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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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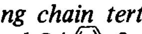
The long chain tertiary phosphine ligands ($P(C_nH_{2n+1})_3$ *and*  *have been used to prepare the following series of platinum, palladium and rhodium complexes:* cis-$[PtL_2Cl_2]$, trans-$[PdL_2Cl_2]$, trans-$[PtL_2HCl]$ *(L = trialkylphosphine only),* $[PtL_4]$ *and* trans-$[RhL_2Cl(CO)]$. *The complexes 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-$[PdL_2Cl_2]$ *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* $[Pd\{P(C_nH_{2n+1})_2C_nH_{2n}\}Cl]_2$ *which differ in the sizes of their Pd–P–C rings together with some unmetallated chloride bridged dimer* $[Pd\{P(C_nH_{2n+1})_3\}Cl_2]_2$.

Introduction

We have recently described the preparation of two series of tertiary phosphines, trialkylphosphines, $P(C_nH_{2n+1})_3$ where n = 10–19 inclusive [1] and tris(*p*-alkylaryl)phosphines $P(C_6H_4C_mH_{2m+1})_3$ 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. $[Rh_2Cl_2(CO)_4]$ 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 $RhCl_3 \cdot 3H_2O$ 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-$[PtL_2Cl_2]$

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-$[PdL_2Cl_2]$

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 $[PdL_2Cl_2]$. The proportion of the dark red waxy material increased with increasing phosphine alkyl chain length to the extent that virtually no $[PdL_2Cl_2]$ was formed with phosphines that have fifteen or more carbon atoms in their chains. Physical spectroscopic and analytical data for $[PdL_2Cl_2]$ are given in Tables III and V and for the dark red waxy materials in Table IV.

trans-$[Pt(PR_3)_2HCl]$

Trans-$[Pt(PR_3)_2HCl]$ R = alkyl were prepared by hydrazine hydrate reduction of the corresponding *cis*-$[Pt(PR_3)_2Cl_2]$ 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-$[RhL_2Cl(CO)]$

Trans-$[RhL_2Cl(CO)]$ complexes were prepared from $[Rh_2Cl_2(CO)_4]$ 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 $(A_t - A_\infty)$ 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).

$$PtL_4 \underset{+L,\,k_{-1}}{\overset{-L,\,k_1}{\rightleftharpoons}} PtL_3 \underset{+L,\,k_{-2}}{\overset{-L,\,k_2}{\rightleftharpoons}} PtL_2 \qquad (1)$$

The first stage involves a first order reaction opposed by a second order reaction (2),

$$PtL_4 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PtL_3 + L \qquad (2)$$

for which the integrated rate equation is [12]:

$$\ln\left\{\frac{C_o^2 - C_eC}{(C - C_e)C_o}\right\} = k_1^{obs}\left\{\frac{C_o + C_e}{C_o - Ce}\right\} t \qquad (3)$$

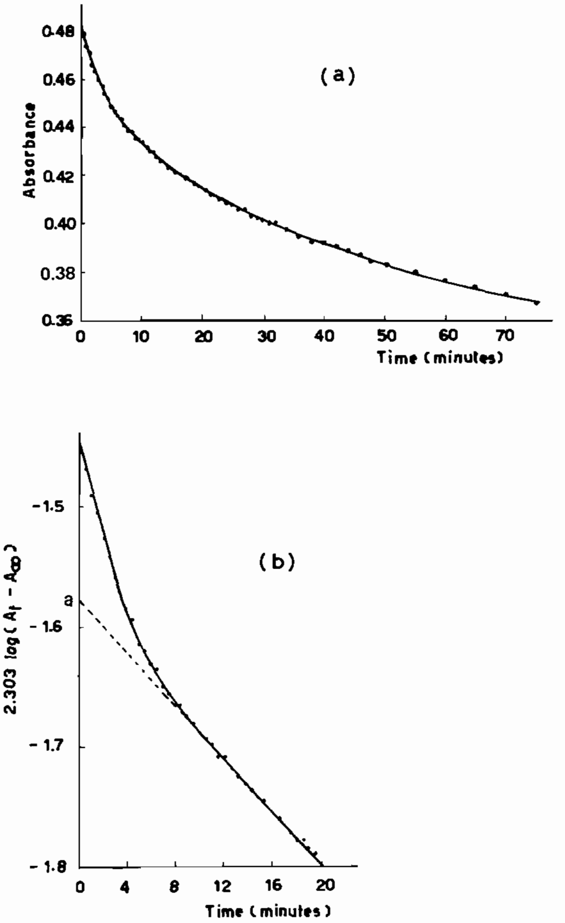


Fig. 1. The dissociation of a 4 × 10^{-4} mol l^{-1} solution of $[\mathrm{Pt}\{\mathrm{P}(C_6H_4\text{-}CH_3)_3\}_4]$ in benzene at 25 °C. (a) Plot of absorbance against time. (b) Plot of 2.303 $\log(A_t - A_\infty)$ against time.

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 × 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 ϵ 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:

$$\left\{\frac{B}{\sqrt{(B^2C_o'^2 + 6BC_o' + 1)}}\right\} \ln\left\{\frac{\frac{1}{2B}\sqrt{(1 + 6BC_o' + B^2C_o'^2)} + C' - (1 + 3BC_o')/2B}{\frac{1}{2B}\sqrt{(1 + 6BC_o' + B^2C_o'^2)} - C' + (1 + 3BC_o')/2B}\right\} = Bk_2^{obs}t + \text{const.} \qquad (6)$$

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. ^1H 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 $[Pt\{P(C_nH_{2n+1})_3\}_2X_2]$.

$P(C_nH_{2n+1})_3$	X	Configuration	Appearance	M. pt. (°C)	Infrared[a] $\nu(Pt-X)$ (cm^{-1})	^{31}P nmr Chemical shift (ppm)[b]	^{31}P nmr J_{Pt-P} (Hz)	Analytical Data Found (Calculated) C	H	X	P
$P(C_4H_9)_3$	Cl	*cis*	White prisms	142	305, 283	+4.9	3518	42.0(43.0)	7.8(8.1)	11.1(10.6)	–
$P(C_8H_{17})_3$	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			64.5(65.2)	11.2(11.4)	4.7(4.9)	–
	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)
$P(C_{14}H_{29})_3$	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			68.3(70.2)	11.9(12.1)	3.9(3.8)	–
	I	*trans*	Yellow crystalline solid	60–62	c			61.7(63.9)	10.9(11.0)	13.1(12.5)	4.1(3.1)

[a] Recorded as nujol mulls. [b] Chemical shifts in $CDCl_3$ measured relative to TMP as external standard. [c] $\nu(M-X)$ for all iodide complexes are assumed to be <200 cm^{-1}.

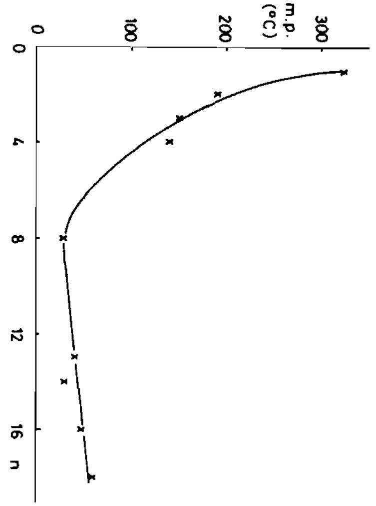


Fig. 2. The effect of chain length on the melting point of *cis*-$[Pt\{P(C_nH_{2n+1})_3\}_2Cl_2]$.

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

$$[M(COD)Cl_2] + 2PR_3 \xrightarrow[\substack{(M = Pd, Pt;\\ R = alkyl\ or\ aryl)}]{} [M(PR_3)_2Cl_2] + COD \qquad (8)$$

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

$$[Rh_2Cl_2(CO)_4] + 4PR_3 \xrightarrow[(R = alkyl\ or\ aryl)]{} 2trans\text{-}[Rh(PR_3)_2Cl(CO)] + 2CO \qquad (10)$$

$$[Pt(PR_3)_2Cl_2] + 2N_2H_4 \xrightarrow[(R = alkyl)]{EtOH/CHCl_3} trans\text{-}[Pt(PR_3)_2HCl] + NH_4Cl + \uparrow N_2 + NH_3 \qquad (11)$$

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 (ν_{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. ^{31}P nmr spectra involve a triplet with $^{195}Pt-^{31}P$ 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]. ^{31}P 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 ($^{195}Pt-^{31}P$ 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 ^{31}P nmr data

TABLE II. Physical, Spectroscopic and Analytical Data for cis-$[Pt\{P(C_6H_4R)_3\}_2X_2]$

R	X	Appearance	M. pt. (°C)	Infrared[a] ν(Pt–Cl) (cm^{-1})	^{31}P nmr[b] δ (ppm)	^{31}P nmr[b] J_{Pt-P} (Hz)	Analytical Data Found (Calculated) C	H	X	P
C_2H_5	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)	–
C_3H_7	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)
C_4H_9	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)	4.7(4.7)
C_5H_{11}	Cl	Yellow hard wax	–	295, 320	−9.3	3694	63.5(65.4)	7.2(7.5)	6.2(5.9)	4.9(5.1)
C_9H_{19}	Cl	Yellow oil	–	295, 320	–	–	–	–	–	–

[a] Recorded as nujol mulls. [b] Chemical shifts measured in $CDCl_3$ relative to TMP as external standard. [c] ν(M–X) for all bromide and iodide complexes are assumed to be <200 cm^{-1}.

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]. ^1H 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_nH_{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_nH_{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:

$$[Pd(COD)Cl_2] + P(C_nH_{2n+1})_3 \rightarrow$$

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

$$+ \text{ dark red or brown complex} \qquad (12)$$

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_nH_{2n+1})$_3$}$_2$$Cl_2$] were either oils or crystalline solids whose microanalyses were consistent with their proposed formulae (Table III). On heating they decomposed rather than melted. In the palladium–chlorine stretching region of the infrared spectrum they showed a single band at 355 cm^{-1} (*cf.* *trans*-[Pd(P_nBu_3)$_2$$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]. ^1H 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_nH_{2n+1})$_3$}Cl_2]$_2$, *I*, (*cf.* [Pd(P^nPr_3)-Cl_2]$_2$ has $\nu_{Pd–Cl}$ at 356 (terminal Cl), 299 (bridging

TABLE III. Physical, Spectroscopic and Analytical Data for *trans*-[Pd{P(C_nH_{2n+1})$_3$}$_2$$Cl_2$].

P(C_nH_{2n+1})$_3$	Appearance	M. pt. (°C)	Infrared ν(Pd–Cl) (cm^{-1})	^{31}P nmr chemical shift[b] δ (ppm)	Analytical Data Found (calculated)			
					C	H	X	P
P(C_4H_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_8H_{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($C_{14}H_{29}$)$_3$	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.

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

Phosphine	Appearance	Infrared (cm^{-1})^{a}	^{31}P nmr δ (ppm)^{b}	Analytical Data Found				Calculated Analyses			
				C	H	Cl	P	C	H	Cl	P
$P(C_{13}H_{27})_3$	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 $[Pd\{P(C_{13}H_{27})_3\}_2Cl_2]$			
								69.9	12.2	5.3	
								(ii) Dimeric $[Pd\{P(C_{13}H_{27})_3\}Cl_2]_2$			
								61.8	10.8	9.3	
								(iii) *o*-Metallated dimer $[Pd\{P(C_{13}H_{27})_2(C_{13}H_{26})\}Cl]_2$			
								64.9	11.2	4.9	
$P(C_{16}H_{33})_3$	Dark brown solid	250–300 br str^{c}		64.6	11.5	3.7	4.8	(i) Monomeric $[Pd\{P(C_{16}H_{33})_3\}_2Cl_2]$			
								72.4	12.5	4.4	3.9
								(ii) Dimeric $[Pd\{P(C_{16}H_{33})_3\}Cl_2]_2$			
								65.2	11.3	8.0	3.5
								(iii) *o*-Metallated dimer $[Pd\{P(C_{16}H_{33})_2(C_{16}H_{32})\}Cl]_2$			
								68.0	11.6	4.2	3.6

^{a}Bands in the region 250–360 cm^{-1} in spectra recorded as nujol mulls. ^{b}Chemical shift in $CDCl_3$ solution measured relative to TMP as an external standard. ^{c}A broad band in which it was not possible to identify individual bands.

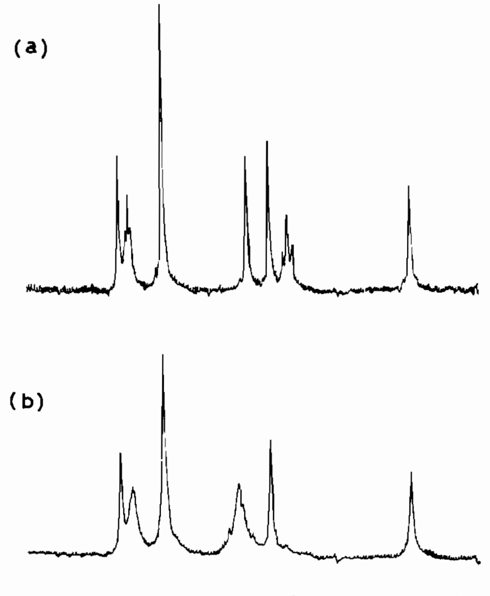
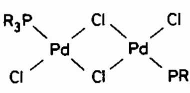
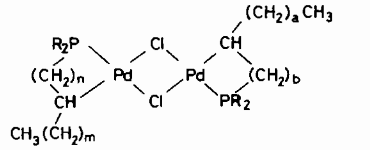


Fig. 3. ^{13}C nmr spectra of (a) *trans*-$[Pd\{P(C_8H_{17})_3\}_2Cl_2]$ and (b) *cis*-$[Pt\{P(C_8H_{17})_3\}_2Cl_2]$ in $CDCl_3$ solution.

Cl *trans* to Cl) and 253 cm^{-1} (bridging Cl *trans* to P^nPr_3)) [22]. The dark colours are consistent with structure *I* since $[Pd(PPr_3)Cl_2]_2$ is deep orange [23]. However *I* does not appear to be the sole dark product formed by reaction 12



I



II

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]. ^{1}H 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 ^{31}P nmr spectrum of the product containing $P(C_{13}H_{27})_3$ shows a single absorption at −3 ppm downfield from TMP which is significantly different to the −7.4 ppm shift observed in *trans*-$[Pd\{P(C_{13}H_{27})_3\}_2Cl_2]$. The presence of a single band argues

TABLE V. Physical, Spectroscopic and Analytical Data for $trans$-$[\mathrm{Pd}\{\mathrm{P}(\mathrm{C_6H_4}\text{-}\mathrm{R})_3\}_2\mathrm{X}_2]$

R	X	Appearance	M. pt. (°C)	Infrared ν(Pd–Cl) ($\mathrm{cm^{-1}}$)[a]	^{31}P nmr δ (ppm)[b]	Analytical Data Found (Calculated) C	H	X	P
C_2H_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)	5.2(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_9H_{19}	Cl	Dark oil	–	365	−18.6	74.4(74.1)	9.5(9.5)	4.7(4.9)	4.8(5.3)

[a] Recorded as nujol mulls. [b] Chemical shifts measured in $CDCl_3$ relative to TMP as external standard. [c] ν(M–X) for all bromide and iodide complexes are assumed to be <200 $\mathrm{cm^{-1}}$.

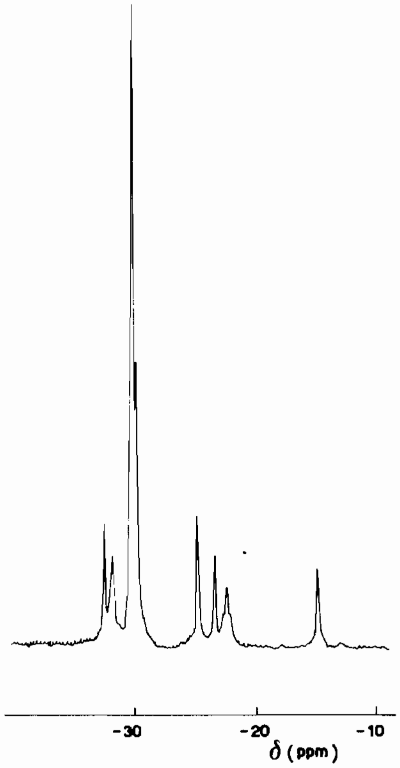


Fig. 4. ^{13}C nmr spectrum of $trans$-$[\mathrm{Pd}\{\mathrm{P(C_{13}H_{27})_3}\}_2\mathrm{Cl_2}]$ in $CDCl_3$ solution.

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

^{13}C 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 simpler complexes. The ^{13}C nmr spectra of $[\mathrm{M(PR_3)Cl_2}]_2$, M = Pd, Pt, R = Et, Pr, ^{n}Bu and $[\mathrm{M(P^nBu^t_2Bu)_2Cl_2}]$ have been described previously [26, 27]. We recorded the spectra of $[\mathrm{M\{P(C_8H_{17})_3\}_2Cl_2}]$ (Fig. 3) and $trans$-$[\mathrm{Pd\{P(C_{13}H_{27})_3\}_2Cl_2}]$ (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 ^{31}P–^{13}C coupling is much larger for odd than even numbered carbon atoms. When the ^{31}P–^{31}P 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 ^{31}P–^{31}P coupling is much less only a doublet is observed. The ^{13}C 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(C₆H₄C_mH_{2m+1})₃}X₂]*

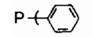
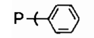
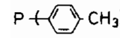
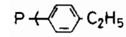
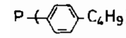
Trans-$[Pd\{P(C_6H_4C_mH_{2m+1})_3\}_2X_2]$ were prepared by reaction 8. Microanalytical results (Table V) were in good agreement with the proposed formulae. For m = 2–5 the products were crystalline, more crystalline and with higher melting (decomposition) points than their platinum analogues. This 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*-$[Pd\{P(C_8H_{17})_3\}_2Cl_2]$ 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 ν_{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. ^1H 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]		^1H NMR[b]			^{31}P NMR[c]		Analytical Data Found (Calculated)		
			$\nu(M-Cl)$ (cm^{-1})	$\nu(M-H)$ (cm^{-1})	δ (ppm)	J_{P-H} (Hz)	J_{Pt-H} (Hz)	δ (ppm)	J_{Pt-P} (Hz)	C	H	Cl
$P(C_{13}H_{27})_3$	Cream crystalline solid	40	283	2170	−16.5	15	1270	−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			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
	3	Bright yellow crystalline		65.0(66.1)	4.5(4.6)	9.7(9.5)
	4	Pale yellow crystalline solid	b	67.8(69.5)	4.9(4.9)	9.8(10.0)
	4	Yellow crystalline solid	−26.3	70.1(71.4)	6.1(6.0)	8.2(8.8)
	4	Yellow crystalline solid	−26.4	75.1(73.0)	6.9(6.9)	8.7(7.9)
	4	Red wax				
$P(C_8H_{17})_4$	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_6D_6 solution relative to TMP as an external standard. ^{b}Insoluble in C_6D_6 at 25 °C.

Trans-[Pt{P(C_nH_{2n+1})$_3$}$_2$HCl]

Trans-[Pt{P(C_nH_{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_nH_{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], ν_{Pt-H} = 2183 cm^{-1}, ν_{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 $J_{^{195}Pt-^1H}$ = 1270–1316 Hz and $J_{^{31}P-^1H}$ = 15 Hz (*cf. trans*-[Pt(PEt$_3$)$_2$HCl], ^{1}H chemical shift = −16.9 ppm, $J_{^{195}Pt-^1H}$ = 1276 Hz and $J_{^{31}P-^1H}$ = 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_nH_{2n+1})$_3$ or P($C_6H_4C_mH_{2m+1}$)$_3$

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_8H_{17})$_3$}$_4$] was a yellow viscous oil, and the attempted preparation of Pt{P($C_6H_4C_4H_9$)$_3$}$_4$] 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_6H_4Me)$_3$ and P(C_6H_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.

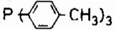
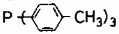
When the [PtL$_4$] complexes were dissolved in benzene solution all but that with L = P($C_6H_4C_4H_9$)$_3$ gave yellow solutions with an absorbance peak at about 330 nm and a shoulder at 360 nm. The absorbance decreased with time; for [Pt(PPh$_3$)$_4$] there was an initial induction period but for all 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($C_{16}H_{33}$)$_3$ $\gg$ PPh$_3$ >  and for loss of the second phosphine k_2^{obs} (reaction 1) are in the order  > P($C_{16}H_{33}$)$_3$ $\geqslant$ 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 for *trans*-[Rh{P(C_nH_{2n+1})$_3$}$_2$Cl(CO)].

P(C_nH_{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_4H_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_8H_{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($C_{18}H_{37}$)$_3$	Cream-brown crystalline solid	56(dec)	310	1940	–13.1	115	73.2(74.8)	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_2Cl(CO)] where L = P(C_nH_{2n+1})$_3$ and P($C_6H_4C_mH_{2m+1}$)$_3$*

Trans-[RhL_2Cl(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-$[\text{Rh}\{\text{P}(\text{C}_6\text{H}_4\text{R})_3\}_2\text{X}(\text{CO})]$

R	X	Appearance	M. pt. (°C)	Infrared[a]		^{31}P NMR[b]		Analytical Data Found (Calculated)			
				ν(M–X)	ν(C=O) (cm^{-1})	δ (ppm)	J_{Rh-P} (Hz)	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)	c	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	c	1970			68.3(67.3)	7.3(7.5)	7.5(7.3)	5.8(5.8)
	I	Yellow crystalline solid	118–120(dec)	c	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	–	c	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_9H_{19}	Cl	Dark oil	–	310	1975	−23.9	126				

[a] Infrared spectra recorded as nujol mulls. [b] Chemical shifts were measured in deuterochloroform solution relative to TMP as an external standard. [c] ν(M–X) for all bromide and iodide complexes are assumed to be <200 cm^{-1}.

TABLE X. Rates of Dissociation of 4×10^{-4} mol l^{-1} Solutions of $[\text{PtL}_4]$ 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	$1.8(5) \times 10^{-3}$	9.5×10^{-5}	1.5×10^{-3}	3.5×10^{-5}
PPh_3[b]	1.4×10^{-3}	1.2×10^{-4}	1.1×10^{-3}	4.0×10^{-5}
$\text{P}(\text{C}_6\text{H}_4\text{CH}_3)_3$	6.2×10^{-4}	1.8×10^{-4}	3.5×10^{-4}	6.7×10^{-5}
$P(C_{16}H_{33})_3$	c	8.9×10^{-5}	c	3.7×10^{-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. [c] Reaction too fast to be studied by the present method.

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*-$[Rh(PMe_3)_2Cl(CO)]$, $\nu_{C=O}$ = 1954, ν_{Rh-Cl} = 302 [32] and *trans*-$[Rh\{P(C_6H_4Me\text{-}p)_3\}Cl(CO)]$, $\nu_{C=O}$ = 1960, ν_{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].

Acknowledgements

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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'_o, 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'_o 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 $(C'_o - C'_e)$ and $(2C'_o - C'_e)$ respectively. At

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_{PtC_1}	J_{PtC_3}
$[PdCl_2\{P(Bu^n)_3\}]_2$[b]	−24.5	−26.6	−24.6	−14.1	–	–	–	–	–	–	–	–	–	–	–	–	32	<5	15	–	–
$[PtCl_2\{P(Bu^n)_3\}]_2$[b]	−22.8	−26.2	−24.6	−14.2	–	–	–	–	–	–	–	–	–	–	–	–	39	<5	15	39	20
trans-$[PdCl_2\{P(Octyl^n)_3\}_2]$	−21.6	−31.9	−31.3	−29.2		−24.1	−22.7	−14.1	–	–	–	–	–	–	–	–	25.4	<5	11.2	–	–
cis-$[PtCl_2\{P(Octyl^n)_3\}_2]$	−24.6	−31.9	−31.1	−29.2		−24.6	−22.7	−14.1	–	–	–	–	–	–	–	–	16.8	<5	6.7	26.8	Not observed
trans-$[PdCl_2\{P(C_{13}H_{27})_3\}_2]$	−21.7	−32.0	−31.3	−29.7					−29.4		−24.1	−22.7	−14.1	–	–	–	27.2	<5	~18	–	–
Red wax containing $P(C_{13}H_{27})_3$ from reaction 12	−21.6 (broad)	−31.9	−31.1 (broad)	−29.7					−29.4		−24.1 (broad)	−22.7	−14.1	–	–	–	c	c	c	–	–
Dark brown product containing $P(C_{16}H_{33})_3$ from reaction 12	Not observed	−32.0	Not observed	−29.7							−29.4		Not observed		−22.7	−14.1	c	c	c	–	–

[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.

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

$$k_2C'_e = k_{-2}(C'_o - C'_e)(2C'_o - C'_e) \qquad (14)$$

from which

$$k_{-2} = \frac{k_2C_e}{(C'_o - C'_e)(2C'_o - C'_e)} \qquad (15)$$

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

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

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

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

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

$$\therefore \int \frac{dC'}{C'^2 - \frac{C'}{B}(1 + 3C'_oB) + 2C'^2_o} = Bk_2t + \text{constant} \qquad (19)$$

$$\therefore \int \frac{dC'}{\left\{C' - \frac{(1 + 3BC'_e)}{2B}\right\}^2 - \left\{\frac{(1 + 6BC'_o + B^2C'^2_o)}{4B^2}\right\}} = Bk_2t + \text{constant} \qquad (20)$$

Integration of equation 20 yields:

$$\left\{\frac{1}{\frac{1}{B}\sqrt{(B^2C'^2_o + 6BC'_o + 1)}}\right\} \times \ln \left\{\frac{\frac{1}{2B}\sqrt{(1 + 6BC'_o + B^2C'^2_o)} + C' - \frac{1}{2B}(1 + 3BC'_o)}{\frac{1}{2B}\sqrt{(1 + 6BC'_o + B^2C'^2_o)} - C' - \frac{1}{2B}(1 + 3BC'_o)}\right\} = Bk_2t + \text{constant} \qquad (21)$$

Minor rearrangement of eqn. 21 yields eqn. 6.

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