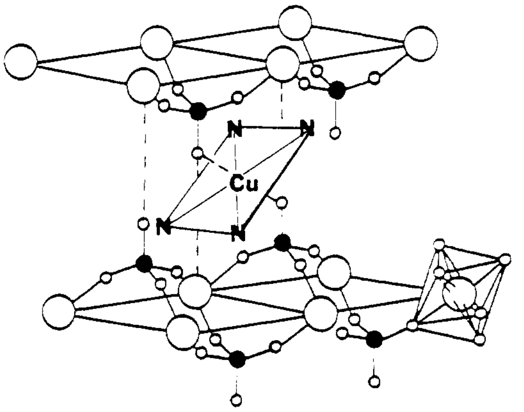

Figure 14. Relative position of the $[Cu(NH_3)_4]^{2+}$ complex in anhydrous zirconium phosphate.

phosphate oxygens that are situated alternatively above and below the planes of zirconium atoms. The different sites within a cavity are created by the different O–O interatomic distances. In $\overline{NH_4NH_4}(2.5{:}48)$, the interlayer distance is 9.38 Å, and in $\overline{NaNa}(2.5{:}48)$, it is 8.5 Å. This allows O–O distances of 5.17 and 4.65 Å in the former and 4.54 and 3.94 Å in $\overline{NaNa}(2.5{:}48)$. In $\overline{NH_4NH_4}(2.5{:}48)$, the O–O distance of 5.17 Å would result in a Cu–O bond length of 2.59 Å if a Cu^{2+} were directly between the two oxygens. This bond length is greater than values that are observed for the axial bond lengths in Cu^{2+} complexes with tetragonal coordination. However, the O–O distance of 4.65 Å would give a Cu–O bond length that is normal.[34] Therefore, in $\overline{NH_4NH_4}(2.5{:}48)$ solids, the Cu^{2+} ion would preferentially situate itself between the pairs of oxygens separated by 4.65 Å, which corresponds to oxygens O_7–O_7'' and its equivalent positions.[50] In $\overline{NaNa}(2.5{:}48)$, the O–O distance of 3.94 Å results in a Cu–O bond length that is slightly smaller than those that are unusually observed. The pairs of oxygens separated by 4.54 Å, which corresponds to oxygens O_{10}–O_7 and O_{10}'–O_7', results in a Cu–O bond length that is consistent with axial bond lengths in Cu^{2+} complexes with tetragonal coordination. The square-planar complex $[Cu(NH_3)_4]^{2+}$, which is approximately 5.5 Å across, could position itself between two P–O^- groups that would then occupy trans axial positions. The plane of the $[Cu(NH_3)_4]^{2+}$ would be in an angle to the Zr layers as illustrated in Figure 14.

Adsorption of ammonia on zirconium phosphates that were not dehydrated resulted in surface ammonia complexes with five NH_3 groups coordinated to the metal. Unlike the ammonia of complexes formed in the interlayer region, a fifth NH_3 molecule would not be prevented from coordinating due to steric hindrance. Threfore it seems probable that a square-pyriamidal ammine complex forms on surfaces of both the $\overline{HH}\cdot H_2O(2.5{:}48)$ and $\overline{NaNa}\cdot 3H_2(2.5{:}48)$ supports rather than the square-planar tetrammine as in the interior.

Registry No. Cu, 7440-50-8; $Zr(HPO_4)_4\cdot H_2O$, 13933-56-7; $Cu(H_2O)_6^{2+}$, 14946-74-8; $Cu(NH_3)_5(H_2O)^{2+}$, 28998-54-1.

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Product Distribution and Stereochemistry in the Reaction of the Unsymmetrical Bis(phosphine) $Ph_2P(CH_2)_6P(Et)Ph$ with Platinum(II) Salts

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The new unsymmetrical bis(phosphine) $Ph_2P(CH_2)_6P(Et)Ph$ has been synthesized, and its reactions with platinum(II) salts have been studied. The formation of the cis or trans isomer with the ligand is critically dependent on the choice of the platinum(II) salt used as the starting material: potassium tetrachloroplatinate(II) yields the cis isomer, and Zeise's salt yields the trans isomer, while bis(benzonitrile)dichloroplatinum(II) gives a cis–trans mixture. The complexes are characterized by ^{31}P NMR and infrared spectroscopy, elemental analysis, and molecular weight data. The ^{31}P NMR spectrum of the trans complex is analyzed and explained in terms of the presence of different dimeric units present in solution. The new symmetrical bis(chiral phosphine) $Ph(Et)P(CH_2)_6P(Et)Ph$ and its platinum(II) complexes have been synthesized in order to confirm the spectral assignments. On the basis of the ^{31}P NMR spectra obtained, it is now possible to predict which unsymmetrical bis(phosphine)–platinum(II) complexes will give ^{31}P NMR spectra capable of complete analysis at 36.4-MHz field strength. The formation of the various isomers is also rationalized.

Introduction

There is much current interest in the synthesis and characterization of chelating bis(phosphine) ligands with chemically and magnetically different phosphorus nuclei attached to the same chelate backbone due to the utility of phosphorus-31 nuclear magnetic resonance as a probe for the investigation and elucidation of the factors that determine the stereochemistry and reactivity of the resulting transition-metal complexes. Symmetrical bis(tertiary phosphines) with flexible chelate backbones have been synthesized by a number of workers and their transition-metal complexes studied.[2-9] The

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synthesis of unsymmetrical bis(phosphines) has proved to be more difficult: ligands of the general formula $Ph_2P(CH_2)_nP(R)Ph$ (n = 1,2,3; R = alkyl) have been prepared,[10-14] but study of their transition-metal complexes has been limited to group 6 metal carbonyl derivatives.[13-15] Recently Grim et al. have prepared bis(*tert*-butylphosphino)(dimethylphosphino)methane and some derivatives of this compound,[16] and Balch and co-workers have examined some bis(tertiary phosphine) complexes of palladium(I).[17]

The importance of steric effects in the chemical behavior of phosphine ligands and their complexes has been increasingly appreciated over the last decade,[18] and recent studies have demonstrated the crucial role that the steric bulk of substituent groups attached to phosphorus plays in determining the pathway,[19] rate,[20] and product distribution[21] in chemical reactions. The unsymmetrical bis(phosphine) discussed here, $Ph_2P(CH_2)_6P(Et)Ph$, is one of a number of phosphines we have developed[22-24] to provide a range of bidentate phosphines with different steric properties at each phosphorus atom so that their resulting complexes could be used to more precisely control reactions in homogeneous catalysts such as asymmetric induction.[25]

Trans-chelated bidentate ligand complexes are of great interest in the investigation of the mechanisms of catalytic reactions.[26] Molecular models show that in a square-planar complex the ligand blocks one side of the square plane, forcing the substrate molecule to approach on the other side. The stereochemistry of coordination of the substrate to the metal is therefore more closely defined, improving the specificity of catalytic reactions. The factors that govern trans chelation in square-planar transition-metal complexes are not clear; for flexible backbone chelates Shaw proposed that the presence of bulky substituent groups on the donor atom produces favorable conformational effects and internal entropy changes which favor the formation of trans-chelated complexes.[27,28] Recent studies by some of us[2,29-31] have shown that the presence of bulky substituent groups on the donor atom may not be a prerequisite for trans chelation. This study demonstrates that the choice of the complex precursor is crucial in determining the stereochemistry of the resulting platinum(II) complexes of the unsymmetrical bis(phosphine) $Ph_2P(CH_2)_6(Et)Ph$ and not the presence of bulky substituent groups on phosphorus.

The stereochemistry of the complexes has been deduced from their ^{31}P NMR and infrared spectra and from molecular weight measurements. The symmetrical bis(chiral ligand) $Ph(Et)P(CH_2)_6P(Et)Ph$ has also been synthesized in order to aid in the interpretation of the spectral data in the unsymmetrical diphosphine complexes. The ligand syntheses themselves are also described. Finally, the formation of the products in each reaction is rationalized, and on the basis of the ^{31}P NMR spectrea obtained, it is now possible to predict which unsymmetrical bis(phosphine)–platinum(II) complexes will give spectra capable of complete analysis at 36.4-MHz field strength.

Experimental Section

Preparation of 1-Bromo-6-(triphenylphosphonio)hexyl Bromide, $[Br(CH_2)_6PPh_3]Br$. 1,6-Dibromohexane (24.4 g, 0.1 mol) was placed in a 250-mL round-bottom flask fitted with a water-cooled reflux condenser, and triphenylphosphine (5.2 g, 0.2 mol) dissolved in 100 mL of benzene was added to the reaction flask. The mixture was heated to reflux by means of an oil bath and was kept at a temperature of 100 °C for a period of 2 h. The mixture was then filtered to isolate the mono(phosphonio) salt in almost quantitative yield (98% based on triphenylphosphine).

Preparation of 1-(Diphenylethylphosphonio)-6-(triphenylphosphonio)hexyl Dibromide, $[Ph_2(Et)P(CH_2)_6PPh_3]Br_2$. An 8.5-g (0.02-mmol) quantity of the mono(phosphonio) salt $[Br(CH_2)_6PPh_3]Br$ and 100 mL of dimethylformamide (DMF) were placed in a 250-mL three-necked round-bottom flask fitted with a water-cooled reflux condenser and a nitrogen inlet. The mixture was stirred continuously by means of a magnetic stirrer, and the reaction was carried out under a nitrogen atmosphere. Diphenylethylphosphine (4.3 g, 0.02 mol) was injected into the reaction vessel by means of a syringe, and the mixture was refluxed for 3 h and then filtered to yield the unsymmetrical bis(phosphonio) salt (98% yield based on the mono(phosphonio) salt).

Preparation of 1-(Ethylphenylphosphinyl)-6-(diphenylphosphinyl)hexane, $[EtPh(O)P(CH_2)_6P(O)Ph_2$. An 11-g (0.02-mol) quantity of the unsymmetrical bis(phosphonio) salt $[Ph_2(Et)P(CH_2)_6PPh_3]Br_2$ was placed in a 500-mL beaker with 200 mL of 20% aqueous sodium hydroxide. The mixture was stirred rapidly by a magnetic stirrer and heated to boiling for a period of 1 h. The benzene produced during the course of the reaction was allowed to boil away. As the reaction proceeded, the solid bis(phosphonio) salt gradually disappeared and a viscous oil formed on the surface of the solution. The mixture was allowed to cool, and the viscous oil was dissolved in 50 mL of benzene after separation. The benzene was then removed by rotary evaporation to yield the bis(phosphine oxide) as an oil. The oil is extremely hygroscopic and retains traces of benzene even under vacuum and hence will not crystallize. The oil was used directly, after pumping under vacuum for 24 h, in the next step of the synthesis.

Preparation of 1-(Ethylphenylphosphino)-6-(diphenylphosphino)hexane, $[Ph(Et)P(CH_2)_6PPh_2]$. An 8-g (0.018-mol) quantity of the unsymmetrical bis(phosphine oxide) was dissolved in 50 mL of dry benzene and placed in a 250-mL three-necked flask fitted with a water-cooled reflux condenser, pressure-equalizing dropping funnel, and nitrogen inlet. The mixture was stirred continuously by means of a magnetic stirrer, and the reaction was carried out under a nitrogen atmosphere. A 50-mL amount of dry, degassed ethanol was then added, and finally a solution of poly(methylhydrosiloxane) (5 g, 0.08 mol) in 50 mL of dry, degassed benzene was allowed to drip into the reaction mixture via the pressure-equalizing dropping funnel. The reaction was very exothermic, and care should be taken to keep the reaction vessel cool (i.e., use of an ice bath is recommended). After

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addition was complete, the mixture was allowed to stir at room temperature for 1 h and then at reflux for a further 1 h to ensure complete reaction. The reaction mixture was then cooled and filtered, and the ligand was recrystallized from an ethanol/benzene solution in 85% yield based on the bis(phosphonio) salt.

Preparation of 1,6-Bis(diphenylphosphino)hexane, [$Ph_2P(CH_2)_6PPh_2$]. The ligand was prepared by the literature route.[2]

Preparation of 1,6-Bis(ethylphenylphosphino)hexane, [$Ph(Et)P(CH_2)_6P(Et)Ph$]. 1,6-Bis(diphenylphosphino)hexane (45.4 g, 0.1 mol) was dissolved in dry dioxane (150 mL) and placed in a 500-mL three-necked flask fitted with a mechanical stirrer, water condenser, and pressure-equalizing dropping funnel. The mixture was degassed by means of a nitrogen purge for 15 min, and then potassium metal (16 g, 0.42 mol) was added, and the mixture was refluxed for 24 h and then cooled to room temperature. Ethyl iodide (65.5 g, 0.42 mol) in 50 mL of degassed, dry dioxane was added to the mixture via the pressure-equalizing dropping funnel over a period of 30 min. The mixture was then filtered and the solvent removed in vacuo to yield the ligand as an oil.

Reaction of $Ph_2P(CH_2)_6P(Et)Ph$ with Zeise's Salt. The ligand (1 mmol) was dissolved in 15 mL of dry acetone and added dropwise over a period of 1 h to a solution of Zeise's salt (1 mmol) dissolved in 25 mL of dry acetone in a 100-mL round-bottom flask. The mixture was stirred continuously by means of a magnetic stirrer. The resulting solution was filtered, and the precipitate was washed with toluene. The acetone/toluene filtrate was evaporated to dryness and the resulting complex recrystallized from an ethanol/toluene mixture and analyzed as $LPtCl_2$. Anal. Calcd: C, 46.4; H, 4.76; Cl, 10.6. Found: C, 46.0; H, 4.4; Cl, 9.6.

Reaction of $Ph_2P(CH_2)_6P(Et)Ph$ with Potassium Tetrachloroplatinate(II). The ligand (1 mmol) and potassium tetrachloroplatinate(II) (1 mmol) were placed in a 100-mL round-bottom flask fitted with a reflux condenser and containing 75 mL of dry ethanol. The mixture was stirred and refluxed for 24 h, during which time the pink K_2PtCl_4 disappeared, yielding a white, insoluble solid. Attempts to dissolve this solid in benzene, acetonitrile, and methylene chloride failed. The solid was filtered, washed with water and acetone, and analyzed as $LPtCl_2$. Anal. Calcd: C, 46.4; H, 4.76; Cl, 10.6. Found: C, 46.9; H, 4.9; Cl, 9.8.

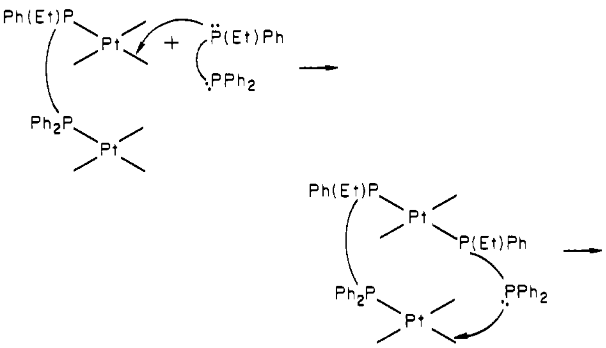
Reaction of $Ph_2P(CH_2)_6P(Et)Ph$ with Bis(benzonitrile)dichloroplatinum(II). The ligand (1 mmol) was dissolved in 15 mL of chloroform and added dropwise over a period of 1 h to a stirred solution of $(PhCN)_2PtCl_2$ (1 mmol) dissolved in 25 mL of chloroform, present in a 50-mL round-bottom flask. The mixture was then stirred for a further 30 min. During the course of the reaction a white solid precipitated, which, after filtration, proved to be insoluble in benzene, acetonitrile, methylene chloride, ethanol, and water. This solid was washed with acetone and dried under vacuum. The filtrate was evaporated to dryness to yield a white solid, which was recrystallized from an ethanol/toluene mixture and analyzed as $LPtCl_2$. Anal. Calcd: C, 46.4; H, 4.76; Cl, 10.6. Found: C, 46.8; H, 5.0; Cl, 10.7.

Reaction of $Ph(Et)P(CH_2)_6P(Et)Ph$ with Zeise's Salt. The ligand (10.5 mmol) was dissolved in 15 mL of dry acetone and added dropwise over a period of 1 h to a solution of Zeise's salt (0.5 mmol) dissolved in 25 mL of dry acetone. The mixture was stirred continuously by means of a magnetic stirrer. The resulting solution was filtered, and the precipitate was washed with toluene. The acetone/toluene mixture was evaporated to dryness and the resulting complex recrystallized from a ethanol/toluene mixture. Anal. Calcd: C, 42.3; H, 5.1; Cl, 11.3. Found: C, 43.2; H, 5.2; Cl, 10.9. ^{31}P NMR spectra were recorded on a Varian CFT-20 spectrometer in $CDCl_3$ using 85% H_3PO_4 as external standard. Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer in a Nujol mull using polyethylene plates. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer in $CDCl_3$ using Me_4Si as internal standard. Mass spectra were recorded on a Du Pont 419B double-focusing mass spectrometer equipped with a Finnigan Incos data system. Analyses were carried out by the microanalytic service at UMIST. Molecular weights were determined by vapor-phase osmometry in chloroform solution.

Results and Discussion

The bis(phosphine) $Ph_2P(CH_2)_6P(Et)Ph$ has been prepared by a novel synthetic route that can be generalized to prepare a wide range of unsymmetrical bis(phosphines) of the general formula $Ph_2P(CH_2)_nPRPh$[22,23] or $Ph_2P(CH_2)_nPR_2$.[24] The method involves the preparation of an unsymmetrical bis(phosphonio) salt, which is subsequently hydrolyzed by aqueous sodium hydroxide to the unsymmetrical bis(phosphine oxide), involving specific cleavage of a phenyl group from each phosphorus atom. The bis(phosphine oxide) is then reduced by poly(methylhydrosiloxane) (PMHS) to the corresponding unsymmetrical diphosphine in good yield. The synthetic route is shown in Scheme I and in eq 1–4.

Scheme I



3a

$$Br(CH_2)_6Br + Ph_3P \xrightarrow{\text{benzene}} [Ph_3P(CH_2)_6Br]Br \quad (1)$$

$$[Ph_3P(CH_2)_6Br]Br + EtPh_2P \xrightarrow{\text{DMF}} [Ph_3P(CH_2)_6P(Et)Ph_2]Br_2 \quad (2)$$

$$[Ph_3P(CH_2)_6P(Et)Ph_2]Br_2 \xrightarrow{\text{NaOH(aq)}} Ph_2(O)P(CH_2)_6P(O)EtPh \quad (3)$$

$$Ph(O)P(CH_2)_6P(O)EtPh \xrightarrow{\text{PMHS}} Ph_2P(CH_2)_6P(Et)Ph \quad (4)$$

The procedure outlined above is experimentally easier than previous routes, as it involves several well-established steps and employs readily available starting materials. The key step in the synthesis is the formation of the mono(phosphonio) salt with triphenylphosphine: this is achieved by carrying out the reaction in a nonpolar solvent such as benzene. The mixture may be warmed to speed up the reaction, but the use of polar higher boiling solvents such as dimethylformamide or nitrobenzene results in the formation of the bis(phosphonio) salt. The required mono(phosphonio) salt is best obtained by using a fivefold excess of 1,6-dibromohexane to triphenylphosphine. The preparation of the unsymmetrical bis(phosphonio) salt is therefore best affected by addition of ethyldiphenylphosphine to the mono(phosphonio) salt $[Ph_3P(CH_2)_6Br]$ in a polar solvent such as DMF. The unsymmetrical bis(phosphonio) salt can be converted to the corresponding bis(phosphine oxide) by the action of aqueous sodium hydroxide: direct reduction to the phosphine using lithium aluminum hydride or sodium metal results in poor yields.[22] Hydrolysis of quarternary phosphonium salts using aqueous sodium hydroxide or aqueous potassium hydroxide is thought to proceed by the mechanism[32-34]

$$R_4P^+ + OH^- \rightarrow R_4POH \xrightarrow{OH^-} R_4PO^- \xrightarrow{\text{slow}} R_3PO + R^- \xrightarrow{H_2O} R_3PO + RH + OH^-$$

If the four groups (R_4) are different, then the one that is ejected in the slow step of the reaction is that which forms the most stable anion, so the phenyl group is preferentially displaced from both ends of the bis(phosphonio) salt to produce

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Table I. ^{13}C NMR Spectral Data for the Ligands $Ph_2P(CH_2)_6P(Et)Ph$(I) and $Ph(Et)P(CH_2)_6P(Et)Ph$ (II)

C resonance	chem shifts[a] and coupling const[b] I	II
ipso	*c*	*c*
ortho	−132.89 (19.3) −132.78 (19.2)	−132.32 (18.1)
meta	−128.61	−128.39
para	−128.32	−128.10
C_A	−20.73 (9.7)	−21.59 (10.6)
C_B	−9.89 (13.6)	−9.78 (13.6)
C_1	*d*	−30.57 (11.5)
C_2	*d*	−25.70 (14.0)
C_3	*d*	−27.62 (9.2)

[a] Measured in ppm relative to Me_4Si internal standard. Negative shifts are downfield from Me_4Si. $CDCl_3$ was used as the lock solvent. [b] Coupling constants are in parentheses and are given in hertz. [c] Signal not observed. [d] Signal too complicated by phosphorus-carbon coupling and resonance overlap for unequivocal assignment of all six nonequivalent carbon resonances.

Table II. Mass Spectral Data for the Ligands $Ph_2P(CH_2)_6P(Et)Ph$ (I) and $Ph(Et)P(CH_2)_6P(Et)Ph$ (II)

m/e[a]	rel intens[b] I	II	ion
378	2.63		$C_{22}H_{28}P_2$
377	17.69		$C_{22}H_{27}P_2$
301		2.8	$C_{18}H_{23}P_2$
300		18.4	$C_{18}H_{22}P_2$
269	13.07		$C_{18}H_{22}P$
222	1.37		$C_{14}H_{23}P$
221	20.18		$C_{14}H_{22}P$
186	2.64		$C_{12}H_{11}P$
185	0.35	1.67	$C_{12}H_{10}P$
183	2.36	1.40	$C_{12}H_8P$
109	2.93	12.6	C_6H_6P
108	4.04	15.3	C_6H_5P

[a] *m/e* values less than 100 were not reported. [b] Relative intensities were compared to that of the *m/e* = 28 base peak. Relative intensities less than 1.0 were not reported.

benzene and the bis(phosphine oxide). The use of boiling aqueous sodium hydroxide means that the benzene produced during the course of the reaction boils away, leaving the oxide as a viscous oil on the surface of the water. The oxide can then be smoothly converted to the free bis(phosphine) by reduction with poly(methylhydrosiloxane)[35] after separation and drying.

The phosphorus-31 NMR spectrum of the ligand shows two resonances at +17.44 and +15.48 ppm upfield from 85% H_3PO_4 external standard. The resonance at +17.44 ppm is assigned to the Ph(Et)P phosphorus and that at +15.48 ppm to the Ph_2P phosphorus.[36] The carbon-13 NMR spectrum shows a complicated aliphatic region for the methylene region of the spectrum due to phosphorus–carbon coupling and signal overlap. The aromatic region and the region where the ethyl group attached directly to phosphorus resonates can be satisfactorily resolved and are displayed in Table I. Note that the two magnetically different phenyl groups can be distinguished by the resonance of the ortho carbon atoms.[36] The mass spectrum of the ligand is shown in Table II. Loss of the ethyl group is a facile process, and indeed the parent ion is not observed—further cleavage by loss of the PPh_2 unit is another feature of the spectrum.

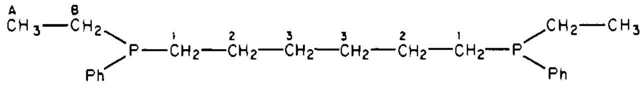

Figure 1. Identification system used for ^{13}C resonance assignment.

Table III. Infrared Data for the Complexes

complex	ν(Pt–Cl), cm^{-1}	geom
$Ph_2P(CH_2)_6P(Et)Ph + K_2PtCl_4$	288, 312	cis
$Ph_2P(CH_2)_6P(Et)Ph + (PhCN)_2PtCl_2$	288, 312	cis
	340	trans
$Ph_2P(CH_2)_6P(Et)Ph + K[PtCl_3(C_2H_4)]$	341	trans
$Ph(Et)P(CH_2)P(Et)Ph + K[PtCl_3(C_2H_4)]$	340	trans

The symmetrical bis(phosphine) $Ph(Et)P(CH_2)_6P(Et)Ph$ was prepared by the synthetic route outlined by eq 5–7.

$$Br(CH_2)_6Br + 2LiPPh_2 \xrightarrow{THF} Ph_2P(CH_2)_6PPh_2 + 2LiBr \quad (5)$$

$$Ph_2P(CH_2)_6PPh_2 + 4K \xrightarrow{dioxane} K_2[PhP(CH_2)_6PPh] + 2KPh \quad (6)$$

$$K_2[PhP(CH_2)_6PPh] + 2KPh + 4EtI \rightarrow Ph(Et)P(CH_2)_6P(Et)Ph + 2EtPh + 4KI \quad (7)$$

The method can be used as a general synthetic route to bis(chiral phosphines) of the type $RPhP(CH_2)_nPPhR$, R = alkyl.

A single ^{31}P resonance is observed and appears at +16.3 ppm in the phosphorus-31 NMR spectrum upfield from 85% H_3PO_4 external standard. The carbon-13 NMR spectrum (see Table I) shows three distinct regions; the aromatic region, the aliphatic region where the methylene bridge carbon atoms resonate, and the aliphatic region where the carbon atoms in the ethyl groups attached directly to phosphorus resonate (see Figure 1).

All the signals can be identified, and the coupling constants observed are in agreement with the literature values for similar monodentate[37] and bidentate[38,39] phosphines. The mass spectrum of the ligand is shown in Table II.

The reaction of $Ph_2P(CH_2)_6P(Et)Ph$ with potassium tetrachloroplatinate(II) yields the white insoluble solid $PtLX_2$ (L = ligand). The infrared spectrum of the solid shows two bands in the metal–chloride stretching region at 288 and 312 cm^{-1}, characteristic of cis chlorine atoms.[40,41] This complex is formulated as the cis polymer due to the lack of solubility of the complex. It has been noted that reaction of the symmetrical ligand $Ph_2P(CH_2)_6PPh_2$ with palladium(II) chloride gives a trans polymeric material,[2] and the polymeric nature of the product in both cases appears to be a consequence of the length of the methylene chain. It was noted that ligands of the type $Ph_2P(CH_2)_nPPh_2$ (n = 8, 10) gave essentially dimeric species while when $n \approx 12$ a trans-chelated monomer was isolated on reaction of the ligands with palladium(II) chloride.

The reaction of bis(benzonitrile)dichloroplatinum(II) with the unsymmetrical ligand $Ph_2P(CH_2)_6P(Et)Ph$ also yields, in part, a white insoluble solid possessing a far-infrared spectrum identical with that obtained in the reaction of the ligand with

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Table IV. Species Observed in the Phosphorus-31 Nuclear Magnetic Resonance Spectra from the Reactions Given

	chem shift,[a] ppm	coupling const (J(Pt-P)), Hz
(1) Reaction of $Ph_2P(CH_2)_6P(Et)Ph$ with Zeise's Salt		
resonance A	−12.3	2547
resonance B	−9.0	2474
resonance C	−10.7[b]	2500[c]
(2) Reaction of $Ph_2P(CH_2)_6P(Et)Ph$ with Bis(benzonitrile)dichloroplatinum(II)[d]		
resonance A	−12.4	2564
resonance B	−8.7	2484
resonance C	−10.7[b]	2500[c]
(3) Reaction of $Ph_2P(CH_2)_6PPh_2$ with Zeise's Salt[30]		
	−12.35	2547
(4) Reaction of $Ph(Et)P(CH_2)_6P(Et)Ph$ with Zeise's Salt		
	−8.9	2475

[a] Samples were run in $CDCl_3$ lock solvent. Chemical shifts were measured relative to 85% H_3PO_4 external standard. [b] Signal appears as a doublet. [c] Estimated value. [d] CH_2Cl_2/C_6D_6 solvent was used for the spectrum.

potassium tetrachloroplatinate(II) (i.e., the cis isomer). A soluble trans isomer was also isolated and examined by ^{31}P NMR and infrared spectroscopy (see Tables III and IV).

In contrast, the reaction of $Ph_2P(CH_2)_6P(Et)Ph$ with Zeise's salt leads to the formation of a yellow solid, which is analyzed as $PtLCl_2$. The far-infrared spectrum of this complex shows only one band at 340 cm^{-1}, characteristic of trans chlorine atoms.[40,41] The ^{31}P NMR spectrum of this soluble solid shows the presence of a number of distinct chemical species present in solution (see Table IV), and all of these species exhibit $J(^{195}Pt-^{31}P)$ in the region for trans bis(phosphine) complexes.[42,43] The spectrum is shown in Figure 2a along with the schematic representation of our interpretation of the spectrum (Figure 2b).

Comparison of the spectrum with that of *trans*-$[Ph_2P(CH_2)_6PPh_2]PtCl_2$[44] allows the identification of resonance A and its ^{195}Pt satellites as a unit possessing *two* mutually trans diphenylphosphino groups—it is clear therefore that the species in solution cannot be monomeric. A molecular weight determination on the complex in chloroform solution gave a molecular weight of 1495, indicating that the species present are at least dimeric. Similarly, comparison of the spectrum with that of *trans*-$[Ph(Et)P(CH_2)_6P(Et)Ph]PtCl_2$ allows the identification of resonance B and its ^{195}Pt satellites as a unit possessing *two* mutually trans ethylphenylphosphino groups. A structure (**3a**) consistent with the ^{31}P NMR, infrared, and molecular weight data is shown in Figure 3.

The other possible dimeric structure that could be envisioned for the complex (**3b**) is also shown in Figure 3. Such a unit possesses a diphenylphosphino group and an ethylphenylphosphino group mutually trans to one another. Two chemically and magnetically nonequivalent phosphorus atoms such as these in a trans orientation in a platinum(II) complex are expected to show a $J(P-P^1)$ in the region of 500 Hz,[45] and the central portion of the ^{31}P NMR spectrum of such a complex (i.e., that not coupled to ^{195}Pt) should exhibit an AB splitting pattern: a four-line system with $J(P-P^1)$ being the separation between lines 1 and 2 or lines 3 and 4. The general appearance of the AB spectrum depends only on the ratio of $J(P-P^1)$ to $\nu_0\delta$ (the chemical shift difference between the two nonequivalent phosphorus nuclei). Examination of the ^{31}P NMR spectrum of the free ligand shows that $\nu_0\delta$ is very small—less than 2 ppm. This, together with the large expected value for $J(P-P^1)$ means that the ratio $J(P-P^1):\nu_0\delta$ will be very large. The spectrum expected in such a case would be two extremely large central components and two extremely small outer components with the possibility that the latter two peaks may not be observable.[45,46] In this situation the analysis of the spectrum is impossible as one cannot measure the value for $J(P-P^1)$ due to the absence of lines 1 and 4 in the AB spectrum. This is the type of spectrum that is observed for the

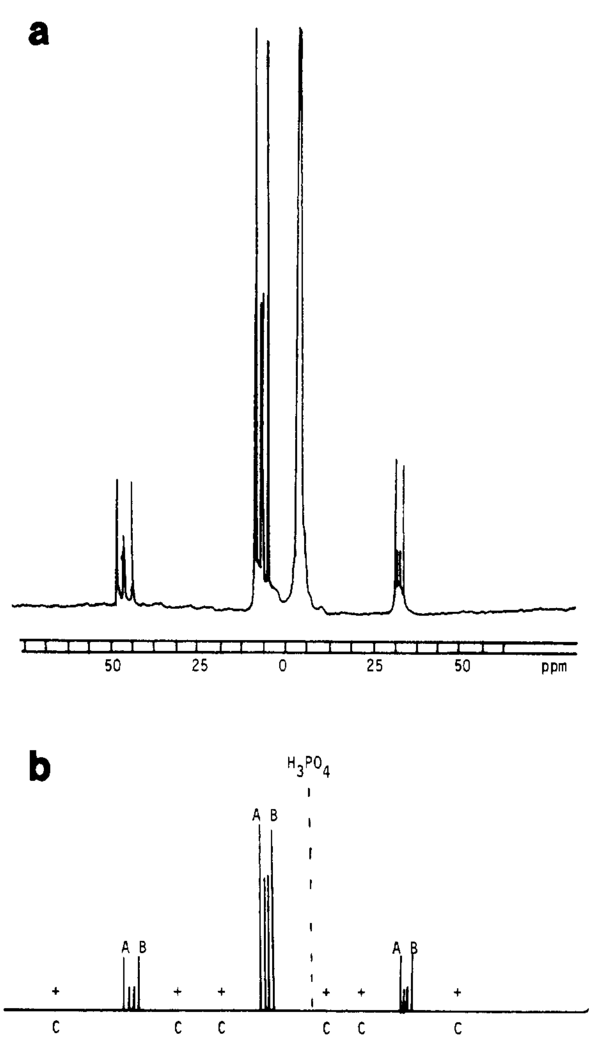
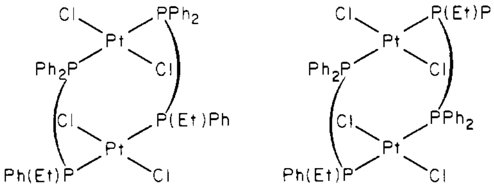


Figure 2. ^{31}P NMR (a) and schematic (b) spectra of *trans*-$[Ph_2P(CH_2)_6P(Et)Ph]PtCl_2$: (+) too weak to be observed; (A) resonance from mutually trans Ph_2P units; (B) resonance from mutually trans Ph(Et)P units.



3a **3b**

Figure 3. Possible dimeric units for the complex *trans*-$[Ph_2P(CH_2)_6(Et)Ph]PtCl_2$.

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Table V. Phosphorus-31 NMR Data for the *cis*-$[Ph_2P(CH_2)_6P(Et)Ph]PtCl_2$ Complex[a]

^1J(Pt-P), Hz	3728, 3629	δ(P)	−17.5, −2.8
^2J(P-P), Hz	15.8		

[a] Sample was run in $CDCl_3$ lock solvent. Chemical shifts were measured relative to 85% H_3PO_4 external standard.

complex shown in Figure 2. The two very intense inner lines for the AB spectrum are observed but not the outer two components. A similar situation exists for the analysis of the ABX system where there is coupling to ^{195}Pt. Presumably at higher field strengths (>36.4 MHz) the two outer components would be observable. Allen and Sze[45] noted that *trans*-$[PtCl_2(n\text{-}Bu_3P)(Et_3P)]$ does not give a first-order ^{31}P NMR spectrum. The chemical shift difference between $(n\text{-}Bu)_3P$ and Et_3P in the free ligands is 12 ppm, so the results obtained here, for a 2-ppm chemical shift separation between the phosphorus nuclei in the free unsymmetrical bis(phosphine) ligand, are not surprising.

An almost identical spectrum is observed for the soluble products from the reaction of $Ph_2P(CH_2)P(Et)Ph$ with bis(benzonitrile)dichloroplatinum(II), indicating the presence of trans-bonded dimeric units in solution.

The integrated areas of the A and B resonances are identical, in keeping with the proposed assignments. However, the ratio of the integrated areas of A and C or B and C are not fixed but should relate to the relative amounts of the different isomers present. The ratio of A:B:C in all spectra of the trans isomers, whether prepared from Zeise's salt or obtained from bis(benzonitrile)dichloroplatinum(II), is 1:1:1, which indicates that isomer **3a** is present in 66% abundance, while isomer **3b** is present in 33% abundance. The integrated areas of the resonances do not vary with the different preparative routes employed here.

The predominance of isomer **3a** may be explained in terms of kinetic control dictating the course of the reaction. Mononuclear trans chelation is prevented because the chelate chain length is of an unsuitable size,[2] so each phosphorus nucleus in the ligand must coordinate to a separate platinum metal center (see Scheme I). The platinum–chloride bond trans to the ethylphenylphosphino group will be labilized to a greater extent than that trans to the diphenylphosphino group. This, coupled with the greater basicity (and hence greater nucleophilicity) of the next incoming ethylphenylphosphino group from another uncoordinated ligand, will promote coordination of the second ethylphenylphosphino group trans to the first, resulting in preferential formation of the symmetrical dimer **3a**.

It would be expected that **3b** would be the product favored on thermodynamic grounds and hence isomerization from **3a** to **3b** should be observed. However, both **3a** and **3b** undergo facile isomerization to the cis isomer, which is more stable than either of the trans isomers (see below).

Addition of a trace of excess unsymmetrical bis(phosphine) to a solution of the trans species followed by the application of heat results in cis–trans isomerization: the spectrum of the cis complex is shown in Figure 4, and the relevant ^{31}P NMR data is displayed in Table V. The spectrum of the cis complex is unexceptional, with all values for both the chemical shifts and the coupling constants being in agreement with the literature values for similar systems.[45]

The formation of the cis or the trans isomer of the complex is therefore critically dependent on the choice of the platinum(II) salt used as the starting material. Zeise's salt gives the trans isomer, and potassium tetrachloroplatinate(II) gives the cis isomer, while bis(benzonitrile)dichloroplatinum(II) yields a mixture of the two. The trans species are clearly at least dimeric as evidenced by the ^{31}P NMR and molecular weight data while the cis species forms as an insoluble polymer.

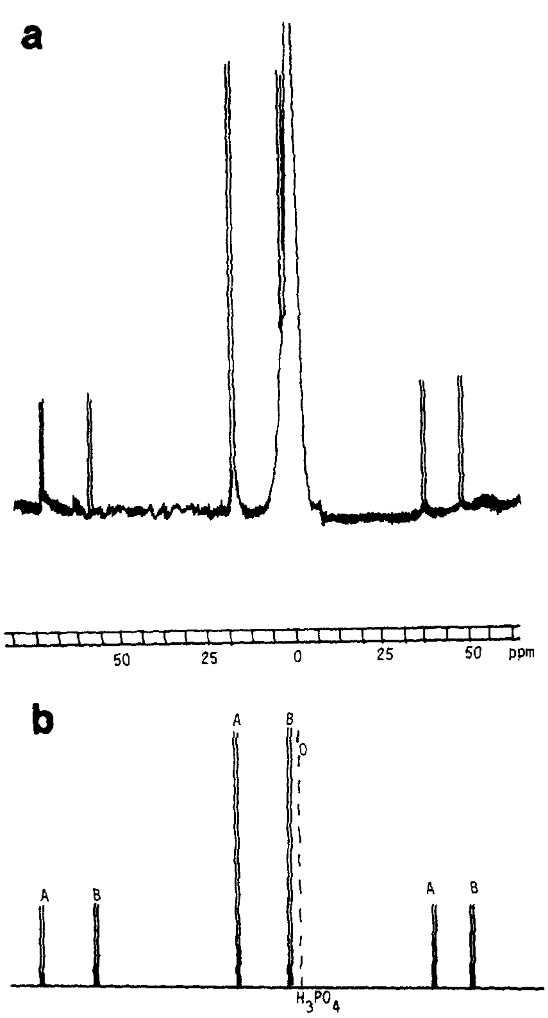

Figure 4. ^{31}P NMR (a) and schematic (b) spectra of *cis*-$[Ph_2P(CH_2)_6P(Et)Ph]PtCl_2$. Resonances A and B and their ^{195}Pt satellites are due to the two chemically and magnetically distinct ^{31}P nuclei present in the complex.

It has long been known that the cis isomers of square-planar platinum(II) phosphine complexes are thermodynamically more stable than their corresponding trans analogues;[46,48] also the use of polar solvents favors the formation of the cis isomer,[43] so the isolation of the cis moiety from the reaction of potassium tetrachloroplatinate(II) with $Ph_2P(CH_2)_6P(Et)Ph$ is easily rationalized. The literature preparation of bis(benzonitrile)dichloroplatinum(II) results in the formation of the cis isomer,[49,50] and the product expected from its reaction with $Ph_2P(CH_2)_6P(Et)Ph$ in chloroform is therefore the cis complex. However, isomerization does occur to give ca. 20% of the trans isomer under conditions that exclude the presence of excess bis(phosphine). This is an interesting observation as most mechanisms proposed for cis–trans isomerization in platinum(II) complexes have involved catalysis by excess phosphine.[51] Addition of excess bis(phosphine) to the solution does indeed catalyze the isomerization of the trans species to produce a soluble cis species (vide supra) characterized by ^{31}P NMR and infrared spectroscopy. The use of Zeise's salt gives exclusively the trans isomer due to the high trans-labilizing effect of the ethylene group,[52,53] which allows the formation

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of the kinetically favored product, i.e., the trans isomer. Due to the length of the chelate backbone the trans isomer is not monomeric—dimeric 18-membered macrocycles being the preferred conformation.

Attempts to separate the trans species by column chromatography or vacuum sublimation failed.

Conclusions

The synthetic procedures outlined in this paper allow the synthesis of novel unsymmetrical bis(phosphines) with long flexible chelate backbones of the type $Ph_2P(CH_2)_nPR_2$ and $Ph_2P(CH_2)_nP(R)Ph$ (R = alkyl) and bis(chiral phosphines) of the type $Ph(R)P(CH_2)_nP(R)Ph$ (R = alkyl), ligands of great interest in homogeneous catalysis and asymmetric synthesis. The ligand synthesized and examined in this study, $Ph_2P(CH_2)_6P(Et)Ph$, can form cis or trans complexes with platinum(II) depending upon the reaction conditions employed and the starting materials used. The chemical shift difference between the two phosphorus nuclei (ca. 2 ppm) does not allow complete analysis of the ^{31}P NMR spectrum of the trans platinum(II) complex of the ligand. This and other observations[45] make it clear that the chemical shift separation between two chemically and magnetically nonequivalent phosphorus nuclei should be greater than 12 ppm to allow complete resolution at 35.4-MHz field strength for trans bis(phosphine) complexes.

Shaw has pointed out[4] that there are many examples where long-chain flexible bidentate ligands preferentially give open-chain polynucear rather than large-ring chelate complexes, and the formation of chelate rings vs. open-chain isomers can be explained in terms of ring strain and entropy factors. However, the formation of cis and trans isomers in these cases cannot be rationalized on these grounds alone. While it is certainly true that the presence of bulky terminal substituents on phosphorus may favor the formation of the trans-chelated complex over its cis analogue, many trans-chelated complexes have been synthesized with phosphorus,[2] arsenic,[29,30] and sulfur[31] donor atoms which do not possess bulky terminal substituents, indicating that other factors may play a vital role in determining the stereochemistry of transition-metal bis(phosphine) complexes.

Complexes of the type *cis*-$[Pt(PR_3)_2Cl_2]$ can be considered to be products of thermodynamic control—a stronger platinum–phosphorus bond being formed when the coordinated phosphorus is trans to a chlorine (which possesses a weak trans influence). A general preparation for this type of complex is the reaction of potassium tetrachloroplatinate (II) with the ligand in a polar solvent. In certain cases, for instance, when R = alkyl, a cis/trans mixture of isomers will either result at room temperature or result after heating the product of the reaction.[43,54] However, when one or two of the substituents is a phenyl group, the product is exclusively the cis isomer, indicating that the basicity of the donor phosphorus may play a role in determining the reaction product.

For ligands that possess two phenyl groups attached to the donor phosphorus atom, it is necessary to react the phosphine with a precursor that will give the product of kinetic control[44]—for example, Zeise's salt[55] or the chlorine-bridged dimer $[Pt_2(PR_3)_2Cl_4]$[43]—in order to obtain the trans isomer. The choice of such a precursor is not necessary for the synthesis of trans-palladium(II)–phosphine complexes; the product of kinetic control (the trans isomer) is formed in almost all cases.[2,56–61] These results and the results obtained in this paper indicate that the choice of a suitable complex precursor is critical for the synthesis of trans-chelated complexes of platinum(II), and such complexes can be readily synthesized by the employment of kinetically labile starting substrate.

Registry No. I, 82195-38-8; II, 83152-25-4; **3a**, 83152-26-5; **3b**, 83152-29-8; $[Br(CH_2)_6PPh_3]Br$, 83152-22-1; $[Ph_2(Et)P(CH_2)_6PPh_3]Br_2$, 83152-23-2; $EtPh(O)P(CH_2)_6P(O)Ph_2$, 83152-24-3; *cis*-$[Ph_2P(CH_2)_6P(Et)Ph]PtCl_2$, 83152-27-6; *cis*-$(PhCN)_2PtCl_2$, 15617-19-3; *trans*-$([Ph(Et)P(CH_2)_6P(Et)Ph]PtCl_2)_2$, 83152-28-7; 1,6-dibromohexane, 629-03-8; triphenylphosphine, 603-35-0; diphenylethylphosphine, 607-01-2; 1,6-bis(diphenylphosphino)hexane, 19845-69-3; ethyl iodide, 75-03-6; Zeise's salt, 16405-35-9; potassium tetrachloroplatinate(II), 10025-99-7.

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^{13}C NMR Spectra of Some New Iridium(I) Complexes: Evidence for Reductive Character in H_2 Addition and the Cis and Trans Influences of Nitriles

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Syntheses of the new complexes $[Ir(cod)(PPh_3)(RCN)]A$ and $[IrH_2(cod)(PPh_3)(RCN)]A$ (cod = 1,5-cyclooctadiene; A = BF_4; R = Me, *p*-$MeOC_6H_4$, C_6H_5, *p*-$CH_3COC_6H_4$, and *p*-$NO_2C_6H_4$) are reported. ^{13}C NMR spectroscopy suggests the addition of H_2 takes place with an increase, rather than the more usual decrease, of electron density at the metal. The data also reveal the presence of cis and trans influences of R on the cod δ(C(vinyl)), which are in the same direction, the trans being ca. 3.5 times greater than the cis influence.

The term oxidative addition as applied to eq 1 carries with

$$\underset{\mathbf{1}}{L_nM} + XY \rightarrow \underset{\mathbf{2}}{L_nM(X)(Y)} \qquad (1)$$

it the implication that the metal has been oxidized in the process. We have suggested that some additions of this type seem not to give rise to oxidation of the metal but rather to reduction.[3,4] In these cases the electron density at the metal

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