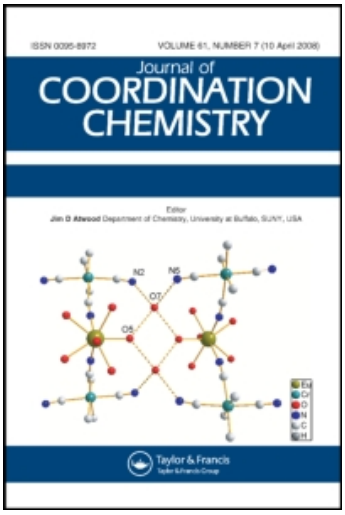

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SYNTHESIS, CHARACTERIZATION, AND COORDINATION CHEMISTRY OF LONG CHAIN *n*-ALKYLDIPHENYLPHOSPHINE LIGANDS

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SYNTHESIS, CHARACTERIZATION, AND COORDINATION CHEMISTRY OF LONG CHAIN *n*-ALKYLDIPHENYLPHOSPHINE LIGANDS

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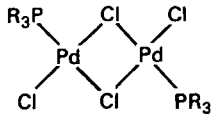
A series of alkyldiphenylphosphines with straight-chain alkyl groups, $PPh_2(C_nH_{2n+1})$, where $n = 5 - 20$, their oxides, $P\{O\}Ph_2(C_nH_{2n+1})$, and sulfides, $P\{S\}Ph_2(C_nH_{2n+1})$, where $n = 1 - 20$, have been prepared. The tertiary phosphines are air sensitive and the lower members of the series ($n < 9$) are colourless, viscous liquids whereas the higher homologues are white waxy solids. The phosphine oxides and sulfides are air stable white crystalline solids. The alkyldiphenylphosphines were reacted with $[PtCl_2(COD)]$ (COD = 1,5-cyclooctadiene) to form *cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ complexes. All of the compounds were characterized by $^{31}P\{^1H\}$ NMR spectroscopy. Mass spectrometry was further used to characterize all of the alkyldiphenylphosphines, their oxides, and sulfides, and *cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ complexes, where $n = 1$, 3, and 5.

Keywords: alkyldiphenylphosphine, synthesis, platinum, complexes, mass spectroscopy

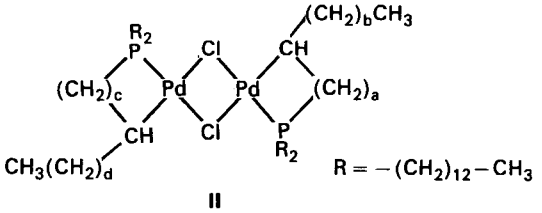
INTRODUCTION

There has been considerable interest in the reaction chemistry of the trialkylphosphine ligands, $P(C_nH_{2n+1})_3$, and the related *para*-substituted triarylphosphines, $P(p\text{–}C_6H_4\text{–}C_mH_{2m+1})_3$.[1–3] Metal complexes of these ligands with long straight-chain alkyl groups (*i.e.*, the higher homologues of these series) are readily soluble in hydrocarbon solvents[3], a useful property for many applications, including the preparation of potential homogeneous catalysts for the activation of alkanes[4] and the preparation of new reagents for the solvent extraction of metals. The major problem in developing significant reaction chemistry for such long-chain trialkyl and *para*-substituted triarylphosphine complexes is the ease with which metallation of the alkyl chains can occur in certain cases. Since many sites along the chain may be susceptible to metallation, such a process can potentially give rise to a large number of products. This situation has been encountered by Hartley and co-workers in their well-known studies of complexes containing long-chain trialkylphosphines.[3]

One of the systems studied by these workers was the reaction of $[PdCl_2(COD)]$ (COD = 1, 5-cyclooctadiene) with 2 equivalents of tris(tridecyl)phosphine in chloroform solution under a nitrogen atmosphere. In addition to the expected *trans*-$[PdCl_2\{P(n\text{–}C_{13}H_{27})_3\}_2]$ complex, a dark red solid was isolated which was believed to consist of the dimeric chloride bridged complex, $[Pd_2(\mu\text{–}Cl)_2Cl_2\{P(n\text{–}C_{13}H_{27})_3\}_2]$, **I**, and a mixture of different possible isomers of metallated products, **II**.



I



II

* Author for correspondence

This assignment was based on elemental analysis and IR spectroscopic data, where a number of peaks due to Pd–Cl stretching vibrations in the region 265 to 357 cm^{-1} were observed. These peaks were assigned to terminal Pd–Cl stretching vibrations of the dimeric complex, **I**, and the different metallated products, **II**. Since the latter are proposed to result from alkyl chain metallation leading to the formation of rings of different sizes, it was suggested that different degrees of ring strain would result in different Pd–Cl stretching vibrations. ^{31}P and ^{13}C NMR measurements could not confirm the presence of different metallated products and ^{1}H NMR spectroscopy merely confirmed the presence of phosphine ligands. Therefore structures could not be unambiguously assigned to these products and their exact composition remains unknown.

The *n*-alkyldiphenylphosphine ligands, $PPh_2C_nH_{2n+1}$, are well-known[5–21] for $n = 1$–6 and 16. Compounds with n = 1–4 and 6 are commercially available and some limited work has been reported[17,18,22] where n = 7, 8 and 12. The alkyldiphenylphosphines display a rich coordination chemistry.[23–29] It seemed likely that the higher homologues of this series would allow the preparation of metal complexes with enhanced solubility in non-polar media while maintaining resistance to chain metallation. The factors governing metallation of alkyl groups have been discussed extensively by Shaw.[30] Certainly it does not appear obvious that the trialkylphosphines prepared by Hartley and co-workers should be particularly susceptible to chain metallation based on the steric factors proposed by Shaw as being dominant in controlling cyclometallation reactions. The alkyldiphenylphosphines might be expected to resist chain metallation due to substitution of the *gem*-dialkyl grouping by *gem*-diphenyl and also due to the reduction in the number of chains available to participate in the metallation process.

We have prepared alkyldiphenylphosphine ligands, $PPh_2(C_nH_{2n+1})$, with varying length alkyl chains, ($n = 5$–20) with the intention of minimizing the probability of chain metallation in complexes of the higher homologues while maintaining the presence of a lipophilic hydrocarbon tail to ensure solubility in non-polar media. The corresponding crystalline sulfides and oxides were prepared as aids in characterization. Scattered reports of the alkyldiphenylphosphine oxides[16,17,31–45], $P\{O\}Ph_2(C_nH_{2n+1})$, where n = 1–12,14,16,18 and alkyldiphenylphosphine sulfides[16,17,32,37,46–53], $P\{S\}Ph_2(C_nH_{2n+1})$, where n = 1–4,6,8, and 12 have appeared. *Cis*-$[PtCl_2L_2]$ complexes have been prepared by the reaction of $[PtCl_2(COD)]$ (COD = 1,5-cyclooctadiene) with the ligand in chloroform solution. Preliminary studies show that these complexes exhibit interesting reaction chemistry. A comparison of the thermal stabilities of *cis*-$[PtCl_2(PPh_2C_{12}H_{25})_2]$ and *trans*-$[PdCl_2(PPh_2C_{12}H_{25})_2]$ shows that the palladium complex is more thermally sensitive than the platinum complex but that neither is subject to chain metallation. This is in striking contrast to palladium complexes of long-chain trialkylphosphine ligands where metallation appears to be exceptionally facile in certain cases.

RESULTS AND DISCUSSION

All the alkyldiphenylphosphines prepared were found to be quite air sensitive, necessitating the preparation of these compounds under inert atmospheres. These phosphines were prepared by reaction of alkyl bromides or alkyl tosylates with lithium diphenylphosphide in tetrahydrofuran solution. The alkyl tosylates were prepared by tosylation of the corresponding alcohols. Lithium diphenylphosphide was prepared *in situ* by the reaction of triphenylphosphine and excess lithium metal in tetrahydro-

furan, resulting in a deep red solution. The lower members of the series (where $n < 9$) are colourless, viscous liquids, whereas the higher homologues are white waxy solids. The alkyldiphenylphosphine oxides were prepared by reaction of the corresponding phosphines with a slight excess of hydrogen peroxide and the alkyldiphenylphosphine sulfides were prepared by refluxing the corresponding phosphines with elemental sulfur. The alkyldiphenylphosphine oxides and sulfides are air-stable white crystalline solids. The $[MCl_2(P\{C_nH_{2n+1}\}_3)_2]$ complexes where M = Pt, Pd were prepared by reaction of the alkyldiphenylphosphines with $[MCl_2(COD)]$. The alkyldiphenylphosphines, their oxides, sulfides, and platinum(II) derivatives, *cis*-$[PtCl_2L_2]$ are readily soluble in chlorinated solvents such as methylene chloride, chloroform, and carbon tetrachloride. The solubility of these compounds increases in non-polar solvents such as hexane, cyclohexane, and petroleum ether and decreases in polar solvents such as ethanol and methanol, with increase in the length of the alkyl chain.

All of the compounds have been characterized by $^{31}P\{^1H\}$ NMR spectroscopy. Table I gives the ^{31}P NMR chemical shifts of the alkyldiphenylphosphines, alkyldiphenylphosphine oxides, alkyldiphenylphosphine sulfides, and *cis*-dichlorobis-(alkyldiphenylphosphine)platinum(II) complexes for straight chain alkyl groups with 1 to 20 carbon atoms. Plots of the ^{31}P NMR chemical shifts of these compounds versus the length of the alkyl chains are shown in Figures 1–2. Changes in the chemical shifts of the phosphorus nuclei are quite marked on moving from methyl through ethyl to propyl substituents, whereas variation in the alkyl groups after *n*-butyl does not affect the ^{31}P NMR chemical shifts of these compounds. The phosphorus chemical shift differences for the first three alkyldiphenylphosphines have

TABLE I
$^{31}P\{^1H\}$ NMR Data for $PPh_2C_nH_{2n+1}$ and Derivatives

n	$PPh_2C_nH_{2n+1}$	$P\{O\}Ph_2C_nH_{2n+1}$	$P\{S\}Ph_2C_nH_{2n+1}$	*cis*-$[PtCl_2L_2]$ $L = PPh_2C_nH_{2n+1}$	
	δ(P), ppm[a]	δ(P), ppm[a]	δ(P), ppm[a]	δ(P), ppm[a]	^1J(Pt, P), Hz
1	−27.1 (28.1)[15,b]	30.1	35.8 (32.5)[48]	−1.0 (−1.2)[15,b]	3624
2	−11.4 (12.5)[15,b]	34.1 (35)[33]	45.3	9.6 (9.6)[15,b]	3623
3	−16.9 (17.6)[10,b]	32.4	42.5	7.8 (6.9)[15,b]	3650
4	−16.2 (17.1)[13,b]	32.7	42.8	7.2 (7.0)[15,b]	3653
5	−16.2	32.7	42.8	7.2	3650
6	−16.0	32.3	42.7 (42)[19]	7.2	3650
7	−16.0	32.6	42.7	7.2	3650
8	−16.0	32.6	42.7	7.1	3647
9	−16.1	32.7	42.8	7.1	3647
10	−15.9	32.5	42.8	7.1	3650
11	−16.0	32.9	42.7	7.1	3650
12	−16.2	32.7	43.1 (41.5)[53]	7.1	3650
13	−16.1	32.7	42.7	7.1	3650
14	−16.0	32.7	42.7	7.1	3650
15	−16.2	32.8	42.7	7.1	3650
16	−16.0	32.5	42.7	7.1	3650
17	−16.0	32.9	42.7	7.1	3653
18	−16.2	32.8	42.7	7.1	3650
19	−16.0	32.9	42.7	7.1	3650
20	−16.3	32.7	42.7	7.1	3647

[a]Chemical shifts are relative to external 85% H_3PO_4 with $CDCl_3$ as the solvent unless indicated otherwise, positive shifts representing deshielding. [b]Solvent: CD_2Cl_2. Literature reported values are given in the parentheses.

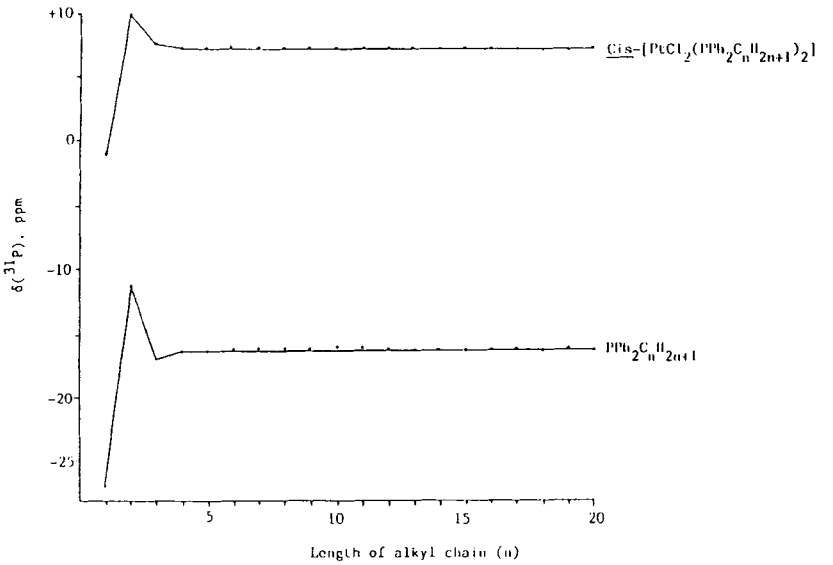


FIGURE 1 Plot of $\delta(^{31}P)$ ppm *vs* length of alkyl chain for *cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ and $PPh_2C_nH_{2n+1}$ showing the effect of alkyl chain length on the ^{31}P chemical shifts.

been explained by Grim, McFarlane, and Davidoff in their studies of group contributions to phosphorus-31 chemical shifts of tertiary phosphines, on the basis of the inductive and hyperconjugative effects of these alkyl groups.[10] Hyperconjugation of the α protons with phosphorus results in the following resonance structures.

$$R_2\ddot{P}CR_2H \leftrightarrow R_2\bar{\ddot{P}}{=}CR_2\overset{+}{H}$$

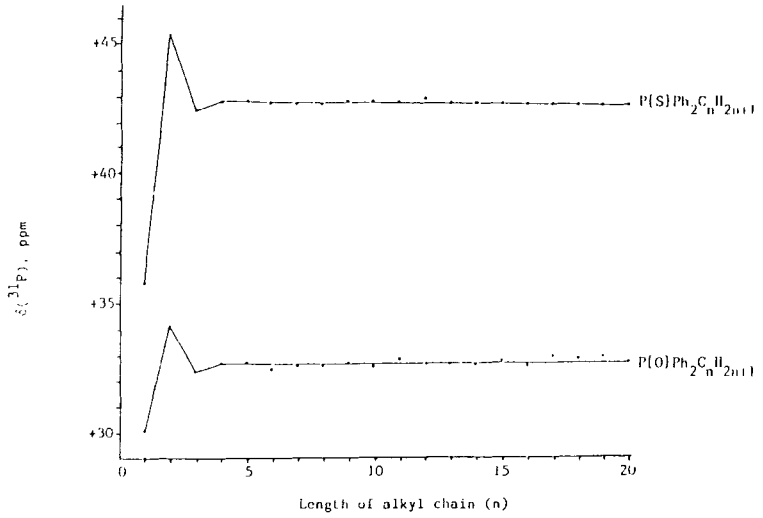


FIGURE 2 Plot of $\delta(^{31}P)$ ppm *vs* length of alkyl chain for $P\{O\}Ph_2C_nH_{2n+1}$ and $P\{S\}Ph_2C_nH_{2n+1}$ showing the effect of alkyl chain length on the ^{31}P chemical shifts.

Thus, PPh_2CH_3 will have the most shielded phosphorus nucleus, on the basis of hyperconjugative effects alone, as it has 3 α protons. When one hydrogen is replaced by a methyl group there is an increase in the inductive effect of the alkyl group, but the hyperconjugative effects are reduced. Table I shows that $PPh_2C_2H_5$ has the most deshielded phosphorus nucleus, whereas PPh_2CH_3 has the most shielded phosphorus nucleus in the series of alkyldiphenylphosphines, indicating that the hyperconjugative effect due to one hydrogen atom is much stronger than the inductive effect due to one methyl group. In moving from ethyl to propyl, inductive effects are responsible for the shielding of the phosphorus nucleus by 5 ppm. Further increases in the number of methylene groups ($n > 4$) does not affect the ^{31}P NMR chemical shifts of these compounds, as this does not change the inductive effects of the alkyl groups to any significant extent. The same arguments are valid for the alkyldiphenylphosphine oxides, sulfides, and *cis*-$[PtCl_2L_2]$ complexes.

The ^1H NMR spectroscopic data for the alkyldiphenylphosphines, $PPh_2(C_nH_{2n+1})$, their oxides, and sulfides measured at 90 MHz are given in Table II. The methyl protons in methyldiphenylphosphine couple with phosphorus with a coupling constant, $^2J(P, H)$ of 4 Hz, whereas in the case of ethyldiphenylphosphine the methyl group has a coupling constant $^3J(P, H)$ of 16 Hz. This is an example of three bond coupling being larger than two bond coupling. From the 90 MHz ^1H NMR spectrum we were unable to extract any coupling constant information, $^2J(P, H)$ for the methylene protons of the ethyl group in ethyldiphenylphosphine for direct comparison with $^3J(P, H)$ of its methyl protons. The methyl regions in the ^1H NMR spectra of these phosphines show well defined coupling whereas methylene signals are generally observed as multiplets or broad resonances. Phenyl protons are observed as multiplets in the characteristic aromatic region. The ^1H NMR spectra of all the alkyldiphenylphosphines with an alkyl chain longer than propyl are very similar and not particularly informative. The ^1H NMR spectra of the alkyldiphenylphosphine oxides and alkyldiphenylphosphine sulfides resemble those of the alkyldiphenylphosphines. At 400 MHz, in the case of ethyldiphenylphosphine sulfide the methylene protons exhibit a well defined doublet of quartets with a coupling constant $^2J(P, H)$ of 11 Hz, as compared to the coupling constant $^3J(P, H)$ of 20 Hz for the methyl protons.

The IR spectra of these compounds are entirely as expected and so only the IR spectra of octadecyldiphenylphosphine, its oxide and sulfide will be discussed as these are representative examples of their series. The characteristic band at $\nu = 1203\ cm^{-1}$ was observed due to the P=O stretching vibration in octadecyldiphenylphosphine oxide which is comparable to the reported[32] P=O stretching frequency of $\nu = 1293\ cm^{-1}$ for methyldiphenylphosphine oxide. In the case of octadecyldiphenylphosphine sulfide characteristic bands for P=S at $\nu = 619, 610\ cm^{-1}$ were observed comparable to the reported[50] P=S stretching frequencies of $\nu = 618, 609\ cm^{-1}$ for methyldiphenylphosphine sulfide. Other than these characteristic bands the IR spectra of octadecyldiphenylphosphine, octadecyldiphenylphosphine oxide and octadecyldiphenylphosphine sulfide were very similar.

We were able to obtain molecular ion peaks for all of the phosphines, phosphine oxides, phosphine sulfides, (Table III) and *cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ complexes, where n = 1,3, and 5 (Table IV) that we analyzed using mass spectrometry. As there seem to be no mass spectroscopic studies reported on alkyldiphenylphosphines, their sulfides, or *cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ complexes and only a single paper[38] on alkyldiphenylphosphine oxides with a limited range of straight-chain alkyl groups (methyl, ethyl, propyl and decyl), we take this opportunity to describe the mass spectra of these compounds in detail. The alkyl chain of the alkyldiphenylphosphine ligand fragments in a similar manner to the long chain trialkylphosphines studied by Hartley

TABLE II
^{1}H NMR Data for $PPh_2C_nH_{2n+1}$ and Derivatives

n	$PPh_2C_nH_{2n+1}$ $\delta(^1H)$, ppm[a]				$P\{O\}Ph_2C_nH_{2n+1}$ $\delta(^1H)$, ppm[a]				$P\{S\}Ph_2C_nH_{2n+1}$ $\delta(^1H)$, ppm[a]			
	$-P(C_6H_5)_2$	$-PCH_2-$	$-(CH_2)_n-$	$-CH_3$	$-P\{O\}(C_6H_5)_2$	$-P\{O\}CH_2-$	$-(CH_2)_n-$	$-CH_3$	$-P\{S\}(C_6H_5)$	$-P\{S\}CH_2-$	$-(CH_2)_n-$	$-CH_3$
1	7.18–7.48, m			1.56, d, $^2J(P, H)$ = 4 Hz	7.40–7.83, m			2.00, d, $^2J(P, H)$ = 13 Hz	7.41–7.94, m			2.26, d, $^2J(P, H)$ = 14 Hz
2	7.24–7.48, m	1.93–2.18, m		1.08, d of t, $^3J(P, H)$ = 16 Hz, $^3J(H, H)$ = 7 Hz	7.42–7.86, m	2.18–2.39, m		1.18, d of t, $^3J(P, H)$ = 17 Hz, $^3J(H, H)$ = 7 Hz	7.41–7.95, m	2.28–2.67, m		1.20, d of t, $^3J(P, H)$ = 20 Hz, $^3J(H, H)$ = 7 Hz
3	7.21–7.51, m	1.93–2.10, m	1.21–1.72, m	1.00, t, $^3J(H, H)$ = 7 Hz	7.42–7.86, m	2.11–2.40, m	1.46–1.80, m	1.01, t $^3J(H, H)$ = 7 Hz	7.36–7.95, m	2.20–2.58, m	1.48–1.85, m	1.00, t, $^3J(H, H)$ = 7 Hz
4–20	7.18–7.51, m	2.11–1.94, br	1.22–1.59, br	0.85–0.86, t, $^3J(H, H)$ = 7 Hz	7.35–7.84, m	2.24–2.30, br	1.22–1.74, br	0.87–0.88, t, $^3J(H, H)$ = 6 Hz	7.36–7.95, m	2.16–2.58, br	1.50–1.81, br	0.88–0.89, t, $^3J(H, H)$ = 7 Hz

[a] Spectra were obtained for $CDCl_3$ solutions using 1% tetramethylsilane as an internal standard.

and coworkers.[1] Once the alkyl chain is fragmented, the resulting PPh_2 group fragments in a fashion comparable to that reported for triphenylphosphine.[54] Mass spectra of $PPh_2(C_5H_{11})$, $P\{O\}Ph_2(C_5H_{11})$, $P\{S\}Ph_2(C_5H_{11})$, and cis-$[PtCl_2(PPh_2C_5H_{11})_2]$ (Figures 3–6) have been chosen as representative examples of their respective series and proposed fragmentation patterns are shown in schemes 1–4 respectively. The mass spectrum of $PPh_2(C_5H_{11})$ shows an intense peak for the molecular ion and other peaks due to the loss of CH_3, C_2H_5, C_3H_7, C_4H_9, and C_5H_{11} from the side chain. The base peak results from the loss of C_4H_9 from the parent ion. As previously reported by Hartley, we also observe an intense peak for the PPh_2H fragment, resulting from the loss of C_5H_{10} from the parent ion. The mass spectrum of PPh_3 shows a peak for the PPh_2 fragment, from cleavage of a phenyl group from phosphorus. The fragmentaton of PPh_2 observed by us is comparable to that previously reported. The fragmentation patterns observed in the mass spectra of the alkyldiphenylphosphine oxides are similar to the respective alkyldiphenylphosphines with increases in the mass units of each fragment by 16. Since the bond energy of P=O is greater than that of the P–C bond, the P=O moiety remains intact throughout much of the fragmention process. The fragmentation of the $P\{O\}Ph_2$ fragment is similar to that observed in the mass spectrum of $P\{O\}Ph_3$.[54] These results are also comparable to mass spectra of the alkyldiphenylphosphine oxides reported by Jelus and co-workers.[38] The mass spectra of the alkyldiphenylphosphine sulfides are similar to those of the oxides except in the case of the sulfides we were able to observe a low intensity peak due to loss of sulfur from the parent ion resulting in the alkyldiphenylphosphine ion. This can be explained on the basis of the lower bond energy of P=S by comparison to P=O. After the loss of the alkyl side chain, fragmentation of $P\{S\}PPh_2$ was found to be similar to that reported for $P\{S\}PPh_3$.[54] There are only a few reports published concerning the mass spectroscopic studies of platinum complexes[55–63] and none on long-chain tertiary phosphine complexes. The mass spectra of *cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ complexes, where n = 1,3, and 5 give molecular ions of reasonable intensities (Table IV). The isotopic distributions of naturally abundant platinum and chlorine result in different possible isotopomers, which are responsible for the characteristic isotopic patterns which are shown in Figure 7. The observed isotopic patterns in the mass spectra of *cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ complexes (Figure 6b) are of course further effected by the isotopic abundances of carbon and hydrogen. These isotopic patterns and m/e values were used in assigning platinum-containing fragments. Scheme 4 shows our suggested fragmentation pattern for *cis*-$[PtCl_2(PPh_2C_5H_{11})_2]$. In the fragmentation process Pt–Cl, Pt–P, and P–C bonds are broken. The ligand once detached from the metal center undergoes its own fragmentation similar to the fragmentation pattern of the free ligand as shown in scheme 1. Our attempts to obtain a mass spectrum of *trans*-$[PdCl_2(PPh_2C_{12}H_{25})_2]$ were unsuccessful because of the rapid decomposition of this complex under the mass spectroscopic conditions used to study the *cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ complexes (n = 1,3, and 5). This result is in agreement with our observations on the thermal stability of solutions of the platinum and palladium complexes of these long chain ligands (*vide infra*).

The reactions of the $PPh_2C_nH_{2n+1}$ ligands with $[PtCl_2(COD)]$ are of interest since it is known that the corresponding reactions of electronically similar tertiary phosphines with $[PtCl_2(COD)]$ are governed by the steric bulk of the ligands involved. Thus, small ligands (*e.g.*, PPh_2CH_3) produce *cis*-$[PtCl_2(PR_3)_2]$, larger ligands (*e.g.*, $P\{n\text{-}C_6H_{11}\}_3$) produce $[Pt_2(\mu\text{–}Cl)_2Cl_2(PR_3)_2]$ and/or *trans*-$[PtCl_2(PR_3)_2]$, and very large ligands (*e.g.*, $P\{\text{mesityl}\}_3$) do not react at all. We found that the isolated product from reactions of $PPh_2(C_nH_{2n+1})$, where $n = 1$–20, with $[PtCl_2(COD)]$ was the corresponding *cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ complex in every case. However, when the

TABLE III
Mass Spectroscopic Data for $PPh_2C_nH_{2n+1}$ and Derivatives.[a]

	$PPh_2C_nH_{2n+1}$, m/e			$P\{O\}Ph_2C_nH_{2n+1}$, m/e			$P\{S\}Ph_2C_nH_{2n+1}$, m/e		
n	M^+	Base Peak	Selected Peaks	M^+	Base Peak	Selected Peaks	M^+	Base Peak	Selected Peaks
1	200(100)	200	185(45), 183(71)	216(100)	216	201(78)	232(100)	232	217(30), 185(8), 183(2)
2	214(100)	214	186(25), 185(57), 183(86)	230(12)	201	229(11), 202(65)	246(48)	217	185(26), 183(24)
3	228(92))	199	200(14), 186(40), 185(26), 183(96)	224(38)	215	243(28), 216(42), 202(54), 201(91)	260(18)	217	185(23), 183(18)
4	242(53)	199	200(45), 186(8) 185(13), 183(45)	258(10)	215	216(64), 202(32), 201(48)	274(13)	217	185(35), 183(39)
5	256(55)	199	200(50), 186(38), 185(16), 183(57)	272(17)	215	216(70), 202(28), 201(30)	288(14)	217	185(20), 183(16)
6	270(81)	199	200(53), 186(53), 185(15), 183(51)	286(19)	215	216(93), 202(80), 201(70)	302(15)	217	185(18), 183(15)
7	284(84)	199	200(59), 186(91) 185(16), 183(48)	300(16)	215	216(80), 202(71), 201(57)	316(16)	217	185(24), 183(21)
8	298(57)	186	200(52), 199(88), 185(17), 183(48)	314(19)	215	216(78), 202(91), 201(61)	330(11)	217	185(17), 183(18)
9	312(51)	186	200(56), 199(90), 185(17), 183(44)	328(19)	215	216(84), 202(86), 201(59)	344(12)	217	185(18), 183(17)

10	326(59)	186	200(55), 199(80), 185(16), 183(41)	342(14)	215	216(85), 202(88), 201(45)	358(14)	217	185(20), 183(19)
11	340(43)	186	200(57), 199(82), 185(18), 183(39)	356(15)	215	216(80), 202(95), 201(75)	372(11)	217	185(10), 183(8)
12	354(24)	186	200(52), 199(70), 185(15), 183(30)	370(18)	202	216(87), 215(88), 201(47)	386(12)	217	185(13), 183(12)
13	368(38)	186	200(48), 199(62), 185(15), 183(30)	384(25)	202	216(93), 215(98), 201(67)	400(9)	217	185(14), 183(12)
14	382(25)	186	200(39), 199(50), 185(14), 183(36)	398(18)	202	216(88), 215(95), 201(60)	414(12)	217	185(15), 183(11)
15	396(20)	186	200(39), 199(60), 185(17), 183(30)	412(25)	202	216(92), 215(80), 201(38)	428(15)	217	185(10), 183(14)
16	410(23)	186	200(48), 199(59), 185(17), 183(28)	426(20)	202	216(94), 215(94), 201(40)	442(15)	217	185(14), 183(17)
17	424(26)	186	200(52), 199(74), 185(35), 183(65)	440(27)	202	216(91), 215(68) 201(34)	456(14)	217	185(13), 183(17)
18	438(16)	186	200(34), 199(38), 185(8), 183(18)	454(22)	202	216(90), 215(65), 201(31)	470(16)	217	185(10), 183(14)
19	452(20)	186	200(55), 199(60), 185(35), 183(65)	468(12)	202	216(92), 215(67), 201(34)	484(18)	217	185(17), 183(20)
20	466(13)	186	200(52), 199(55), 185(16), 183(20)	482(15)	202	216(93), 215(67), 201(35)	498(15)	217	185(14), 183(18)

[a] Relative abundances measured by peak height and normalized to a value of 100 units for the base peak are given in parentheses.

TABLE IV
Major Fragments in Mass Spectra of *Cis*-$[PtCl_2(PPh_2C_nH_{2n+1})_2]$ Complexes (n = 1, 3, and 5)

Cis-$[PtCl_2L_2]$ Complex	m/e	Relative Intensity[a], %	Assignment
$L = PPh_2CH_3$	664–672	15	M^+
	629–635	6	$[M-Cl]^+$
	594–598	12	$[M-2Cl]^+$
	394–398	9	$[M-2Cl-L]^+$
	377–384	5	$[M-2Cl-L-CH_3]^+$, $[M-2Cl-CH_3-2H]^+$
	313–320	6	$[M-2Cl-L-C_6H_5-2H]^+$ $[M-2Cl-L-C_6H_5-4H]^+$
	301–305	6	$[Pt-PC_6H_4]^+$
	235	31	$[PPh_2CH_3Cl]^+$
	215	100	$[PPh_2CH_3]^+$
	185	39	$[PPh_2]^+$
	183	63	$[PPh_2-2H]^+$
$L = PPh_2C_3H_7$	720–728	10	M^+
	685–691	4	$[M-Cl]^+$
	643–656	7	$[M-2Cl]^+$, $[M-Cl-C_3H_6]^+$
	599–611	7	$[M-2Cl-C_3H_7-2H]^+$, $[M-2Cl-C_3H_7]^+$
	561–570	6	$[M-2Cl-2C_3H_7]^+$, $[M-2Cl-2C_3H_7-2H]^+$, $[M-2Cl-C_3H_6-C_3H_7]^+$
	420–424	8	$[M-2Cl-L-2H]^+$
	377–381	7	$[M-2Cl-L-C_3H_7-2H]^+$
	301–305	16	$[Pt-PC_6H_4]^+$
	263	60	$[PPh_2C_3H_7Cl]^+$
	228	100	$[PPh_2C_3H_7]^+$
	199	82	$[PPh_2CH_2]^+$
	186	28	$[PPh_2H]^+$
	185	19	$[PPh_2]^+$
	183	75	$[PPh_2-2H]^+$
$L = PPh_2C_5H_{11}$	776–784	23	M^+
	741–747	5	$[M-Cl]^+$
	705–712	18	$[M-C_5H_{11}]^+$
	670–676	4	$[M-Cl-C_5H_{11}]^+$
	635–639	17	$[M-2Cl-C_5H_{11}]^+$
	599–605	2	$[M-Cl-2C_5H_{11}]^+$
	562–569	12	$[M-2Cl-2C_5H_{11}]^+$, $[M-2Cl-2C_5H_{11}-H]^+$, $[M-2Cl-C_5H_{11}-C_5H_{10}]^+$
	484–490	2	$[M-Cl-L]^+$
	442–451	24	$[M-Cl-2C_5H_{11}-2C_6H_5]^+$, $[M-Cl-2C_5H_{11}-2C_6H_5-2H]^+$
	376–383	10	$[Pt(PPh_2)]^+$, $[Pt(PPh_2)-2H]^+$
	333	5	$[PPh_3C_5H_{11}]^+$
	301–305	11	$[Pt-PC_6H_4]^+$
	291	60	$[PPh_2C_5H_{11}Cl]^+$
	256	54	$[PPh_2C_5H_{11}]^+$
	199	100	$[PPh_2CH_2]^+$
	186	42	$[PPh_2H]^+$
	185	20	$[PPh_2]^+$
	183	67	$[PPh_2-2H]^+$

[a] Relative intensities (%) are measured by peak height and normalized to a value of 100 units for the base peak. Height of the most intense peak was used in the case of the observed m/e ranges where mixtures of isotopomers are present.

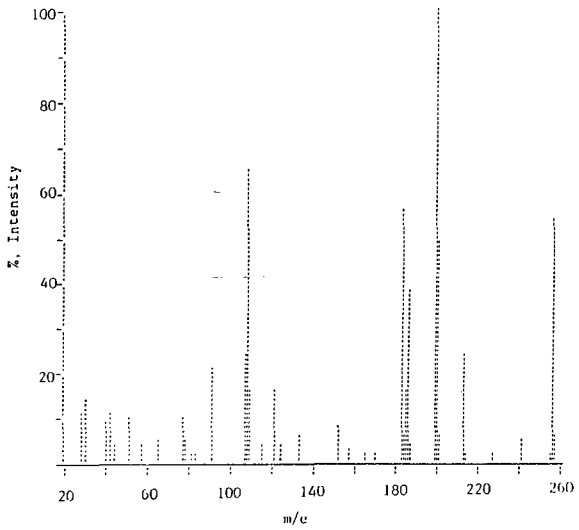


FIGURE 3 Mass spectrum of $PPh_2C_nH_{2n+1}$.

reaction of $[PtCl_2(COD)]$ with two equivalents of $PPh_2C_{12}H_{25}$ in $CDCl_3$ solution was monitored in situ by $^{31}P\{^1H\}$ NMR spectroscopy, we observed formation of both the *cis*- and *trans*- isomers of $[PtCl_2(PPh_2C_{12}H_{25})_2]$, with the *cis* isomer predominant. This observation suggests that the halo-bridged complex $[PtCl_2(\mu\text{–}Cl)_2(PPh_2C_{12}H_{25})_2]$ may be formed initially which undergoes bridge cleavage to produce *trans*-$[PtCl_2(PPh_2C_{12}H_{25})_2]$, followed by isomerization to the *cis*-isomer.

The susceptibility of *cis*-$[PtCl_2(PPh_2C_{12}H_{25})_2]$ to metallation under extreme conditions was examined. Heating of a sealed tube containing a deuteriochloroform solution of the complex at 403K for 24 hours, followed by examination by $^{31}P\{^1H\}$ NMR spectroscopy, showed that no metallation occurred and only the original

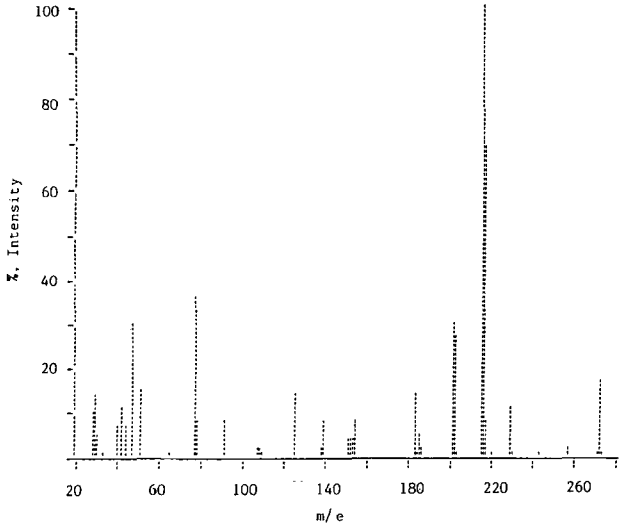


FIGURE 4 Mass spectrum of $P\{O\}Ph_2C_nH_{2n+1}$.

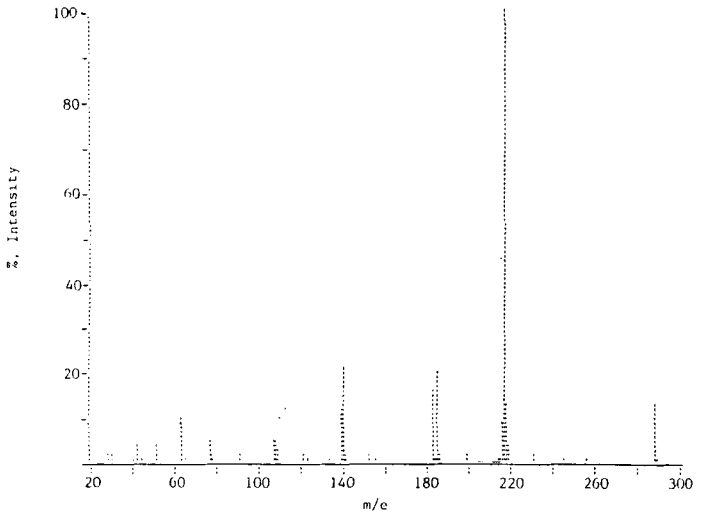


FIGURE 5 Mass spectrum of $P\{S\}Ph_2C_nH_{2n+1}$.

complex was present, with no evidence of thermal decomposition. The reaction of $[PdCl_2(COD)]$ with 2 equivalents of $PPh_2C_{12}H_{25}$ in $CDCl_3$ solution was similarly monitored *in situ* by NMR spectroscopy, and produced a single detectable species with a chemical shift typical of *trans*-$[PdCl_2(PPh_2R)_2]$ complexes, $\delta(^{31}P) = 16.5$ ppm. The *trans*-geometry was confirmed by examination of the ν(Pd–Cl) region of the IR spectrum of the isolated product. Heating a sealed tube of the complex in $CDCl_3$ solution at 403K for 24 hrs, followed by examination by $^{31}P\{^1H\}$ NMR spectroscopy, showed only the presence of the original *trans*-$[PdCl_2(PPh_2C_{12}H_{25})_2]$ complex plus a trace of free $PPh_2C_{12}H_{25}$. Visual inspection of the sample indicated the formation of small amounts of palladium metal, showing that the palladium complex is more thermally sensitive than its platinum analogue, although no evidence for metallation was obtained in either case. This contrasts with reports of complexes containing long-chain trialkylphosphine ligands, of the type $[MCl_2(P\{C_nH_{2n+1}\}_3)_2]$, where metallation is exceptionally facile in certain cases where M = Pd.

EXPERIMENTAL

All synthetic manipulations were performed under a nitrogen atmosphere in Schlenk-ware. Tetrahydrofuran (THF) was pre-dried over KOH pellets before distilling from sodium benzophenone ketyl. Saturated solutions of ammonium chloride were always freshly prepared before use. Pyridine was kept over KOH pellets for 24 hours, then distilled from barium oxide, and stored over molecular sieves. The *p*-toluenesulfonyl chloride was recrystallized from hexane. Methyldiphenyl-, ethyldiphenyl-, *n*-propyl-diphenyl-, and *n*-butyldiphenylphosphines were purchased from Strem Chemicals, Inc. The long-chain alkyl bromides, $n\text{-}C_nH_{2n+1}Br$, used for the preparation of the corresponding alkyldiphenylphosphines, were purchased from Aldrich Chemical Company, Inc., (n = 5–16, 18) and Alfa Products, Inc., (n = 20). The *n*-heptadecyl- and *n*-nonadecyl halides (chlorides, bromides or iodides) were not available commercially at the time of this study. *n*-Heptadecyl and *n*-nonadecyl tosylates used for the preparation of the corresponding alkyldiphenylphosphines were prepared from

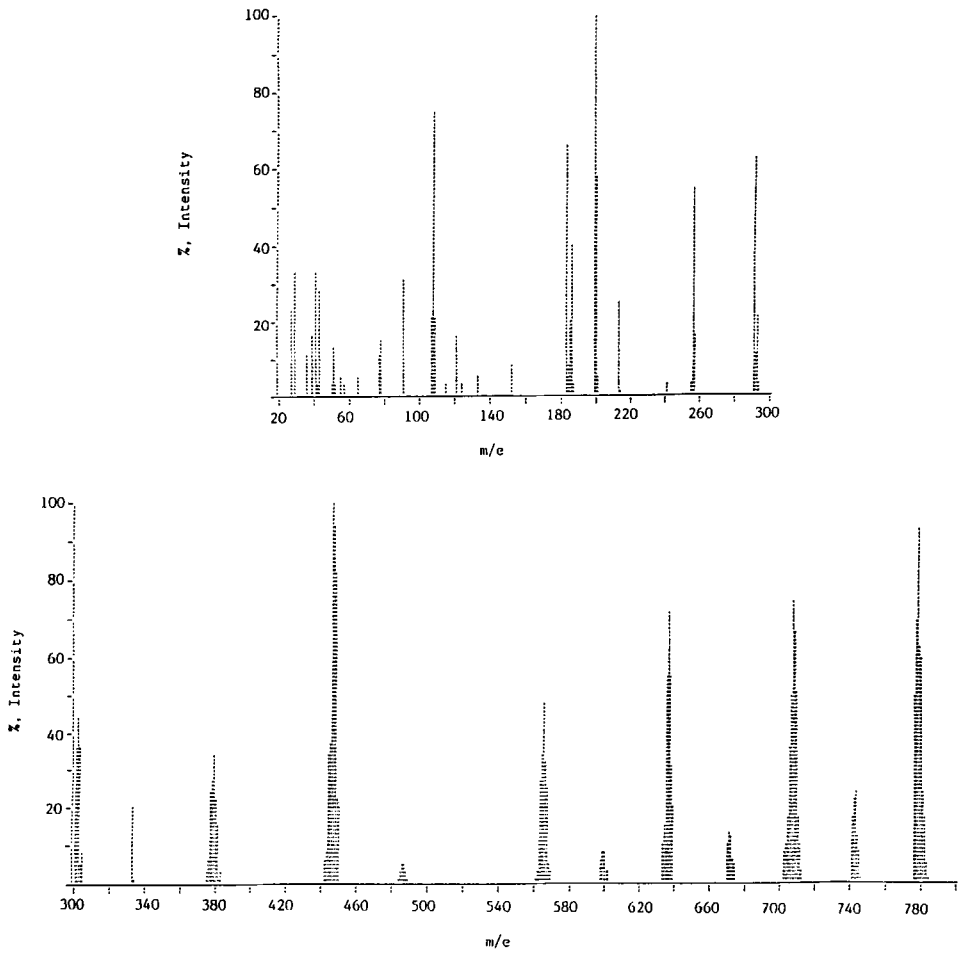
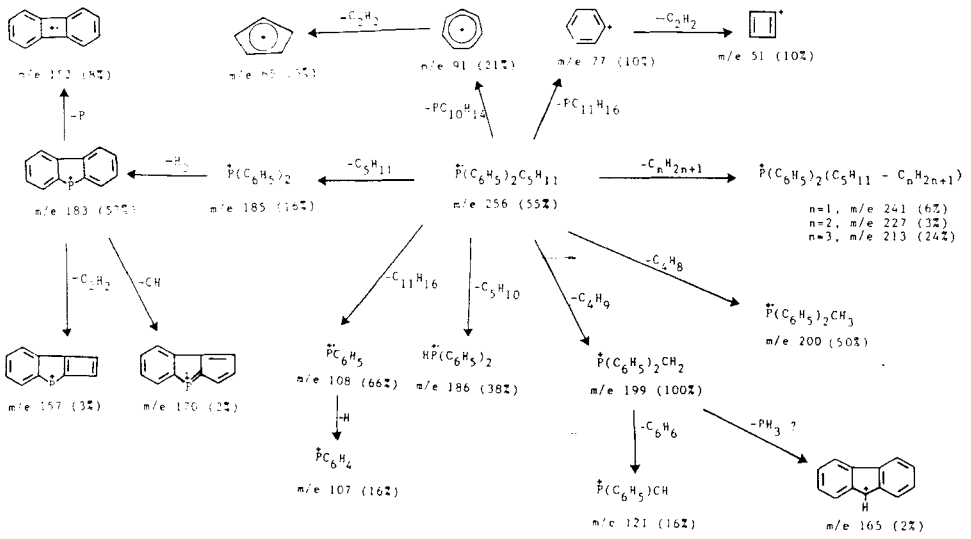
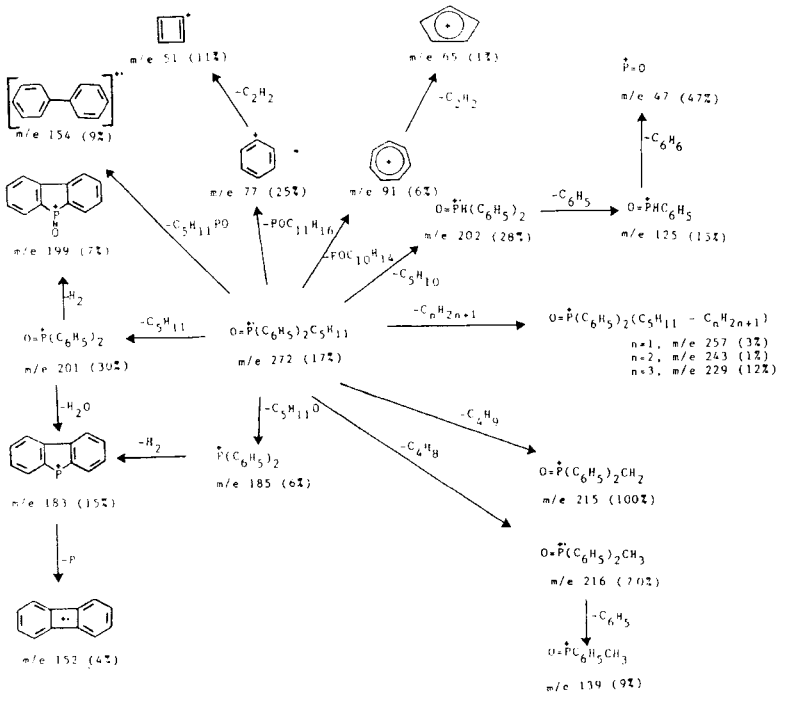


FIGURE 6 a: Mass Spectrum of *cis*-$[PtCl_2(PPh_2C_5H_{11})_2]$, m/e 20–300. b: Mass Spectrum of *cis*-$[PtCl_2(PPh_2C_5H_{11})_2]$, m/e 300–800.

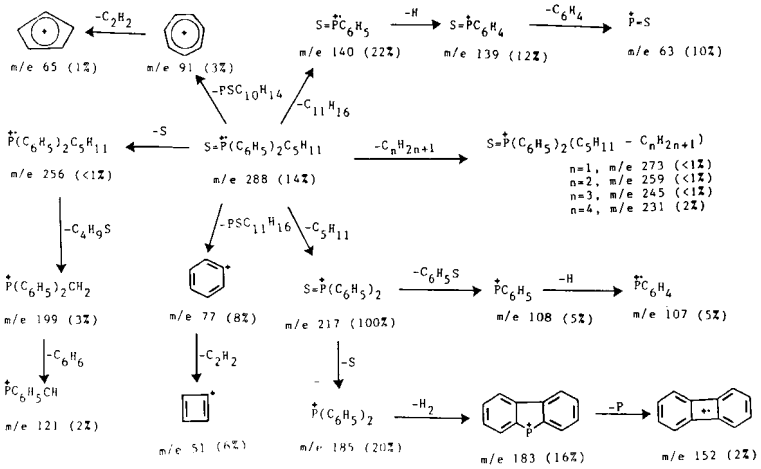
1-heptadecanol (Lancaster Synthesis Ltd) and 1-nonadecanol (Reidel De Haen Ag Seelge Hannover) respectively. $[PtCl_2(COD)]$[64] and $[PdCl_2(COD)]$[65] were prepared by literature methods. NMR spectra for the air sensitive alkyldiphenylphosphines were obtained as deoxygenated $CDCl_3$ solutions in 5 mm NMR tubes under nitrogen. All the $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL FX 90Q spectrometer operating in the Fourier-transform mode with 85% H_3PO_4 as the external reference and $CDCl_3$ as the solvent. More positive values of the chemical shift represent deshielding. ^1H NMR spectra were run on a JEOL FX 90Q spectrometer or a Varian VXR 400 spectrometer operating in the Fourier-transform mode using 1% $SiMe_4$ as an internal standard in $CDCl_3$ solvent. IR spectra were determined as KBr pellets on a Nicolet 60 SX spectrometer. All of the mass spectra were recorded on a Nuclide 12–90 G mass spectrometer. The spectra were run at an electron beam energy of 70 eV with an emission current of 50 μA and at an accelerating potential of 4 kV. Samples were introduced as neat liquids or solids into the mass spectrometer through the



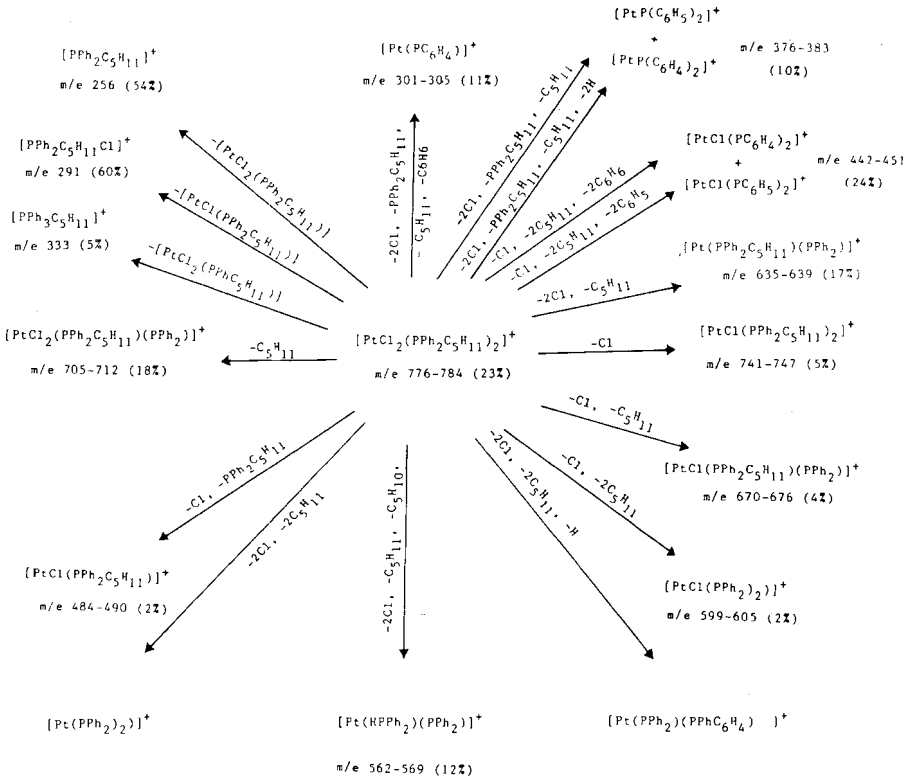
SCHEME 1 Fragmentation pattern for pentyldiphenylphosphine; the percentage intensities are shown in parentheses.



SCHEME 2 Fragmentation pattern for pentyldiphenylphosphine oxide; the percentage intensities are shown in parentheses.



SCHEME 3 Fragmentation pattern for pentyldiphenylphosphine sulfide; the percentage intensities are shown in parentheses.



SCHEME 4 Fragmentation pattern for *cis*-dichlorobis(pentyldiphenylphosphine)platinum(II), with the ligand pentyldiphenylphosphine fragments similar to scheme 1; the percentage intensities are shown in parentheses.

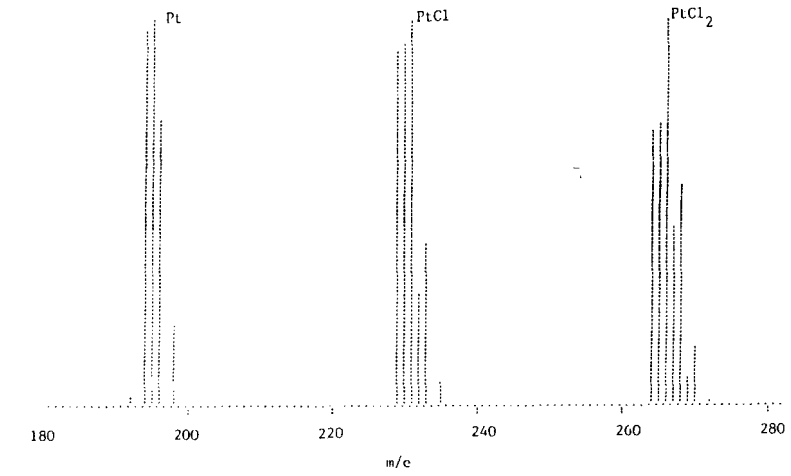


FIGURE 7 Characteristic isotopic patterns for $PtCl_2$, PtCl, and Pt fragments.

direct probe insertion at probe temperatures varying from 25 to 250°C. The relative intensities were estimated by measurement of the heights of the peaks and the mass number of each ion was established by comparison with standards. The heights of the peaks and their respective masses in the mass spectra of $PPh_2(C_5H_{11})$, $P\{O\}Ph_2(C_5H_{11})$, $P\{S\}Ph_2(C_5H_{11})$, and cis-$[PtCl_2(PPh_2C_5H_{11})_2]$ were entered into a computer programme for obtaining Figures 3–6 respectively.

Preparation of the Alkyldiphenylphosphines

All the alkyldiphenylphosphines, with the exception of those where n = 1,2,3,4 (commercially available, *vide supra*), 17 and 19 (*vide infra*) were prepared by reacting the corresponding alkyl bromides with lithium diphenylphosphide in tetrahydrofuran solution.[11] Lithium diphenylphosphide was prepared *in situ* by the reaction of triphenylphosphine and excess lithium metal in tetrahydrofuran.[66,67] A specific example is given below for illustrative purposes. To a stirring solution of triphenylphosphine (37.51 g, 0.143 mol) in dry THF (200 cm^3) in a Schlenk flask, an excess of freshly cut small pieces of lithium metal (5 g) was added. This reaction mixture was stirred at room temperature for 3 h. After this time almost all the triphenylphosphine had reacted to produce a deep red solution of lithium diphenylphosphide. The unreacted lithium metal was filtered off and *t*-butyl chloride (9.26 g, 0.1 mol) was added slowly over a period of 10 minutes to convert phenyllithium into isobutene, benzene, and lithium chloride. Lithium chloride was filtered from the solution. Tridecyl bromide (26.33 g, 0.1 mol) in THF (50 cm^3) was added slowly to the clear red solution of lithium diphenylphosphide over a period of 30 minutes and stirred for an additional 2 h. The colour of the solution changed from red to yellow during the addition of tridecyl bromide. Deoxygenated, saturated aqueous ammonium chloride solution (100 cm^3) was added to the reaction mixture and the solution was stirred for 5 minutes. The organic layer was separated, dried over anhydrous Na_2SO_4, and filtered. After evaporating the solvent, the resulting residue was washed with cold methanol 4 times to give a white waxy solid of tridecyldiphenylphosphine (30.00 g, 81%), which was found to be free of any phosphorus containing impurities by $^{31}P\{^1H\}$ NMR

spectroscopy. The alkyldiphenylphosphines where n < 10 were purified by distillation under reduced pressure. Heptadecyldiphenylphosphine and nonadecyldiphenylphosphine were prepared from the reaction of lithium diphenylphosphide with the respective alkyl tosylates. The alkyl tosylates were made from the corresponding alcohols. A specific example is as follows. To a stirred solution of 1-nonadecanol (2.85 g, 0.01 mol) in dry pyridine (50 cm^3) *p*-toluenesulfonyl chloride (1.91 g) was added in small portions over a period of 5 minutes at 0°C and the mixture was stirred in an ice bath for 5 h. The pyridine was then neutralized with chilled aqueous HCl (5 M, 100 cm^3). The precipitate was filtered and recrystallized from methanol to yield nonadecyl tosylate (3.07 g, 70 %). Nonadecyldiphenylphosphine was prepared by reaction of nonadecyl tosylate with lithium diphenylphosphide in a manner similar to the experiment described above for the preparation of tridecyldiphenylphosphine.

Preparation of the Alkyldiphenylphosphine Oxides

The alkyldiphenylphosphine oxides were prepared by reaction of the alkyldiphenylphosphines with a slight excess of hydrogen peroxide.[68] A specific example is as follows. A suspension of tridecyldiphenylphosphine (2.63 g, 0.01 mol) was stirred at room temperature in H_2O_2 (6% w/v, 15 cm^3) for 3 h. The tridecyldiphenylphosphine oxide was then extracted with chloroform (3 × 30 cm^3). All fractions were combined and dried over anhydrous Na_2SO_4. The chloroform solution was evaporated to dryness and the resulting residue was recrystallized from acetone to produce a white crystalline solid of tridecyldiphenylphosphine oxide (2.51 g, 90 %).

Preparation of the Alkyldiphenylphosphine Sulfides

The alkyldiphenylphosphine sulfides were prepared by reaction of the alkyldiphenylphosphines with elemental sulfur.[69] A specific example is as follows. Tridecyldiphenylphosphine (2.63 g, 0.01 mol) was refluxed with elemental sulfur (0.32 g, 0.01 mol) in benzene for 2 h. The benzene was then evaporated to dryness and the resulting tridecyldiphenylphosphine sulfide was recrystallized from hexane to produce a white crystalline solid of tridecyldiphenylphosphine sulfide (2.37 g, 90 %).

Preparation of cis-$[PtCl_2L_2]$ *(L = alkyldiphenylphosphine)*

The *cis*-$[PtCl_2L_2]$ complexes were prepared by reaction of the alkyldiphenylphosphines with $[PtCl_2(COD)]$. A specific example is as follows. Tridecyldiphenylphosphine (0.736 g, 0.002 mol) was stirred with $[PtCl_2(COD)]$ (0.374 g, 0.001 mol) in chloroform for 30 minutes. At this time the *cis*-$[PtCl_2L_2]$ complex was precipited by careful addition of hexane and subsequently filtered and dried *in vacuo* (0.903 g, 91 %).

Preparation of trans-$[PdCl_2(PPh_2C_{12}H_{25})_2]$

Trans-$[PdCl_2(PPh_2C_{12}H_{25})_2]$ was prepared by reaction of $PPh_2C_{12}H_{25}$ with $[PdCl_2(COD)]$. Dodecyldiphenylphosphine (0.708 g, 0.002 mol) was stirred with $[PdCl_2(COD)]$ (0.286 g, 0.001 mol) in chloroform for 30 minutes. At this time the *trans*-$[PdCl_2(PPh_2C_{12}H_{25})_2]$ complex was precipitated by slow addition of hexane and subsequently filtered and dried *in vacuo* (0.751, 85 %).

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