]$_2$; the crystal structure of which has

been reported[12]. The oxidative-addition of iodomethane to

trans-[Rh($\mu$-Cl)(CO)(PPh$_3$)]$_2$ (Scheme 2) also gave pseudo first-order kinetics.

As shown in Table 1 the rate of oxidative-addition ($k_{obs}$) of iodomethane to

the monomeric trans-[RhCl(CO)(PPh$_3$)$_2$] is only slightly slower than that

observed for the dimeric trans-[Rh($\mu$-Cl)(CO)(PPh$_3$)]$_2$ although a direct

comparison cannot be made due to the possibility of halide exchange in the

monomeric system[2].

*Reaction of trans-[RhI(CO)(PPh$_3$)$_2$] with iodomethane.* During the preparation

of this complex it was found to dissociate a phosphine ligand to give an

equilibrium amount of the dimer [Rh($\mu$-I)(CO)(PPh$_3$)]$_2$, III[4]. Also the

extreme oxygen sensitivity of trans-[RhI(CO)(PPh$_3$)$_2$] was noted[4] and so care

was taken to exclude oxygen from the reaction cell. As there was a possibil-

ity of a reversible oxygen absorption onto the surface of trans-[RhI(CO)(PPh$_3$)$_2$],

samples were placed under high vacuum before use. A reversible oxygen absorp-

tion onto the surface of [RhCl(PPh$_3$)$_3$] has previously been reported[13]. The

reaction of trans-[RhI(CO)(PPh$_3$)$_2$] with iodomethane was monitored by the

decrease of $\nu_{CO}$ at 1980cm$^{-1}$ and was found to follow a second-order rate law

in the early stages of the reaction. This suggested the dimer trans-

[Rh($\mu$-I)(CO)PPh$_3$)]$_2$, III, plays an important part in the oxidative-addition.

The initial products heave $\nu_{CO}$ 2060cm$^{-1}$ (assigned to the rhodium(III)  acyl

product X). After a time a new carbonyl absorption due to a rhodium(III)

alkyl species with $\nu_{CO}$ 2048cm$^{-1}$ was observed. The time taken for the

appearance of $\nu_{CO}$ 2048cm$^{-1}$ increased when oxygen was rigorously excluded

from the cell, and coincided with the emergence of a phosphine oxide

absorption at 1130cm$^{-1}$ in the IR spectrum. Thus, as shown in Scheme 3,

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## Scheme 3

$2[RhI(CO)(PPh_3)_2]$

II  $\nu_{CO}$ 1980cm$^{-1}$

$k_A \Updownarrow k_{AA}$

$2OPPh_3 \xleftarrow[k_P]{O_2} 2PPh_3$  +  $[Rh(\mu-I)(CO)(PPh_3)]_2$

$\nu_{PO}$ 1130cm$^{-1}$     III  $\nu_{CO}$ 1980cm$^{-1}$

$+2MeI, k_C \Updownarrow k_{-C}, -2MeI$
$+2PPh_3 \quad\quad -2PPh_3$

$k_{-D}, -2\ MeI, -2PPh_3$

$k_D$

$+2MeI \quad k_E$

$+2MeI$
$+2PPh_3$



VII$^{*}$, $\nu_{CO}$ 2048cm$^{-1}$

IX, $\nu_{CO}$ 2060cm$^{-1}$

X, $\nu_{CO}$ 1705cm$^{-1}$

$+ 2\ OPPh_3$
$- 2CO$

 . 2MeI

XII

Reaction route A via IX and X.
Reaction route B via VII.

\* VI is in equilibrium with the acyl isomer VIII shown in Scheme 2.

initially there is a rapid reaction of trans-$[Rh(\mu-I)(CO)(PPh_3)]_2$, with

iodomethane to give IX and X, which is then followed by a slow reaction to

give the final products via the rhodium(III) alkyl complex having $\nu_{CO}$

$2048cm^{-1}$ (assigned the structure VII). The change from reaction route A to

reaction route B in Scheme 3 occurs due to removal of the free dissociated

phosphine by oxidation to phosphine oxide, which is too poor a donor to be

able to break the halide bridges of $[Rh(\mu-I)I(CO)Me(PPh_3)]_2$ to give monomeric

products. In the presence of triphenylphosphine the halide bridges of both

$[Rh(\mu-I)I(CO)(Me)(PPh_3)]_2$, VII, and $[Rh(\mu-I)I(COMe)(PPh_3)]_2$, VIII, would be

expected to be rapidly broken to yield the monomers IX and X. Complexes

VII and VIII, X = Cl, are known to react rapidly with free triphenylphosphine

to yield monomeric species[9]. In a situation where the reaction occurs under

a nitrogen atmosphere, route B would not occur.

The reaction mechanism shown in Scheme 3 was tested by FACSIMILE and

found to give a good fit, with the sum of the squares of the residuals

= 4231. The rate constants for each step are shown in Table 1. This

reaction was analysed using the equations 1-5. The fit between

$$ II\ +\ II\ \rightleftharpoons\ III\ +\ 2P \tag{1} $$

$$ III\ +\ 2P\ +\ 2MeI\ \rightleftharpoons\ 2IX \tag{2} $$

$$ III\ +\ 2P\ +\ 2MeI\ \rightleftharpoons\ 2X \tag{3} $$

$$ III\ \longrightarrow\ VII \tag{4} $$

$$ P\ +\ \tfrac{1}{2}O_2\ \longrightarrow\ PO(inactive) \tag{5} $$

P = triphenylphosphine, PO = phosphine oxide.

The calculated and observed absorbances for the reaction of trans-$[RhI(CO)(PPh_3)_2]$

with iodomethane at 20°C, when analysed in terms of Scheme 3, are shown in

Figures 1a and 1b. Analysis of this reaction by a mechanism having IX in

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Fig. 1(a). Computer fitting for model using equations 1-5.
Predicted absorbance for $\underline{\text{II}}$ at 1980cm$^{-1}$ (---), predicted absorbance
for $\underline{\text{X}}$ at 1705cm$^{-1}$ (--·-), experimental absorbance at 1980cm$^{-1}$ (-···-)
and experimental absorbance at 1750cm$^{-1}$ (——).

116.
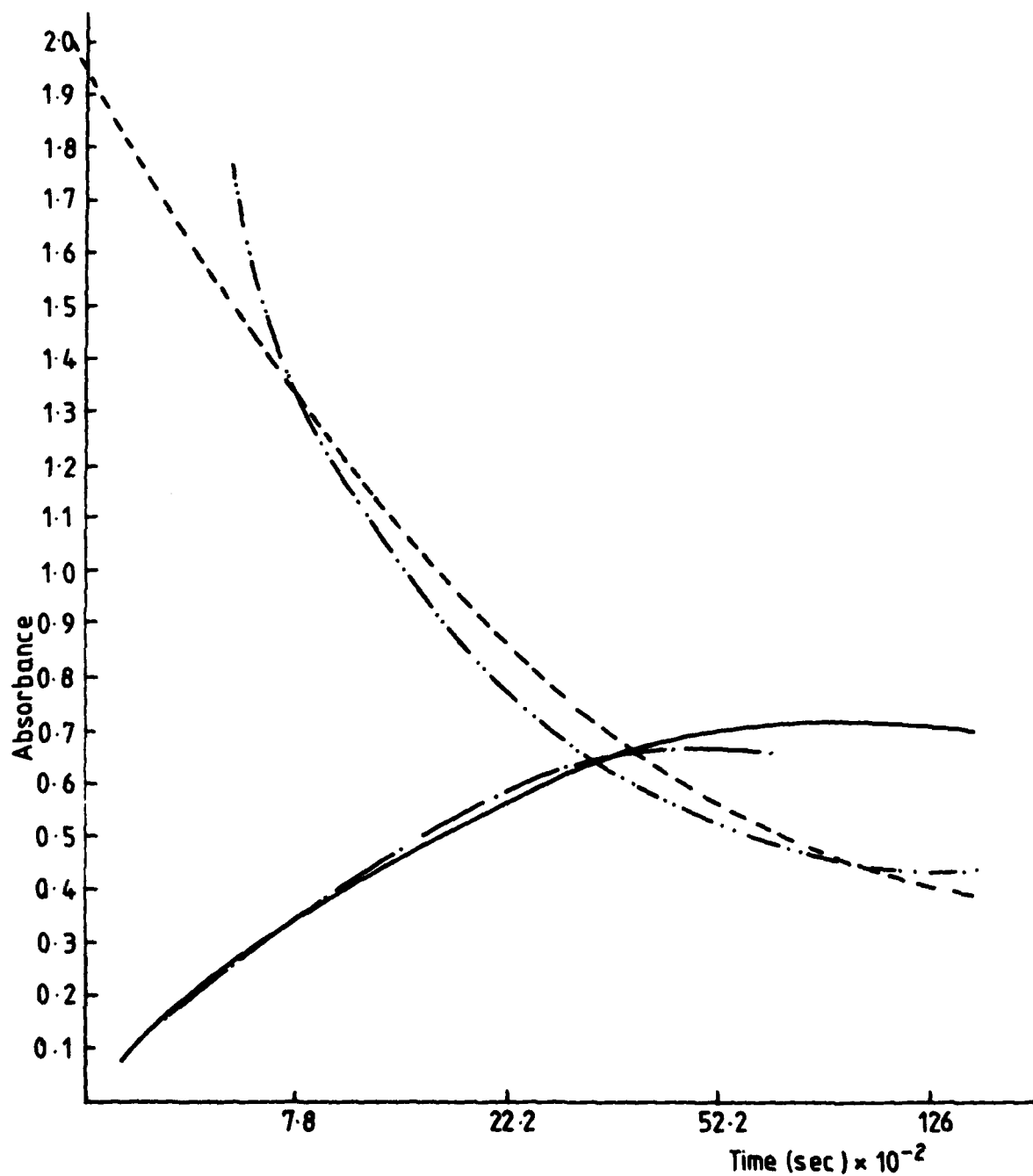
Fig. 1(b). Computer fitting for model using equations 1-5.
Predicted absorbance for $\underline{IX}$ at 2060cm$^{-1}$ (---), predicted absorbance for $\underline{VII}$ at 2048cm$^{-1}$ (——), experimental absorbance at 2060 cm$^{-1}$ (-···-) and experimental absorbance at 2048cm$^{-1}$ (-··-).

117.
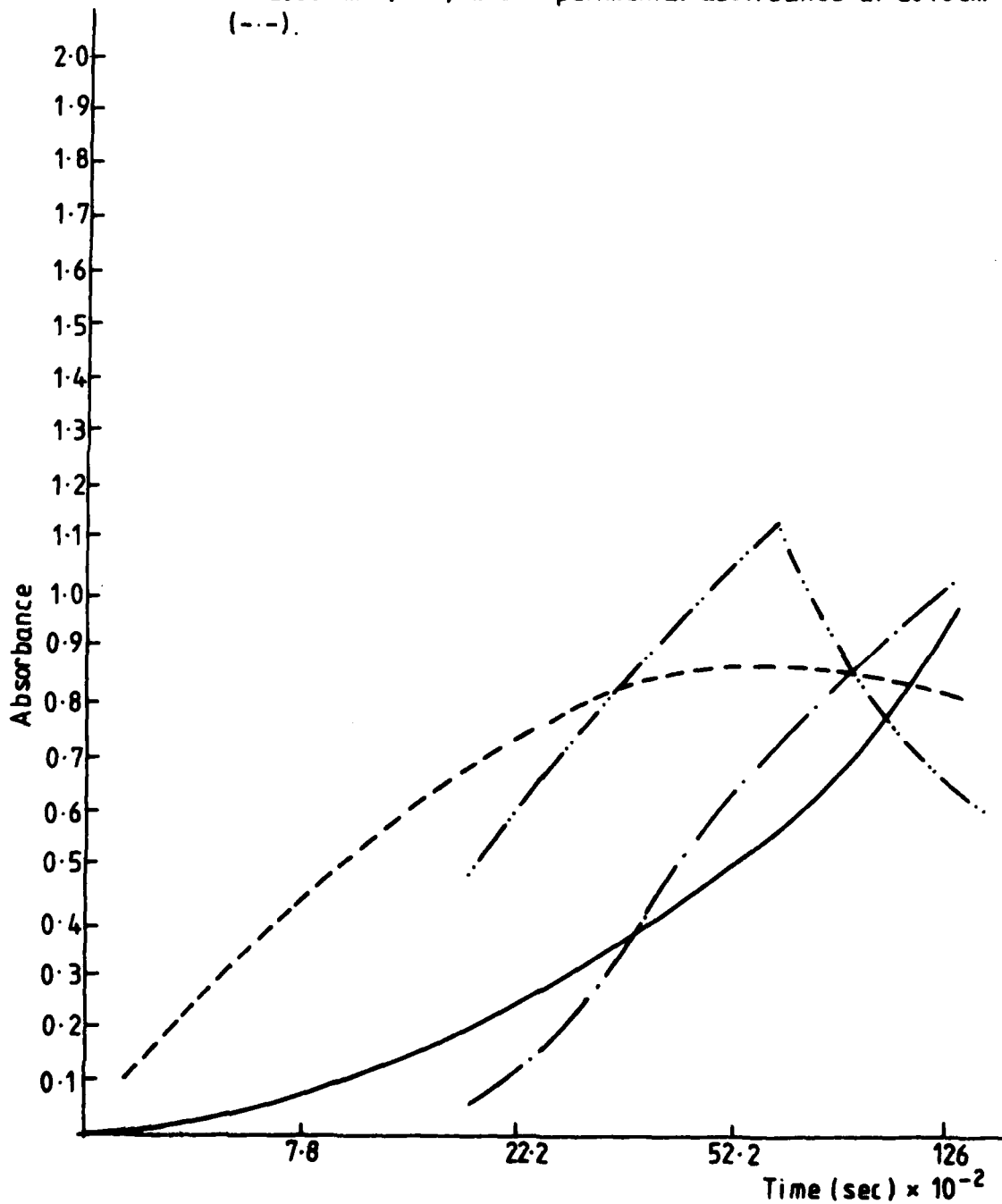
Fig. 1(c).  Computer fitting for model using equations 1,2,6,4 and 5. Predicted absorbance for $\text{II}$ at 1980 cm$^{-1}$(---), predicted absorbance for $\text{X}$ at 1705 cm$^{-1}$(-·-), experimental absorbance at 1980cm$^{-1}$(-·-) and experimental absorbance at 1705cm$^{-1}$ (——).

118.
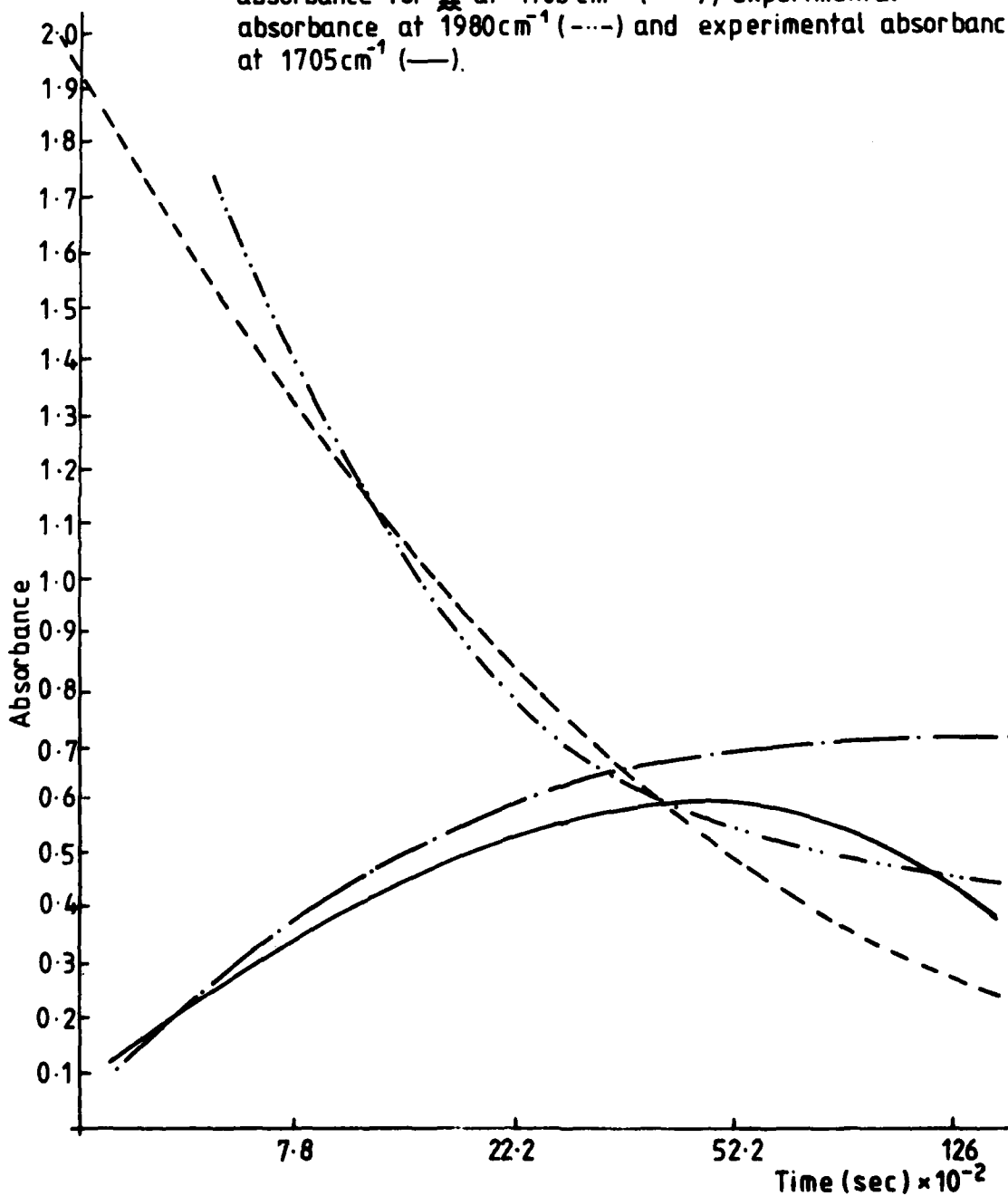
Fig. 1(d). Computer fitting for model using equations 1, 2, 6, 4 and 5.
Predicted absorbance for Ⅸ at $2060 cm^{-1}$ (---), predicted
absorbance for Ⅶ at $2048 cm^{-1}$ (——), experimental absorbance
at $2060 cm^{-1}$ (-···-) and experimental absorbance at $2048 cm^{-1}$
(-··-).

119.

equilibrium with $\underset{\sim}{X}$ by use of equations 1, 2, 6, 4 and 5 gave a poorer fit (Figures 1c and 1d), with the sum of the squares of the residuals = 36,426.

$$\underset{\sim}{\text{IX}} \rightleftharpoons \underset{\sim}{X} \tag{6}$$

IR spectroscopy shows that the final reaction product slowly loses carbon monoxide. The final product has ^{1}H NMR and IR spectra and microanalysis[14] consistent with the structure $\underset{\sim}{\text{XII}}$ in Scheme 3.

## Discussion

The results presented here and in earlier work[2,5] suggest a mechanism of oxidative-addition of 1-haloalkanes to trans-$[RhX(CO)(PR_3)_2]$, $\underset{\sim}{\text{II}}$, X = Cl and Br, R = phenyl or para-substituted aryl, where acyl ($\underset{\sim}{\text{IV}}$) and alkyl ($\underset{\sim}{\text{V}}$) complexes are formed independently from $\underset{\sim}{\text{II}}$ as shown in Scheme 4.

Scheme 4

$$\underset{\sim}{\text{II}} \underset{k_2}{\overset{K_1}{\rightleftharpoons}} \underset{\sim}{\text{IV}} \searrow \underset{\sim}{V}$$
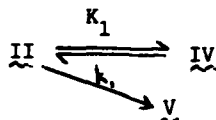
This has been explained by use of a mechanism involving the anionic intermediate $[RhX_2(CO)(PR_3)]^-$ formed on dissociation of phosphine and formation of a quaternary phosphonium salt by reaction with the 1-haloalkane[2]. The addition of 1-bromopropane to $\underset{\sim}{\text{II}}$, X = Br and R = p-EtC$_6$H$_4$, yields only the rhodium(III) acyl product $\underset{\sim}{V}$, as shown in Scheme 1. This supports the general mechanism shown in Scheme 4 although in this case the formation of $\underset{\sim}{\text{IV}}$ does not occur as the value $K_1$ does not favour its formation. A mechanism involving formation of the acyl complex $\underset{\sim}{V}$ without a rhodium(III) alkyl complex as intermediate is unlikely. It is improbable that this intermediate is the anionic acyl complex $[RhBr_3(CO)Pr\{P(p-EtC_6H_4)_3\}]^-$ formed by the oxidative-addition of 1-bromopropane to $[RhBr_2(CO)\{P(p-EtC_6H_4)_3\}_2]^-$ as this reaction was

120.

found not to be catalysed by the addition of added bromide ion. An alternative simpler explanation is that the intermediate is an isomer of IV, in which carbonyl insertion into the rhodium(III) methyl bond is sterically favoured (ie isomer IV (b) in Scheme 5) and rapidly occurs to give the acyl complex V.

The mechanism of oxidative-addition of iodomethane to trans-[RhI(CO)(PPh$_3$)$_2$], although complicated by dimerisation, also proceeds via an equilibrium between the rhodium(I) dimer, and rhodium(III) acyl and alkyl complexes as shown in Scheme 6. This is more complicated because the reaction also involves cleavage of the halide bridges of a dimeric rhodium(III)

Scheme 6

III

IX    X
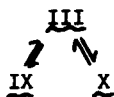
acyl or alkyl complex. The rise in conductivity reported to occur during this reaction[5] could be explained by reaction of iodomethane with dissociated phosphine to give [Ph$_3$PMe]$^+$I$^-$, and reaction with the phosphine oxide, produced during the course of this reaction, to give an equilibrium amount of [Ph$_3$POMe]$^+$I$^-$. The rate of oxidation of phosphine to phosphine oxide is faster than reported in the absence of rhodium complexes[16]. In the example shown in Table 1 where oxygen was initially vigorously excluded from the reaction cell, it was impossible to prevent slow ingress into the pumping loop over the 6 hr run. Without the complex present free phosphine would show little oxidation under these conditions.

The oxidative-addition of iodomethane to trans-[Rh($\mu$-X)(CO)(PPh$_3$)]$_2$ was found to be dependent on the halide in the order, I > Cl. The addition of 1-bromoalkanes to trans-[RhX(CO)(PR$_3$)$_2$] II, X = Br; PR$_3$ = P(p-Et C$_6$H$_4$)$_3$ and PEt$_2$Ph[15] is slow (Table 1) due to the lower electrophilicity of the substrate. The rate of oxidative-addition has been found to be dependent on the coordin-ated phosphine of trans-[RhX(CO)(PR$_3$)$_2$]. When X = Br the order R = p-Et C$_6$H$_4$ > Ph

121.

## Scheme 5



trans-$[RhX(CO)(PR_3)_2]$ + R'X'

II

$K_1$

IV(a)

IV(b)

k    Fast

V

122.
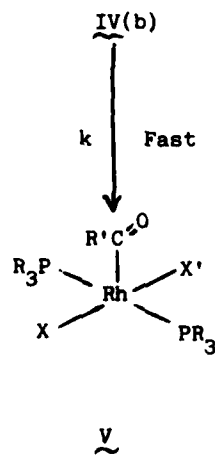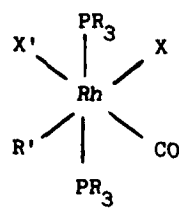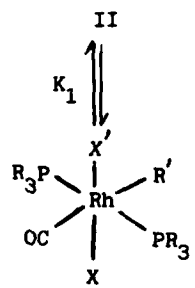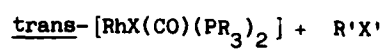
was found.

In conclusion the oxidative-addition of iodomethane to _trans-_
$[Rh(\mu-X)(CO)(PPh_3)]_2$ involves nucleophilic attack of the metal complex on
the carbon of the iodomethane.  The enhanced reactivity of _trans-_
$[Rh(\mu-I)(CO)(PPh_3)]_2$ to oxidative-addition has led to this being the
reactive species in the apparent reaction of iodomethane to _trans-_
$[RhI(CO)(PPh_3)_2]$.

## Acknowledgements

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14. The moisture sensitive brown complex XII was precipitated from the iodomethane solution by addition of dry petroleum ether (40–60°) in 36% yield. $^1H$ NMR (CDCl$_3$) gave $\delta$ 8.0–8.9 (m, 10H), 3.2 (d, J = 11.7Hz, 1H), 2.18 (S, 1H) ppm. IR spectroscopy (nujol mull) gave $\nu_{PO}$ 1110cm$^{-1}$ and absorption at 1090cm$^{-1}$ typical of coordinated phosphine. Anal. Calcd for $C_{38}H_{36}I_3OP_2Rh$: C 43.3; H 3.4 % Found: C, 43.5, H, 3.5 %.

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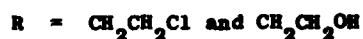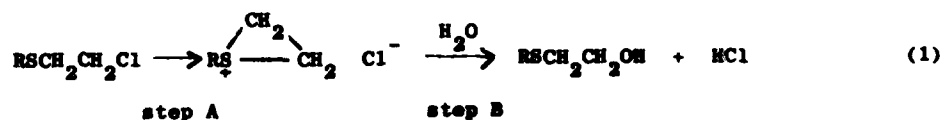16. Floyd, M B; Boozer, C E J. Am. Chem. Soc., 1963, 85, 984.

# Chapter 6

## The Decomposition of Mustard and its Derivatives

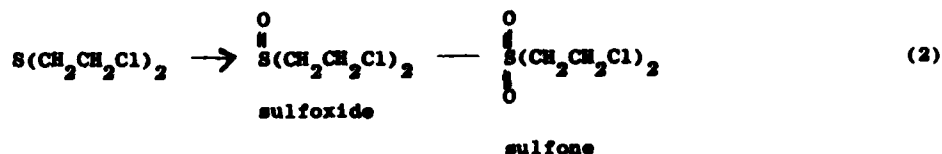## Promoted by Rhodium(I) Tertiary Phosphine Complexes

1. **Introduction**.

   Classically mustard can be degraded by one of two methods.

   (i)   By hydrolysis, which is pH independent since step A is rate determining in reaction sequence (5)[1]. Two hydrolyses are required to yield the inactive thiodiglycol:

$$RSCH_2CH_2Cl \longrightarrow R\overset{+}{S}\underset{CH_2}{\overset{CH_2}{<\quad|}}\quad Cl^- \xrightarrow{H_2O} RSCH_2CH_2OH \; + \; HCl \qquad (1)$$

$$\text{step A} \qquad\qquad \text{step B}$$

   $R = CH_2CH_2Cl$ and $CH_2CH_2OH$

   (ii)  By oxidation as shown in reaction sequence 2, although the sulfone[2] has some vesicant activity.

$$S(CH_2CH_2Cl)_2 \longrightarrow \overset{O}{\underset{}{\overset{\|}{S}}}(CH_2CH_2Cl)_2 \;\; \overset{}{\longrightarrow} \;\; \overset{O}{\underset{\underset{O}{\|}}{\overset{\|}{S}}}(CH_2CH_2Cl)_2 \qquad (2)$$

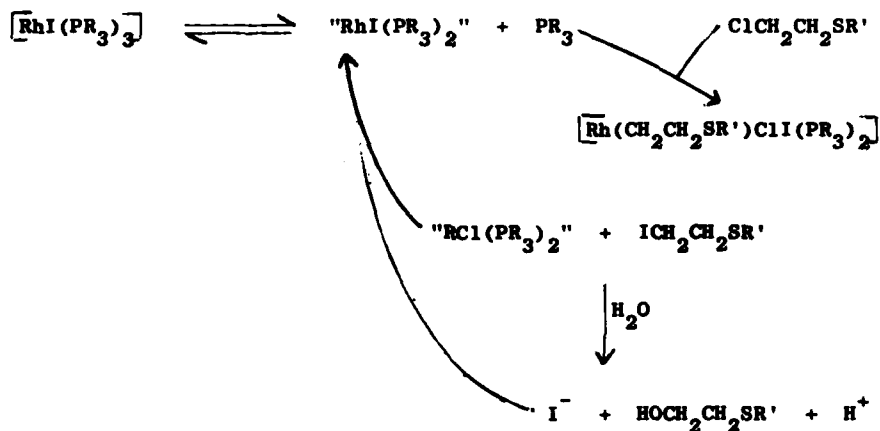$$\text{sulfoxide}$$

$$\text{sulfone}$$

   Both of these degradation routes could be promoted by rhodium(I).

   (iii) **Hydrolysis Promoted by Rhodium(I) Complexes**.

   Halide exchange reactions of trans-$[RhX(CO)(PR_3)_2]$, described in Chapter 3, could be used to catalyse the hydrolysis of mustard. Exchanging iodo for chloro in bis(2-chloroethyl)sulphide may make hydrolysis occur faster as iodide is a better leaving group (Scheme 1). It has already been shown that bromide is a better leaving group than chloride in reactions involving a similar three-membered cyclic intermediate[3].

## Scheme 1

$$[RhI(PR_3)_3] \rightleftharpoons \text{"}RhI(PR_3)_2\text{"} + PR_3 \qquad ClCH_2CH_2SR'$$

$$[Rh(CH_2CH_2SR')ClI(PR_3)_2]$$

$$\text{"}RCl(PR_3)_2\text{"} + ICH_2CH_2SR'$$

$$\downarrow H_2O$$

$$I^- + HOCH_2CH_2SR' + H^+$$

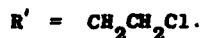R   =   phenyl, para-substituted phenyl or alkyl.

R'   =   $CH_2CH_2Cl$ or $CH_2CH_2OH$.

### (iv)   Oxidation Promoted by Rhodium Complexes.

Rhodium-oxygen complexes have been used to oxidise a variety of organic molecules including alkenes[4,5] and phosphines[6,7]. A catalytic process could use this type of oxidation to produce the inactive sulfoxide as shown in Scheme 2.
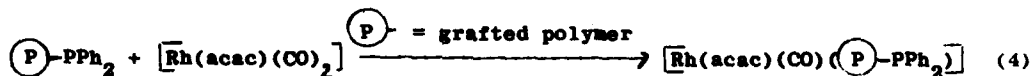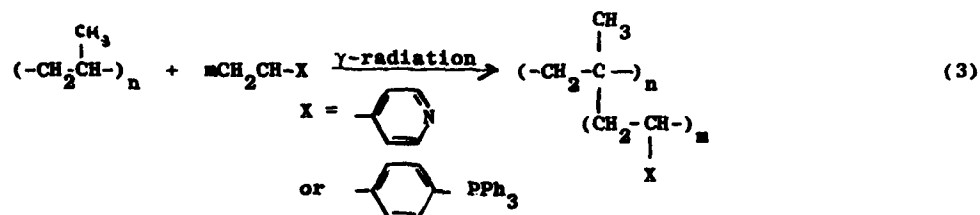
## Scheme 2



126.

$R' = CH_2CH_2Cl.$
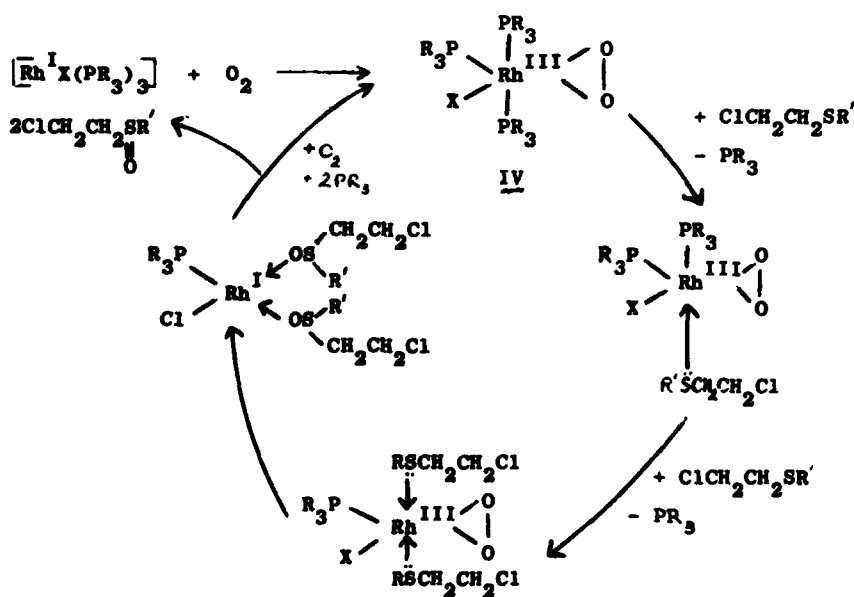
$R =$ phenyl, _para_-substituted phenyl or alkyl.

$I = +1$ oxidation state.

$III = +3$ oxidation state.

## 2. The Application of Rhodium Catalysed Deactivation of Mustard.

The most cost effective use would be in self-decontaminating paints and cloth. A series of rhodium complexes bound to polypropylene have been developed in our laboratory as shown in equations 3 and 4, therefore any catalytic process developed for mustard decontamination could be adapted for use in paints

$$
\text{(-CH}_2\text{CH-)}_n \ \overset{\text{CH}_3}{\underset{\phantom{x}}{|}} \ + \ \text{mCH}_2\text{CH-X} \ \xrightarrow{\gamma\text{-radiation}} \ \text{(-CH}_2\text{-C-)}_n \tag{3}
$$

$$\text{P}\!-\!\text{PPh}_2 + \left[\overline{\text{Rh(acac)(CO)}_2}\right] \xrightarrow{\ \ \text{P} = \text{grafted polymer}\ \ } \left[\overline{\text{Rh(acac)(CO)}(\text{P}\!-\!\text{PPh}_2)}\right] \tag{4}$$
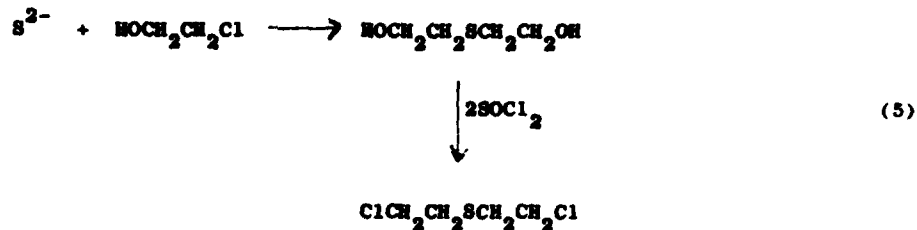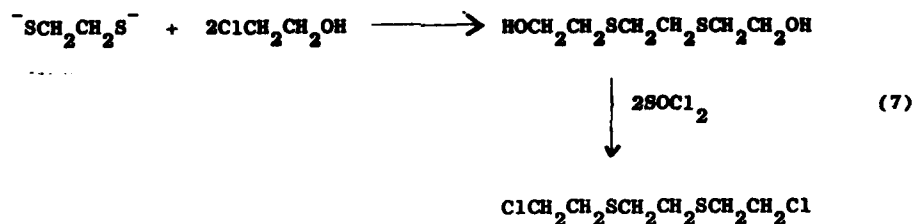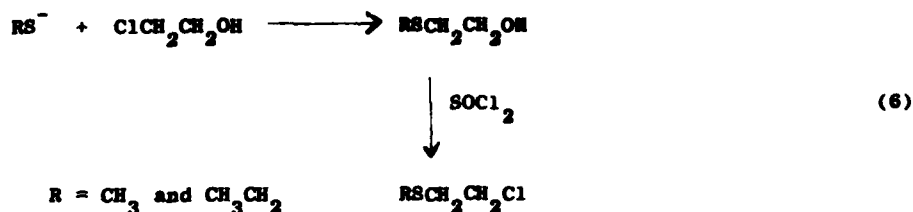
and cloths, by binding the rhodium into the paint or cloth. Alternatively the very soluble tertiary phosphines developed in Chapter 2 could be used to ensure that the rhodium complexes dissolved freely in paints and polymers.

## 3. Decontamination Studies.

### a. Preparation of Mustard, Half-Mustard and Sesqui-Mustard.

Mustard[9], half-mustard[10] and sesqui-mustard[11] were prepared as described in the literature (reactions 5-7).

$$
S^{2-} + \text{HOCH}_2\text{CH}_2\text{Cl} \longrightarrow \text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}
$$

$$
\Big\downarrow 2\text{SOCl}_2 \tag{5}
$$

$$
\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}
$$

$$RS^- + ClCH_2CH_2OH \longrightarrow RSCH_2CH_2OH$$

$$\downarrow SOCl_2 \qquad\qquad (6)$$

$$R = CH_3 \text{ and } CH_3CH_2 \qquad RSCH_2CH_2Cl$$

$$^-SCH_2CH_2S^- + 2ClCH_2CH_2OH \longrightarrow HOCH_2CH_2SCH_2CH_2SCH_2CH_2OH$$

$$\downarrow 2SOCl_2 \qquad\qquad (7)$$

$$ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$$

b.   The Rate of Hydrolysis of Mustard by Water.

The rate of hydrolysis of mustard by water is dependent on stirring rate, and so the rate of hydrolysis was measured in a series of uncatalysed reactions as a control to compare with catalysis experiments.  In all cases the same experimental procedure was employed as described below.  The results are shown in Table 1.

Experimental Procedure:  Bis(2-chloroethyl)sulphide (0.25ml, 0.32g, $2.0 \times 10^{-3}$ mole) was pipetted into 25ml of water and stirred for 10 mins. The mustard was extracted by dichloromethane (50ml) and the concentration of mustard determined on a Pye-Unicam 204 Chromatograph equipped with a flame ionisation detector using a 2.8m column containing 5% OV1 on diatonite[12,13]. Figure 1 shows the linear relationship between the concentration of mustard and the area of the GC peak.

c.   Attempted Catalysis of Mustard Hydrolysis by $\left[RhI(PPh_3)_3\right]$.

An attempt was made to promote mustard hydrolysis by catalysing the exchange of chloride for iodide as in Scheme 1 (R = Ph).  Excess iodide was added as $NPr_4^+I^-$, which was soluble in mustard, to help initiate the reaction. The mixture was stirred for 10 mins in water.  The mustard was then extracted, as described in section b, and its concentration determined by GC.  The result is shown in Table 1.

Fig. 1.    Standard curve for Sulfur Mustard. Peak
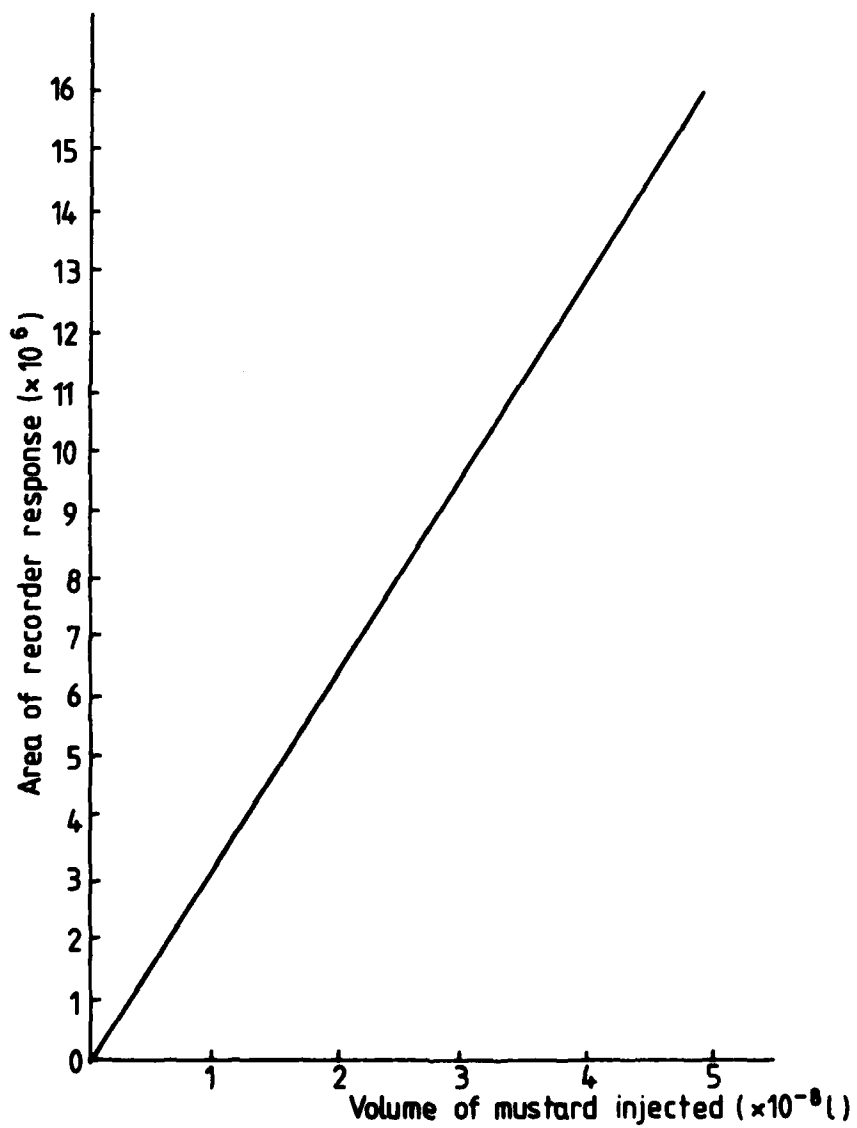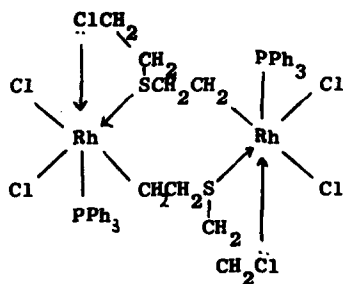area response plotted against amount injected.

## Table 1

### The Decontamination of Mustard in the Presence and

### Absence of Promoters

| Decontaminant | Promoter | Time (min) | % Decontamination |
|---|---|---|---|
| Water | None | 10 | 4% |
| Water | None | 30 | 24% |
| Water | None | 60 | 44% |
| Water | $[RhI(PPh_3)_3]$ | 10 | 14% |
| Oxygen in $CH_2Cl_2$ | $[RhCl(O_2)(PPh_3)_3]$ | 48 hrs | 42% |

d.   Attempted Catalytic Oxidation of Mustard by $[RhCl(PPh_3)_3]$.

An attempt was made to promote the oxidation of mustard by the oxidation shown in Scheme 2 (R = Ph). Oxygen complexes formed from $[RhCl(PPh_3)_3]$[14] are known to catalyse the oxidation of organic compounds such as olefins[4,5] and therefore it was hoped that this and the oxygen complex described in Chapter 3 (reference 3) might promote the oxidation of mustard. $[RhCl(PPh_3)_3]$ underwent oxidative-addition on treatment with bis(2-chloroethyl)sulphide. The air stable product was isolated by precipitation with benzene. ^{1}H-NMR and IR spectroscopy and elemental analysis were consistent with the structure I. The rhodium(III) complexes formed by oxidative-addition of alkylhalides usually decompose either via reductive elimination[15] or, in the presence of air via oxidation as described in section 1. The unusual stability of I to both oxidation and reductive elimination probably is due to the chelating effect of the mustard ligand.

$$ClCH_2$$
$$CH_2$$
$$SCH_2CH_2$$

$$Cl \quad PPh_3 \quad Cl$$
$$\diagdown \quad \diagup$$
$$Rh \qquad Rh$$
$$\diagup \quad \diagdown$$
$$Cl \quad CH_2CH_2S \quad Cl$$
$$PPh_3 \quad CH_2$$
$$CH_2Cl$$

**I**

e.    Catalytic Oxidation of Mustard by $[RhCl(O_2)(PPh_3)_3]$.

To avoid the competing oxidative-addition of mustard to $[RhCl(PPh_3)_3]$ forming **I**, the rhodium-oxygen complex, $[RhCl(O_2)(PPh_3)_3]$ was used as the catalyst instead of $[RhCl(PPh_3)_3]$ in Scheme 2. The reaction mixture was stirred in air under dry conditions, the results are shown in Table 1.

f.    **Summary of Decontamination Studies**.

From these initial studies $[RhCl(O_2)(PPh_3)_3]$ is a promising candidate for further studies in the catalytic degradation of the mustard agents. Further investigation into the stability of the complex **I** may also lead to a catalytic process for mustard degradation.

This novel approach to the decontamination of mustard agents also lends itself to a system where the metal complex may be strongly bound to polymer materials. This is by the use of radiation grafted polymers which functionalise inert polymers with ligand moieties. This is also a specialised research area in which our laboratories have considerable expertise.

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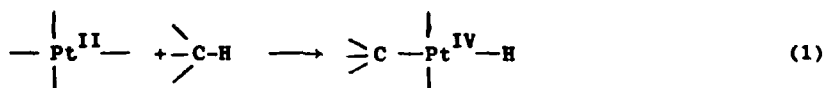
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## Carbon Hydrogen Bond Activation Using Platinum(O) Complexes

1. ### Introduction

A major objective of the original grant application was the activation of C-H bonds. Classically this has been achieved using platinum(II) complexes by an oxidative-addition reaction (reaction 1).[1,2] The product of reaction 1 is a

$$— \overset{|}{\underset{|}{Pt^{II}}} — \quad + \overset{\backslash}{\underset{/}{-}}C-H \quad \longrightarrow \quad \overset{|}{\underset{}{\gtrdot}}C — \overset{|}{\underset{|}{Pt^{IV}}} — H \tag{1}$$

platinum(IV)-alkyl complex and these have a very limited chemistry. By contrast platinum(II)-alkyl complexes have a much wider chemistry.[2] Accordingly we attempted to prepare platinum(II)-alkyl complexes by the oxidative-addition of C-H bonds to platinum(O) complexes. In chapter 5 we have shown that tertiary phosphine platinum(O) complexes readily undergo oxidative-addition with methyl iodide.[3] In the present chapter we show firstly that tertiary phosphine platinum(O) complexes readily undergo oxidative-addition with the relatively inert C-Cl bond of dichloromethane and that, in the absence of more reactive bonds undergo oxidative-addition with C-H bonds, for example in pentafluorobenzene.

The fundamental aim of the work described in the present chapter was to try to generate coordinatively unsaturated platinum(O) species in solution in the presence of an organic substrate since it was envisaged that these species would be highly reactive and possibly bring about oxidative-addition of a C-H bond according to reaction 2. Some compounds $[ML_2]$, M = Pd, Pt; L = large bulky phosphine have been prepared [4-7] and been shown to be highly reactive towards
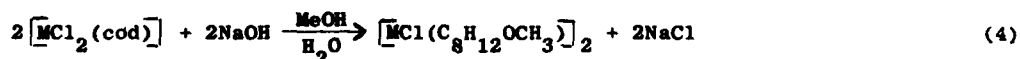
$$Pt^{O} \; + \; R\text{-}H \; \rightleftharpoons \; R\text{-}Pt^{II}\text{-}H \tag{2}$$
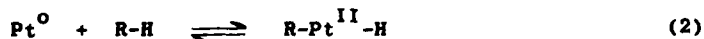
oxidative-addition[8-10].

Recently , it has been demonstrated that DBU (DBU = 1,8-diazabicyclo$[\overline{5},4,\overline{0}]$-undec-7-ene) will remove HCl from trans-$[\overline{P}tHCl(PPh_3)_3]$ in the presence of a weak ligand, L, according to equation 3.

$$\text{trans-}[\overline{P}tHCl(PPh_3)_2] \; + \; DBU \; + \; L \; \xrightarrow{C_6H_6} \; [\overline{P}tL(PPh_3)_2] \; + \; +DBU.HCl \tag{3}$$
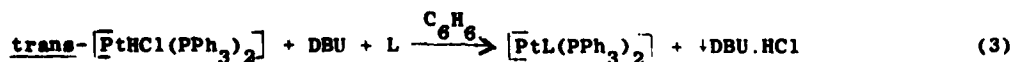
DBU.HCl is a white solid, insoluble in benzene.  Our original plan, therefore,

was to prepare a series of hydride complexes, trans-$[\text{PtHCl}(PR_3)_2]$ and investigate

the reaction in equation 3 to see if it would be possible to generate, in situ, species

of the type $[\text{Pt}(PR_3)_2]$ when no other ligands are present.

2.    Preparation of Hydride Complexes.

Although we have previously reported[12] the preparation of trans-$[\text{PtHCl}(PR_3)_2]$,

R = n-alkyl, by the hydrazine reduction of cis-$[\text{PtCl}_2(PR_3)_2]$, a more convenient

route for both platinum(II)[13] and palladium(II)[14] hydride complexes is shown in

equations 4 and 5 (M = Pd, Pt).

$$2\,[\text{MCl}_2(\text{cod})] \;+\; 2\text{NaOH} \xrightarrow[\text{H}_2\text{O}]{\text{MeOH}} [\text{MCl}(C_8H_{12}OCH_3)]_2 \;+\; 2\text{NaCl} \tag{4}$$

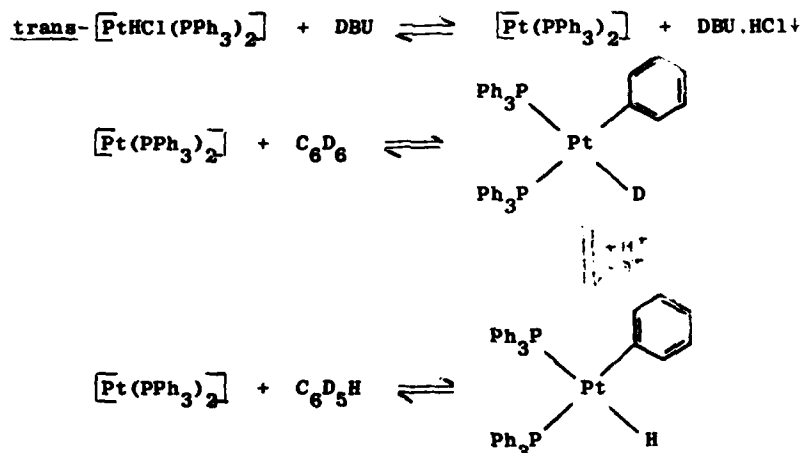$$[\text{MCl}(C_8H_{12}OCH_3)]_2 \;+\; 4PR_3 \xrightarrow{\text{MeOH}} 2\,[\text{MHCl}(PR_3)_2] \;+\; 2C_8H_{12}OCH_3 \tag{5}$$

We have used this reaction to prepare the hydride complexes of platinum(II) with the

long alkyl chain phosphines.  The reactions with $P(\underline{n}-C_4H_9)_3$, $P(\underline{n}-C_8H_{17})_3$ and

$P(\underline{n}-C_{14}H_{29})_3$ were carried out using a mixture of aqueous methanol and chloroform

to ensure homogeneity of the reaction mixture.  However, the reaction does not

succeed using PPh$_3$ and the corresponding hydride had to be prepared by the

literature procedure[15].  With $P(\underline{n}-C_4H_9)_3$ and $P(\underline{n}-C_8H_{17})_3$, the complexes were

isolated as waxes, while for $P(\underline{n}-C_{14}H_{29})_3$ a low-melting off-white solid was obtained.

Each complex showed a strong $\nu$(M-H) band in the infrared spectrum.  However, the

$P(\underline{n}-C_{14}H_{29})_3$ derivative proved to be a mixture of products from the microanalytical

data (Table 1).

Table 1:  Microanalytical Data for $[\text{PtHCl}(PR_3)_2]$ (Found (Calculated))

|  | C(%) | H(%) | P(%) |
|---|---|---|---|
| $[\text{PtHCl}\{P(\underline{n}-C_4H_9)_3\}_2]$ | 46.1(45.3) | 8.6(8.7) | 9.4(9.7) |
| $[\text{PtHCl}\{P(\underline{n}-C_8H_{17})_3\}_2]$ | 60.1(59.3) | 10.4(10.7) | 6.5(6.4) |
| $[\text{PtHCl}\{P(\underline{n}-C_{14}H_{29})_3\}_2]$ | 66.3(68.3) | 11.9(11.9) | 5.4(4.2) |
| $[\text{PtHCl}(PPh_3)_2]$ | 56.9(57.2) | 4.3(4.1) | 8.1(8.2) |

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3.  **Attempted D/H Exchange Experiments Using trans-$[PtHCl(PPh_3)_2]$.**

It was hoped that a reaction of the type shown in Scheme 1 might occur under the conditions used. Any exchange that would take place may be detected by ^{1}H nmr spectroscopy.

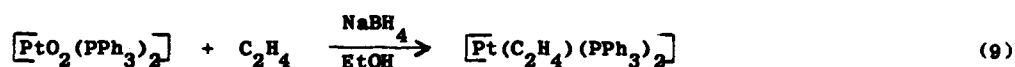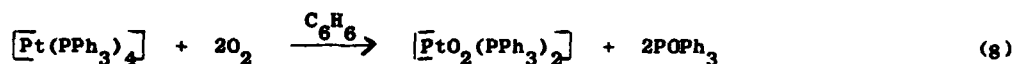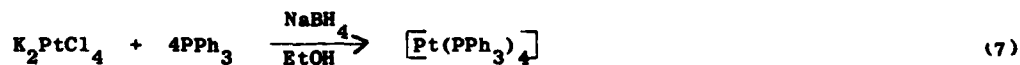$$trans-[PtHCl(PPh_3)_2] + DBU \rightleftharpoons [Pt(PPh_3)_2] + DBU.HCl\downarrow$$

$$[Pt(PPh_3)_2] + C_6D_6 \rightleftharpoons$$



$$[Pt(PPh_3)_2] + C_6D_5H \rightleftharpoons$$



<u>Scheme 1</u>

The reaction was carried out under nitrogen using dry, degassed solvents. To a warm, stirred solution of trans-$[PtHCl(PPh_3)_2]$ (0.2g, 0.26 mmol) in $d^6$-benzene (3ml) was added a solution of DBU (0.06g, 0.39 mmol) in $d^6$-benzene (3ml). An immediate colour change from colourless to yellow was noted (indicative of platinum(0) species in solution). After stirring for 2h only a small amount of precipitate was formed. This was filtered off and glacial acetic acid (3ml) added. The mixture was stirred at 80°C for 10h. Analysis of the products showed that no exchange had taken place and most of the trans-$[PtHCl(PPh_3)_2]$ could be recovered unchanged. It thus appeared that under the above conditions only a very small quantity of a platinum(0) species was formed and that equilibrium 6 lies heavily on the left. In the presence of further ligands, such as phenylacetylene[22], $[Pt(PhC\equiv CH)(PPh_3)_2]$ may be formed in

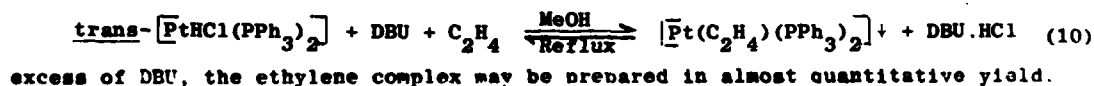$$trans-[PtHCl(PPh_3)_2] + DBU \rightleftharpoons [Pt(PPh_3)_2] + DBU.HCl \qquad (6)$$
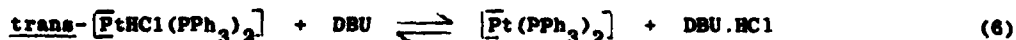
almost quantitative yield. We decided to investigate the possibility of preparing

$[Pt(C_2H_4)(PPh_3)_2]$ using this method with a view to removing the olefin by hydrogenation.

An authentic samples of $[Pt(C_2H_4)(PPh_3)_2]$ was prepared by a standard literature procedure [16] (equations 7-9) in 60% yield based on $K_2PtCl_4$. $[Pt(C_2H_4)(PPh_3)_2]$ could

$$K_2PtCl_4 \ + \ 4PPh_3 \ \xrightarrow[\text{EtOH}]{\text{NaBH}_4} \ [Pt(PPh_3)_4] \qquad\qquad (7)$$

$$[Pt(PPh_3)_4] \ + \ 2O_2 \ \xrightarrow{\text{C}_6\text{H}_6} \ [PtO_2(PPh_3)_2] \ + \ 2POPh_3 \qquad\qquad (8)$$

$$[PtO_2(PPh_3)_2] \ + \ C_2H_4 \ \xrightarrow[\text{EtOH}]{\text{NaBH}_4} \ [Pt(C_2H_4)(PPh_3)_2] \qquad\qquad (9)$$

also be prepared in 30% yield via the reaction shown in equation 10. Using a 5-fold

$$\text{trans-}[PtHCl(PPh_3)_2] \ + \ DBU \ + \ C_2H_4 \ \xrightarrow[\text{Reflux}]{\text{MeOH}} \ [Pt(C_2H_4)(PPh_3)_2]\downarrow \ + \ DBU.HCl \quad (10)$$

excess of DBU, the ethylene complex may be prepared in almost quantitative yield. ($[Pt(C_2H_4)(PPh_3)_2]$ requires: C,61.4%; H,4.6%; P,8.3%: found: C,60.9%;H,4.6%; P,8.8%.)

### 4.  Attempted D/H Exchange Experiments Using $[Pt(C_2H_4)(PPh_3)_2]$.

It was believed that using $[Pt(C_2H_4)(PPh_3)_2]$, a reaction, such as that shown in Scheme 2, might occur. The reaction was carried out using dry, degassed solvents.



Scheme 2

136.
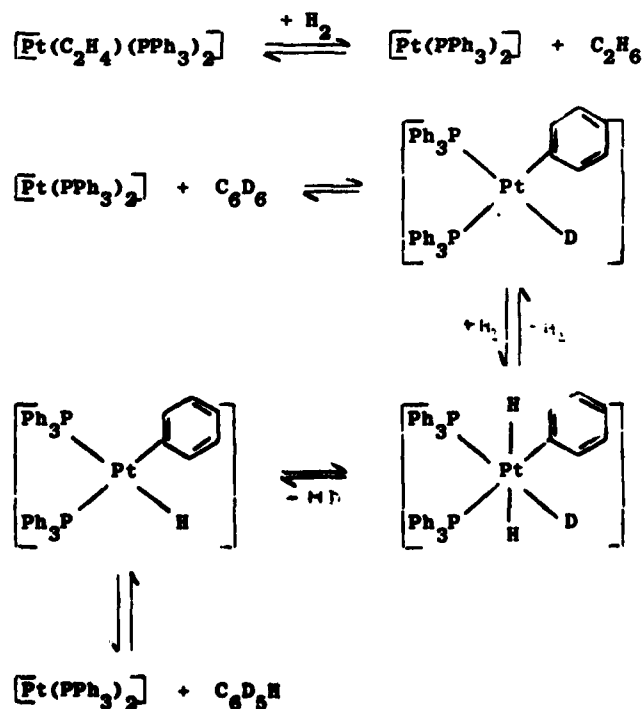
A solution of $[\overline{Pt}(C_2H_4)(PPh_3)_2]$ (0.25g, 0.33 mmol) in $d^6$-benzene (5ml) was stirred under an atmosphere of hydrogen. The solution turned a deep-red colour within a few minutes. From this solution a brown solid could be isolated. Stirring the reaction mixture for $6\frac{1}{2}$h at room temperature did not bring about any deuterium-hydrogen exhcnage in deuterobenzene.

The brown solid that could be isolated from the reaction mixture did not appear to be a hydride, but the ir and $^1$H nmr spectra indicated that the only ligand present was PPh$_3$. Therefore it is likely that a reaction such as that described in equation 11 had taken place. Cluster compounds of this type are known

$$n[\overline{Pt}(PPh_3)_2] \longrightarrow [\overline{Pt}_n(PPh_3)_{2n}] \tag{11}$$

from attempts to isolate $[Pt(PPh_3)_2]$ [17].

## 5. The Oxidative-Addition Reactions of $[Pt(C_2H_4)(PPh_3)_2]$

During the characterisation of $[Pt(C_2H_4)(PPh_3)_2]$ it was noticed that solutions of the complex in chloroform deposited a solid on standing at room temperature for a few days. On further examination it was found that a C-Cl bond of the solvent had oxidatively-added to the metal complex. Furthermore, a number of different products could be isolated depending on reaction conditions. Although oxidative-additions of halogenomethanes to $[Pt(L)(PPh_3)_2]$ where L = alkene or alkyne, have been reported,[18-20] reaction of the present complex with CHCl$_3$ under ambient conditions has not. In particular close examination of this system has led to rather unexpected results in that product formation depends on a number of factors such as the presence of oxygen, reaction time, temperature and concentration.

All the solvents used were dried and purified by distillation. Ethanol was removed from CHCl$_3$ before use. The following is a summary of the work carried out.

(1) If $[Pt(C_2H_4)(PPh_3)_2]$ is stirred in CHCl$_3$ (0.1mol dm$^{-3}$) under nitrogen for 7 days, a white precipitate, $\underline{I}$, forms from a bright yellow solution. This

solid, $\underset{\sim}{\text{I}}$, was shown by IR spectroscopy and microanalysis to be

cis-$\left[\text{PtCl}_2(\text{PPh}_3)_2\right]$ ($\left[\text{PtCl}_2(\text{PPh}_3)_2\right]$ requires: C,54.7%; H,3.8%; P,7.8%;

found: C,54.0%; H,3.9%; P,7.8%). This complex could also be prepared in the

presence of air but was only formed under these conditions when the concentration

exceeded 0.12mol.dm$^{-3}$ either in air or under $\text{N}_2$.

(ii) The addition of n-hexane or diethyl ether to the yellow solution obtained

in (i) caused the deposition of a yellow solid, $\underset{\sim}{\text{II}}$, which was shown by IR

spectroscopy and elemental analysis to be $\left[\text{Pt}(\text{CHCl}_2)\text{Cl}(\text{PPh}_3)_2\right]$.
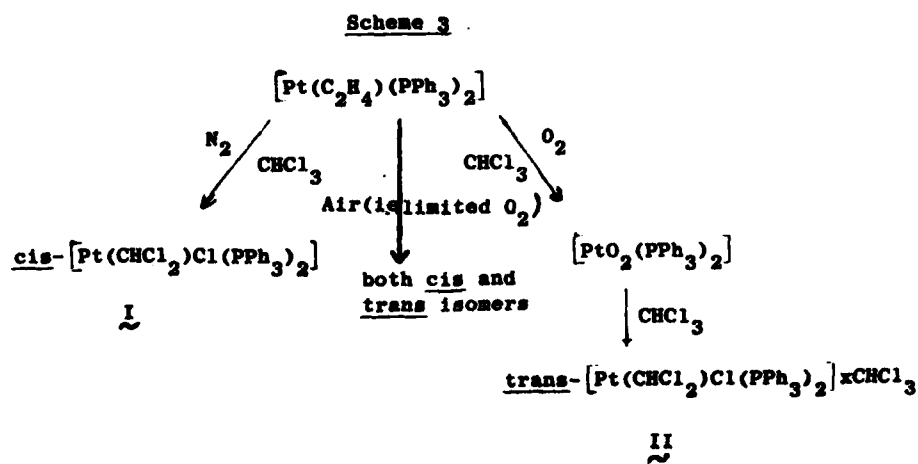
($\left[\text{Pt}(\text{CHCl}_2)\text{Cl}(\text{PPh}_3)_2\right]$ requires: C, 53,0%; H, 3.7%; P,7.4%; found: C,53.3%;

H,3.8%; P,7.6%). Further, in each experiment where chloroform was used, a

yellow solution was obtained from which this compound was isolated. The IR

spectrum of the product appeared to indicate that the cis-isomer is formed.

This complex is the only product if the reaction is carried out under nitrogen

at concentrations of less than 0.04mol.dm$^{-3}$.

(iii) If the reaction is carried out in air using a concentration of 0.04mol dm$^{-3}$

of $\left[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2\right]$ in $\text{CHCl}_3$, a yellow solid, $\underset{\sim}{\text{II}}$, precipitates from a yellow

solution within 1h. This can be recrystallised from $\text{CHCl}_3$. Both the crude

and recrystallised material have identical IR spectra and in particular show

a strong C-H stretching band due to free $\text{CHCl}_3$ at 2955cm$^{-1}$. Elemental

analysis shows that $\underset{\sim}{\text{II}}$ is probably the solvate $\left|\text{Pt}(\text{CHCl}_2)\text{Cl}(\text{PPh}_3)_2\right|.x\text{CHCl}_3$.

($\left[\text{Pt}(\text{CHCl}_2)\text{Cl}(\text{PPh}_3)_2\right].\text{CHCl}_3$ requires: C,47.6%; H,3.3%; P,6.5%; Cl,22.2%;

found: C, 45.8%; H,3.2%; P,6.8%; Cl,20.7%. The slight discrepancy in the

calculated and found figures is probably due to a non-integral number of

chloroform molecules associated with each molecule of complex). Prolonged

drying of this solvate removes the free chloroform, as indicated by the IR

spectrum and the sample analyses for $\left[\text{Pt}(\text{CHCl}_2)\text{Cl}(\text{PPh}_3)_2\right]$.

($\left[\text{Pt}(\text{CHCl}_2)\text{Cl}(\text{PPh}_3)_2\right]$ requires: C,53.0%; H,3.7%; P,7.4%; found: C,52.1%;

H,3.7%; P,7.6%). The IR spectrum also shows that $\underset{\sim}{\text{II}}$ is probably the

trans-isomer, this isomer being less soluble in the solvated form than

the unsolvated cis-isomer. Work up of the yellow solution after the precipitate II has been removed gives the complex III, cis-$[Pt(CHCl_2)Cl(PPh_3)_2]$.

(iv) If oxygen is bubbled through the solution during the reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with $CHCl_3$ then the known[21] compound $[PtO_2(PPh_3)_2]$ may be isolated, as shown by an intense band in the IR spectrum at $820 cm^{-1}$ due to $\nu(O-O)$ and comparison with an authentic sample. Further, if a suspension of $[Pt(C_2H_4)(PPh_3)_2]$ is stirred in acetonitrile in air for 23h then the sole product is $[PtO_2(PPh_3)_2] \cdot CH_3CN$ ($\nu(O-O)$ at $820 cm^{-1}$, $\nu(C\equiv N)$ at $2245 cm^{-1}$ cf. $\nu(C\equiv N)$ in $CH_3CN$ at $2245 cm^{-1}$; $[PtO_2(PPh_3)_2] \cdot CH_3CN$ requires: C,57.6%; H,4.2%; N,1.8%; P,7.8%; found: C,57.6%; H, 4.2%, N, 1.4%; P, 8.4%). Attempts to purify this compound by recrystallisation from $CHCl_3$ yielded a yellow solid which was identical to trans-$[Pt(CHCl_2)Cl(PPh_3)_2]xCHCl_3$. Thus the presence of oxygen affects the formation of products according to Scheme 3. The formation of cis-$[PtCl_2(PPh_3)_2]$ appears to occur from either I or II but is only generated at high concentrations. It also probably has its origins in a

## Scheme 3

$$[Pt(C_2H_4)(PPh_3)_2]$$

$N_2$ / $CHCl_3$     $CHCl_3$   $O_2$

Air(is limited $O_2$)

cis-$[Pt(CHCl_2)Cl(PPh_3)_2]$     both cis and trans isomers     $[PtO_2(PPh_3)_2]$

I

$CHCl_3$

trans-$[Pt(CHCl_2)Cl(PPh_3)_2]xCHCl_3$

II

photochemical process. Although the reactions were carried out in the dark, owing to the removal of the ethanol stabiliser from the chloroform prior to the experiments, such reactions are known to occur very readily if even the smallest amount of light is allowed to enter.[19,22] It has also been reported

that photolysis of $[PtO_2(PPh_3)_2]$ in $CHCl_3$ in the absence of air gave unidentified side-products assumed to arise from oxidative addition of the solvent,[23] although direct photolysis of $[Pt(C_2H_4)(PPh_3)_2]$ in $CHCl_3$ gives trans-$[PtHCl(PPh_3)_2]$.[24]

These results therefore indicate that the overall system is a very complex one. The product distribution is governed by the presence of oxygen and light, and also by the relative proportions of each. The concentration of the reactants are also important. A further complication to the system is that all reactions have to be carried out at room temperature owing to the ease of formation of the unreactive cluster compounds $[Pt_n(PPh_3)_{2n}]$.[25] It was therefore thought necessary to look for a simpler system.

6. The Preparation of $[Pt(PR_3)_3]$ and their reaction with $C_6HF_5$.

It has been shown[26] that the complex $[Pt\{P(C_2H_5)_3\}_3]$ is extremely reactive and readily reacts both with dihydrogen[26] and the C-H bond in pentafluorobenzene[27]. Since we have already published our work on the analogous, but less reactive compounds $[Pt(PR_3)_3]$, R = alkyl, p-alkylphenyl,[3,12] it was thought that the preparation and a study of the reactions of the complexes $[Pt(PR_3)_3]$ would not only provide systems capable of oxidatively adding activated C-H bonds, but would also give further insight into how the long alkyl chain phosphine ligands would modify their high reactivity. These species may also be handled at higher temperatures. $[Pt(PR_3)_3]$ were prepared by treating $[Pt(cod)_2]$[28] with the appropriate tertiary phosphine.

Due to the relative instability of $[Pt(cod)_2]$ when in solution the complex is usually stirred in suspension in n-hexane to which the reactant is added. On reacting $[Pt(cod)_2]$ with $P(n-C_4H_9)_3$ or $P(-\langle\rangle-C_9H_{19})_3$ in the mole ratio 1 : 3 in n-hexane deep orange solutions formed from which red-orange oils were isolated by evaporation of the solvent. These complexes showed extreme sensitivity to air inasmuch as attempts to obtain microanalyses and $^{31}P$ nmr spectra gave results indicative of the formation of oxidation products. The $^{31}P$ nmr gave no signal attributable to $[Pt(PR_3)_3]$, the intended product, but instead gave signals showing the presence of $[PtO_2(PR_3)_3]$, $OPR_3$ and some minor phosphine oxidation products.

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The reaction with $P(\underline{n}\text{-}C_4H_9)_3$ was further studied, again in the mole ratio of $[Pt(cod)_2]$ to ligand of $1:3$, in an attempt to prepare the tri-coordinate complex $[Pt\{P(\underline{n}\text{-}C_4H_9)_3\}_3]$. This species has been previously reported[6], the method of preparation being removal of one ligand from the tetrakis complex at $70^\circ C$ _in vacuo_. Also the complex $[Pt\{P(C_2H_5)_3\}_3]$ has been reported to react with $C_6HF_5$ to produce _trans_-$[PtH(C_6F_5)\{P(C_2H_5)_3\}_2]$[24] Thus to gain evidence for the existence of $[Pt\{P(\underline{n}\text{-}C_4H_9)_3\}_2]$ after reaction of $[Pt(cod)_2]$ with $P(\underline{n}\text{-}C_4H_9)_3$, the bright yellow oil which was isolated by solvent removal _in vacuo_ was further reacted with $C_6HF_5$ at room temperature for 36 hrs. Removal of excess $C_6HF_5$ _in vacuo_ left a yellow oil which gave an IR spectrum very similar to that reported[29] for _trans_-$[PtH(C_6F_5)\{P(C_2H_5)_3\}_2]$ with $\nu(\text{M-H})$ at $2035\,cm^{-1}$. It has not been possible to identify the hydride signal in the $^1H$ nmr spectrum on our Perkin Elmer R32 90 MHz spectrometer. This is not unexpected due to coupling of this single proton in a large molecule to both $^{195}Pt$ and $^{31}P$ which for _trans_-$[PtH(C_6F_5)\{P(\underline{n}\text{-}C_4H_9)_3\}_2]$ would give a possible pseudo-triplet of triplets.

The complex $[Pt(cod)_2]$ was reacted in a similar fashion in _n_-hexane suspension with the ligand $P(C_{16}H_{33})_3$ which on work-up yielded a sandy-brown solid. As the reactants were again used in a $1:3$ mole ratio the expected product was $[Pt\{P(C_{16}H_{33})_3\}_3]$, however, microanalysis did not support this formulation (Found C,70.9%; H,12.3%; P,4.1%; $C_{144}H_{297}P_3Pt$ requires C,74.7%; H,12.9%; P,4.0%) neither did reaction (attempted) with $C_6HF_5$. By analogy to the reaction of $C_6HF_5$ described above it would be expected for oxidative addition to occur if the tri-coordinate species was present. However, the sandy-brown product was recrystallised unchanged from $C_6HF_5$. It should be noted that it is not inconceivable that the steric bulk of the ligand might inhibit reactions at the metal centre. A possible product might be $[PtO_2\{P(C_{16}H_{33})_3\}_2]$ ($C_{96}H_{198}P_2O_2Pt$ requires C,70.2%; H,12.2%; P,3.8%) and it is difficult to assess this possibility by IR spectroscopy. Work is continuing to characterise these extremely sensitive complexes.

7. Reaction of $[Pt(cod)_2]$ with phosphites $P(OR)_3$

When three equivalents of $P(OC_4H_9)_3$ were reacted with one equivalent of $[Pt(cod)_2]$ as a stirred suspension then the solution became homogeneous within 30 min and assumed a deep yellow colour. Evaporation of the solvent in vacuo gave a mobile pale orange oil which partially solidified on extensive drying. This material gradually darkened to a deep red wax on standing even when kept under nitrogen at $-20^o$C. The microanalysis suggests that only platinum and ligand in the ratio 1:3 remain (Found C,46.3%; H,9.1%; P,10.3%; $C_{36}H_{81}O_9P_3Pt$ requires C,45.7%; H,8.6%; P,9.8%), however, the $^{31}P$ nmr of the wax indicates that the product is not solely the expected $[Pt\{P(OC_4H_9)_3\}_3]$. Unlike the corresponding phosphine complexes, no ligand exchange processes, which are fast on the nmr time-scale, are occurring. At ambient temperature two sharp resonances are seen at 192.6 and 127.7 ppm relative to $H_3PO_4$ as external standard and showing couplings of 6406 and 5395Hz respectively. The signal at 127.7 ppm can be attributed to $[Pt\{P(OC_4H_9)_3\}_4]$ from literature values[30] however, it is more difficult to assign a structure for the species giving rise to the other signal. One consideration is the species $[Pt\{P(OC_4H_9)_3\}_3]$ since the larger $^1J_{Pt-P}$ would be expected for a tri-coordinate Pt(0) species as compared to a tetrakis complex due to increase in s-character of the Pt-P bond in the tri-coordinate complex[31]. However, since the darkening of the wax may well be caused by the presence of colloidal platinum metal then the unknown complex may have the formula $[Pt\{P(OC_4H_9)_3\}_n]$ where n = 1 - 3. For n = 1 or 2 then cluster compounds may result.

When $[Pt(cod)_2]$ was reacted with two equivalents of $P(OC_4H_9)_3$ again a deep red-orange product was formed after work-up. Analysis of this oil was not consistent with a stoichiometry of one platinum atom to two ligands (Found C,44.8%; H,8.4%; $C_{24}H_{54}O_6P_2Pt$ requires C,41.4%; H,7.7%). This suggests the possibility of the ligand (cod) remaining coordinated to the platinum. The $^{31}P$ nmr spectrum of the oil again indicates that a mixture of products is formed. Signals are seen at 192.6 ppm ($^1J_{Pt-P}$ = 6411Hz) and a very closely spaced set of two signals at 161.1 and 160.3 ppm

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with associated larger couplings of 5483 and 5454Hz respectively. Thus, reaction in the mole ration 1 : 2 gives the same unknown product ($\delta$(P) = 192.6 ppm) obtained in the 1 ; 3 mole ratio reaction but also two other species very similar to each other but having a coupling indicative of a Pt(0)-P bond. These species may well contain (cod) as a ligand and account for the high C% value. Repeating this reaction gave the same products but in a differing ratio (assumed from relative intensities). It would seem that altering slightly rates of addition gives a different product distribution. This may well be caused by the $[Pt(cod)_2]$ being reacted in suspension and thus the ratio of $[Pt(cod)_2]$ to ligand in solution is not known.

To counter the above difficulties we have recently performed the 1 : 3 mole ratio reaction using a toluene solution of $[Pt(cod)_2]$ ensuring that $[Pt(cod)_2]$ is always in excess until reaction is complete. This method appears to yield a single product from subsequent studies with $C_6HF_5$.

8.  Reactions of the complexes formed between platinum(0) and $P(OC_4H_9)_3$.

In the work with phosphines described above, the reaction with $C_6HF_5$ was utilised in an attempt to identify products. When the major product was $[Pt\{P(OC_4H_9)_3\}_4]$ then no reaction was seen to occur with $C_6HF_5$ nor with methanol or benzonitrile. Reaction did occur with iodomethane, however, to give $[Pt(CH_3)I\{P(OC_4H_9)_3\}_2]$ which is in the process of full characterisation.

If, however, products which contained complexes other than the tetrakis compound were reacted with $C_6HF_5$ either at ambient temperature for 50 hrs or at 85°C for 4 hrs then reaction did occur. The orange-red oil isolated by solvent removal can be treated with methanol and cooled to precipitate any tetrakis complex present. The infrared spectrum of the remaining oil shows a strong band at 2040 cm$^{-1}$ attributable to $\nu$(M-H) together with evidence for the $C_6F_5$ moiety. The spectrum is similar to that of trans-$[PtH(C_6F_5)\{P(C_2H_5)_3\}_2]$[29] and is therefore probably the $\{P(OC_4H_9)_3\}$ analogue. Further characterisation is proceeding. Heating this material under vacuum (10$^{-2}$ mm Hg) for 4 hrs results in the loss of hydride and $C_6F_5$ as indicated by infrared spectroscopy. However, reaction of this residue with fresh $C_6HF_5$

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reforms the hydrido-complex again. In the course of these reactions the signal in the $^{31}$P nmr attributable to the tetrakis complex increases in intensity relative to other signals. It would thus seem that if the opportunity arises i.e. sufficient ligand at a particular phase of the raction, then the tetrakis complex will form and remain as an unreactive product.

The explanation of the above reactions is unlikely to be simple. If the tri-coordinate species is present it may react as in reaction 12 and if the

$$\left[Pt\{P(OC_4H_9)_3\}_3\right] + C_6HF_5 \rightleftharpoons \left[PtH(C_6F_5)\{P(OC_4H_9)_3\}_2\right] + P(OC_4H_9)_3 \qquad (12)$$
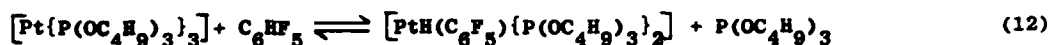
equilibrium shown in equation 13 lies to the right this would explain the increase in the amount of the tetrakis complex.

$$\left[Pt\{P(OC_4H_9)_3\}_3\right] + P(OC_4H_9)_3 \rightleftharpoons \left[Pt\{P(OC_4H_9)_3\}_4\right] \qquad (13)$$

However we must still account for the reaction of $\left[PtH(C_6F_5)\{P(OC_4H_9)_3\}_2\right]$ under heating and vacuum where $C_6F_5$ and H are lost. If the excess phosphite has been taken up to give the tetrakis complex then only "$Pt\{P(OC_4H_9)_3\}_2$" remains. A possible answer is that a small cluster complex forms which can react with $C_6HF_5$ to reverse the reaction.

Elucidation of the mechanisms of the reactions described above requires a study of the $^{31}$P nmr of reactants and products many of which are currently with our spectroscopist.


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# Chapter 8

## Summary

A series of tertiary phosphines and tertiary phosphine oxides containing long alkyl chains have been synthesised. As expected they are very soluble in non-polar solvents, particularly hydrocarbons. As a consequence it is difficult to separate these compounds from intermediates and by-products formed during their synthesis. Accordingly it is necessary to purify all the reactants and to use reactions that give a minimum of side products. The same remarks apply to the synthesis of the transition metal complexes of these ligands.

The transition metal complexes of the tertiary phosphine ligands have been prepared with rhodium(I), palladium(0), palladium(II), platinum(0) and platinum(II). All are very soluble in non-polar organic solvents. This extreme solubility modifies the catalytic properties of these complexes in homogeneous solution, as demonstrated by the enhanced ratio of normal:branched aldehyde formed in the hydroformylation of 1-hexene in the presence of $[RhCl(CO)L_2]$ when para-alkyl groups are present on the triarylphosphine L. The value of extreme solubility on the catalytic properties of the resulting complexes is particularly well demonstrated by the ability of the platinum(II) complexes $[PtL_2Cl_2]$ together with tin(II) chloride to promote the partial hydrogenation of the polyolefins methyl linoleate and methyl linolenate to the corresponding monoolefins with high selectivity. The long alkyl chains enable this reaction to be performed in the absence of added solvent, and this results in the platinum(II) complexes being particularly active and selective catalysts. Undoubtedly many more catalytic reactions will be developed in which the unique and extreme solubility properties of long alkyl chain tertiary phosphine complexes will be found to be very advantageous.

The presence of long alkyl chains on the tertiary phosphines enable them to promote the ability of their low valent transition metal complexes such as those of rhodium(I) and platinum(0) to undergo oxidative-addition. A detailed study of the reaction of alkyl halides with $[RhX(CO)L_2]$, X = halide,

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L = tertiary phosphine, has not only led to a fuller understanding of the reaction mechanism, but in addition has suggested that this reaction may be exploited as a means of promoting the decontamination of mustard. The rhodium complexes can either be dissolved in paints or polymers, using their extreme solubility in non-polar solvents or may be linked to polymers and cloth-like materials by $\gamma$-radiation grafting the tertiary phosphine ligands on to the polymers or cloth. We propose to extend our initial observations in this area.

Finally we have shown that zerovalent platinum complexes containing tertiary phosphine ligands can readily react with C-H bonds as in $C_6HF_5$ to cleave the C-H bond and coordinate the two fragments. We propose to investigate this further as it provides a very exciting route for converting hydrocarbons directly into platinum(II)-carbon complexes, which are known to undergo a wide range of reactions.

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