A ^{31}P Nuclear Magnetic Resonance Investigation of the Structure, Equilibria, and Kinetics of $[Pt(PR_3)_n]$ in Solution

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The compounds $[PtL_4]$ (L = PMe_3, PMe_2Ph, $PMePh_2$, PEt_3, or $PBu^n{}_3$), $[PtL_3]$ [L = PEt_3, $PBu^n{}_3$, $P(p\text{-tolyl})_3$, $P(CH_2Ph)_3$, $PPr^i{}_3$, or $P(C_6H_{11})_3$], and $[PtL_2]$ [L = $PPr^i{}_3$, $P(C_6H_{11})_3$, or $PBu^t{}_2Ph$] have been prepared and shown to exist in solution. In the cases of L = $PMePh_2$, PEt_3, $PBu^n{}_3$, n = 3 and L = $PPr^i{}_3$, $P(C_6H_{11})_3$, n = 2 it has proved possible to measure the equilibrium constant, $\Delta H^\ominus$, and $\Delta S^\ominus$ for $[PtL_{n+1}] \rightleftharpoons [PtL_n] + L$. For $[Pt(PMe_3)_4]$, $[Pt(PMe_2Ph)_4]$, $[Pt(PMePh_2)_4]$, $[Pt(PEt_3)_4]$, $[Pt(PBu^n{}_3)_4]$, $[Pt(PPr^i{}_3)_3]$, and $[Pt\{P(C_6H_{11})_3\}_3]$, the tertiary phosphine exchange is dissociative, while for $[Pt(PPr^i{}_3)_2]$ and $[Pt\{P(C_6H_{11})_3\}_2]$ associative exchange occurs. In the case of $[Pt(PEt_3)_3]$ and $[Pt(PBu^n{}_3)_3]$ both associative and dissociative exchange occur, the relative rates of which depend on the temperature and concentration of free tertiary phosphine. In the cases of $[Pt(PPr^i{}_3)_2]$ and $[Pt\{P(C_6H_{11})_3\}_2]$ a marked solvent effect has been found and attributed to possible toluene co-ordination producing $[Pt(\eta\text{-toluene})(PR_3)_2]$ in equilibrium with $[Pt(PR_3)_2]$. No evidence is found for steric crowding affecting $\Delta H^\ominus$ or $\Delta H^\ddagger$, but $\Delta S^\ominus$ and $\Delta S^\ddagger$ are affected due to interpenetration of the ligands and resulting loss of motional freedom, while previously it has been assumed that interligand steric crowding destabilizes the molecule *via* the enthalpy term.

THERE has been considerable interest in the chemistry of $[ML_n]$ complexes (M = Ni^0, Pd^0, or Pt^0; L = phosphorus ligand) and the use of these compounds in catalysis, although the majority of the work has been restricted to $[M(PPh_3)_n]$, n = 3 or 4.[1] The range of compounds available has been increased by the recent development of a general synthetic method for $[PdL_n]$, n = 2, 3, or 4, based on $[\{Pd(\eta^3\text{-}C_4H_7)Cl\}_2]$.[2] The stoicheiometry and preliminary results on the catalytic properties [3] of these compounds were found to depend on the nature of the tertiary phosphine, but the causes of this dependence deserve further studies. A ^{31}P n.m.r. investigation [4] has permitted in general the determination of the stoicheiometry of $[PdL_n]$ in solution and the activation parameters for ligand exchange, but an accurate study was hampered by the similarity of the ^{31}P chemical shifts of the species in equilibrium.

We have now investigated the solution properties of $[PtL_n]$ complexes, as the presence of $^1J(^{195}Pt\text{-}^{31}P)$ and slower rates of ligand exchange permit a more detailed investigation than for the analogous $[PdL_n]$ compounds. Previous investigations of the equilibria and kinetics of phosphorus-ligand exchange in $[PtL_n]$ systems have been limited to $[Pt\{P(OEt)_3\}_4]$,[5] $[Pt(PR'_3)_4]$,[6] $[Pt(PR'_3)_3]$,[6,7] and $[Pt(PBu^t{}_2Ph)_2]$[8] (R′ = aryl group).

When this work commenced there were methods available for the preparation of specific $[Pt(PR_3)_n]$ compounds yielding $[Pt(PMe_3)_4]$, $[Pt(PMe_2Ph)_4]$, $[Pt(PMePh_2)_4]$, $[Pt(PEt_3)_3]$, $[Pt(PEt_3)_4]$, $[Pt(PR'_3)_3]$, and $[Pt(PR'_3)_4]$.[1,9-13] Subsequently, the preparation of $[Pt(PPr^i{}_3)_3]$, $[Pt(PPr^i{}_3)_2]$, $[Pt\{P(C_6H_{11})_3\}_3]$, $[Pt\{P(C_6H_{11})_3\}_2]$, and $[Pt(PBu^t{}_2Ph)_2]$ have been published either in notes resulting from the present work [14,15] or by other authors.[16,17]

This group of complexes provides a series which allows the investigation of the effect of the size of the phosphorus ligand on the stability of the compound. The ligand size may be quantified either in terms of cone angle as proposed by Tolman [1a] or solid cone angle [18] thus providing a quantitative measurement of the bulk of a tertiary phosphine for comparison with the thermodynamic data from the present investigation.

EXPERIMENTAL

The preparation of the air-sensitive $[PtL_n]$ complexes was carried out under an inert atmosphere of nitrogen purified by passage through Alfa Inorganics De Ox catalyst. Solvents were degassed before use. The n.m.r. tubes were prepared using vacuum-line techniques. Hydrogen-1 n.m.r. spectra were recorded at 100 MHz (Varian HA100), 90 MHz (Bruker HFX-90), or 270 MHz (Bruker HX-270). The ^{31}P n.m.r. spectra were obtained on a JEOL PS-100 n.m.r. spectrometer in 10 mm tubes, sealed under high vacuum, with an internal ^2H reference. High frequency is taken as being positive. At least 10 min were allowed for temperature equilibration. Temperatures were measured by inserting an open tube containing toluene or nitrobenzene into the probe and measuring the temperature after equilibrium using a thermocouple (Comark electronic thermometer). In most cases, the ^{31}P n.m.r. spectra were measured every 10 °C from the freezing point to *ca.* 20 °C above the boiling point of the solvent.

The lineshape analysis was performed using a computer program designed to solve the standard complex rate matrix.[19] Two forms of analysis were used. When only one type of $[Pt(PR_3)_n]$ species was present the problem was treated as a four-site exchange problem with exchange between each of the three signals due to the platinum complex and the free tertiary phosphine. The exchange rate between the three phosphorus signals of the platinum complex was set equal to zero. In solutions containing no free tertiary phosphine a very low concentration of free tertiary phosphine, 0.001%, was assumed to avoid difficulties with infinite rates. Calculation as a three-site problem showed that this procedure did not affect the calculation but avoided making corrections to the rate, *i.e.* when a tertiary phosphine leaves $[^{195}Pt(PR_3)_n]$ to give $[^{195}Pt(PR_3)_{n-1}] + PR_3$ there is a 66% chance that it will co-ordinate to a n.m.r.-inactive platinum isotope. When both $[Pt(PR_3)_n]$ and $[Pt(PR_3)_{n-1}]$ were present, the problem was treated as a seven-site exchange problem, with once again no exchange permitted within a $[Pt(PR_3)_n]$ species and the retention of platinum spin during exchange.

Elemental analyses were performed by F. Pascher, Mikroanalytisches Laboratorium, Bonn. The compound $PBu^t{}_2Ph$ was prepared according to Shaw and co-workers.[20] All the other tertiary phosphines were commercially available (Strem) and were used without further purification.

Tetrakis(allylchloroplatinum) was prepared according to the method given by Lukas.[21]

The complexes $[\mathrm{Pt(PMePh_2)_4}]$ and $[\mathrm{Pt(PMe_2Ph)_4}]$ were prepared according to Clark and Itoh,[11] [Pt(*p*-tolyl)$_3$] was prepared according to Tolman *et al.*,[6] and *trans*-$[\mathrm{PtCl_2(PPr^i_3)_2}]$ was prepared following Leviston and Wallbridge.[22]

Tetrakis(tri-n-butylphosphine)platinum(0).—The compound $[\{\mathrm{Pt(allyl)Cl}\}_4]$ (2.33 g, 2.15 mmol) was suspended in methanol (20 cm^3). The suspension was cooled to −80 °C, $\mathrm{PBu^n_3}$ (11 g, 54 mmol) added, and then slowly warmed to room temperature. The clear yellow solution obtained was left overnight at room temperature. The methanol was evaporated in high vacuum, and the red-orange oily residue was extracted with pentane (30 cm^3). The pentane solution was gradually cooled from −20 to −60 °C to yield large white prismatic crystals. The pentane was siphoned off at −60°C, the crystals were washed with cold pentane, and dried at −80 °C in high vacuum (4.4 g, 51% yield). At room temperature the compound is an orange-red oil (Found: C, 57.8; H, 10.9; P, 12.2; Pt, 19.4. Calc. for $\mathrm{C_{48}H_{108}P_4Pt}$: C, 57.4; H, 10.85; P, 12.35; Pt, 19.4%).

Tris(tri-n-butylphosphine)platinum(0).—The compound $[\mathrm{Pt(PBu^n_3)_4}]$ was kept for 4 h at 70 °C in high vacuum (10^{-6} mmHg).* One molecule of tertiary phosphine was quantitatively lost to yield an orange-red oil.

Tetrakis(triethylphosphine)platinum(0).—This compound may be prepared starting from $[\{\mathrm{Pt(allyl)Cl}\}_4]$ by following the synthesis given above for $[\mathrm{Pt(PBu^n_3)_4}]$. However, it is more convenient to follow the preparative method described by Pearson *et al.*[12] Pure $[\mathrm{Pt(PEt_3)_4}]$ may be obtained by crystallizing the crude product (orange oil) resulting from this reaction after evaporation of the solvent, from acetone in the presence of the tertiary phosphine. Starting from $\mathrm{K_2[PtCl_4]}$ (6 g) and crystallizing from acetone (60 cm^3) containing $\mathrm{PEt_3}$ (3 cm^3), large white crystals were obtained on cooling slowly from room temperature to −30 °C. The solvent was siphoned off, the crystals were washed with cold acetone, and dried in high vacuum (10^{-6} mmHg) at −40 °C (7.3 g, 75% yield).

Tris(triethylphosphine)platinum(0) was obtained by melting $[\mathrm{Pt(PEt_3)_4}]$ in high vacuum according to Muetterties and co-workers.[9]

Tetrakis(trimethylphosphine)platinum(0).—Platinum(II) chloride (2.03 g, 7.64 mmol) was suspended in tetrahydrofuran (thf) (35 cm^3) and $\mathrm{PMe_3}$ (4.1 g, 54 mmol) dissolved in thf (30 cm^3) was added. The mixture was refluxed for 2 h. The white ivory suspension so obtained was siphoned onto potassium amalgam (1%, *ca.* 300 g) and mechanically stirred at room temperature overnight. The thf solution was siphoned off and evaporated. The grey residue was extracted with heptane in small portions (*ca.* 60 cm^3). The heptane solution was concentrated (*ca.* 5 cm^3) and cooled to −80 °C when white needles were obtained. The solution was siphoned off, the crystals washed with cold pentane (−80 °C), and dried (*ca.* 0.9 g, 23% yield) (Found: C, 29.0; H, 7.2; P, 24.9; Pt, 39.25. Calc. for $\mathrm{C_{12}H_{36}P_4Pt}$: C, 28.85; H, 7.25; P, 24.8; Pt, 39.05%).

Tris(tri-isopropylphosphine)platinum(0).—The compound $[\mathrm{PtCl_2(PPr^i_3)_2}]$ (4.0 g, 6.8 mmol), $\mathrm{PPr^i_3}$ (2.4 g, 15 mmol), and potassium amalgam (1%, 300 g) were mechanically stirred overnight in thf (70 cm^3). The red thf solution was siphoned off and the solvent was removed *in vacuo*. The residue was extracted with pentane (50—60 cm^3). On cooling the red pentane solution to −80 °C, yellow crystals separated out. The solvent was siphoned off and the crystals were washed with cold pentane (80 °C). After recrystallization from pentane and drying (10^{-3} mmHg, −30 °C), very air sensitive yellow crystals were obtained (*ca.* 1 g, *ca.* 21% yield) (Found: C, 48.1; H, 9.40; P, 13.6; Pt, 29.1. Calc. for $\mathrm{C_{27}H_{63}P_3Pt}$: C, 48.0; H, 9.40; P, 13.75; Pt. 28.85%).

Bis(tri-isopropylphosphine)platinum(0).—The compound $[\mathrm{Pt(PPr^i_3)_3}]$ loses quantitatively one molecule of $\mathrm{PPr^i_3}$ when melted *in vacuo*, analogously to $[\mathrm{Pd(PPr^i_3)_3}]$, to yield a red-orange oily material which was recognized to be pure $[\mathrm{Pt(PPr^i_3)_2}]$ by comparison of the ^{1}H n.m.r. spectrum with that of the analogous palladium complex.

1—3-η-*Allylbis(tricyclohexylphosphine)platinum*(II) *Hexafluorophosphate*.—The compound $[\{\mathrm{Pt(allyl)Cl}\}_4]$ (3.00 g, 2.77 mmol) was suspended in thf (120 cm^3) and $\mathrm{P(C_6H_{11})_3}$ (3.10 g, 11.07 mmol) dissolved in thf (25 cm^3) was added. A clear pale yellow solution was obtained on heating in a warm water-bath for a few minutes. Silver hexafluorophosphate (2.80 g, 11.07 mmol) dissolved in thf (35 cm^3) was added and AgCl immediately formed. After stirring at room temperature for a few minutes, the suspension was filtered, and, to the clear yellow solution, was added $\mathrm{P(C_6H_{11})_3}$ (3.10 g, 11.07 mmol) dissolved in thf (25 cm^3). The solution was concentrated (*ca.* 150 cm^3) up to the formation of a white crystalline material and diethyl ether was slowly added (400 cm^3). The white crystals were filtered off, washed with toluene, then diethyl ether, and dried *in vacuo* (8.80 g, yield 84.4%). The complex was found (^{1}H n.m.r. spectrum) to be identical with that reported by Attig and Clark.[23]

1—3-η-Allylbis(tribenzylphosphine)platinum(II) hexafluorophosphate was prepared analogously to $[\mathrm{Pt(\eta^3\text{-}C_3H_5)\{P(C_6H_{11})_3\}_2][PF_6]}$. The pure product was obtained by crystallization from acetone–diethyl ether, and was identified by the ^{1}H n.m.r. spectrum.

Tris(tribenzylphosphine)platinum(0).—The salt $[\mathrm{Pt(\eta^3\text{-}C_3H_5)\{P(CH_2Ph)_3\}_2][PF_6]}$ (1.24 g, 1.25 mmol) and $\mathrm{P(CH_2Ph)_3}$ (381 mg, 1.25 mmol) were suspended in absolute methanol (50 cm^3) and sodium methoxide (4 cm^3, 1.38 mol dm^{-3}) was added. The suspension was stirred and kept at 50 °C for 1 h. A yellow solid formed. The mixture was stirred at room temperature overnight. The yellow solid was filtered off, washed with methanol, dried *in vacuo*, and then extracted with toluene (40 cm^3). The toluene solution was concentrated (20 cm^3) and on crystallization at −30 °C yellow crystals were obtained. The mother-liquor was siphoned off, the crystals were washed with toluene–heptane (1 : 1) and dried *in vacuo* (600 mg, 43% yield) (Found: C, 68.45; H, 5.60; P, 8.35; Pt, 17.65. Calc. for $\mathrm{C_{63}H_{63}P_3Pt}$: C, 68.3; H, 5.75; P, 8.40; Pt, 17.6%).

Bis(tricyclohexylphosphine)platinum(0).—The compound $[\{\mathrm{Pt(allyl)Cl}\}_4]$ (810 mg, 0.745 mmol) was suspended in thf (25 cm^3) and then $\mathrm{P(C_6H_{11})_3}$ (1.67 g, 5.9 mmol) dissolved in thf (25 cm^3) was added to yield a pale yellow solution. Potassium t-butoxide (1.36 g, 12.1 mmol) was added to the solution. The mixture was heated at 65 °C overnight and then cooled to room temperature. The thf was evaporated *in vacuo* and the pale yellow residue was dried, heating with warm water for 2 h. The residue was then extracted with warm heptane (50 cm^3) and slowly filtered through sinter frits (G3 and then G4). Pale yellow prismatic crystals were obtained by slowly cooling to room temperature. The heptane was siphoned off and the crystals were washed with pentane and dried *in vacuo* (530 mg). Upon concentration of the mother-liquor (*ca.* 15 cm^3) more

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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa; 1 cal = 4.184 J

crystals were obtained at room temperature and then at 0 °C (350 mg). Overall yield is 39% based on platinum (Found: C, 57.4; H, 8.85; P, 8.10; Pt, 25.5. Calc. for $C_{36}H_{66}P_2Pt$: C, 57.2; H, 8.80; P, 8.20; Pt, 25.8%).

The compound $[Pt\{P(C_6H_{11})_3\}_2]$ may also be obtained in comparable yield by treating $[Pt(\eta^3\text{-}C_3H_5)\{P(C_6H_{11})_3\}_2][PF_6]$ with $K[OBu^t]$ in thf.

Tris(tricyclohexylphosphine)platinum(0).—The compound $[Pt\{P(C_6H_{11})_3\}_2]$ (0.39 g, 0.52 mmol) and $P(C_6H_{11})_3$ (0.31 g, 1.11 mmol) were mixed in heptane (5 cm³). On cooling to −80 °C the solution became deep yellow. Yellow crystals were obtained upon crystallization which contain heptane in the lattice (Pt : heptane is 1 : 1.5) as shown by *X*-ray crystallography [15] (Found: C, 65.35; H, 10.30; P, 7.90; Pt, 16.45. Calc. for $[Pt\{P(C_6H_{11})_3\}_3]\cdot 1.5C_7H_{16}$ ($C_{64.5}H_{123}P_3Pt$): C, 65.3; H, 10.45; P, 7.85; Pt, 16.45%).

Bis(phenyldi-t-butylphosphine)platinum(0).—The compound $[\{Pt(allyl)Cl\}_4]$ (1.0 g, 0.93 mmol) was suspended in thf (30 cm³) and PBu^t_2Ph (2.12 g, 8.0 mmol) was added. A yellowish solution was obtained upon heating with warm water. Potassium t-butoxide (1.8 g, 16.0 mmol) was added. The mixture was heated overnight at 60 °C. The thf was evaporated *in vacuo*. The brownish residue was extracted with toluene (25 cm³) and slowly filtered through sinter frits (G3 and then G4). The toluene solution was evaporated *in vacuo* and the orange-brown oily residue was pumped in high vacuum at 65 °C. The material, which after this vacuum treatment is semi-solid, was dissolved in heptane (25 cm³) and filtered. Pale yellow crystals were obtained upon cooling at −20 °C. The mother-liquor was siphoned off, the crystals washed with pentane, and dried *in vacuo* (0.65 g). Additional crystalline material was obtained upon concentration of the mother-liquor (0.15 g). Overall yield 34% based on platinum (Found: C, 52.5; H, 7.35; P, 9.40; Pt, 30.85. Calc. for $C_{28}H_{46}P_2Pt$: C, 52.6; H, 7.25; P, 9.70; Pt, 30.55%).

RESULTS

Preparation of Complexes.—The complex $[Pt(PMe_3)_4]$ has been previously prepared by treating $[Pt(B_3H_7)(PMe_3)_2]$ with PMe_3.[10] It proved to be more convenient to prepare $[Pt(PMe_3)_4]$, and then the unknown complexes, $[Pt(PPr^i_3)_2]$ and $[Pt(PPr^i_3)_3]$, by the reduction of $[PtCl_2L_2]$ ($L = PMe_3$ or PPr^i_3) with potassium amalgam in the presence of free ligand following essentially the method described by Schunn [13] for the preparation of $[Pt(PEt_3)_4]$. The latter is conveniently prepared as described by Pearson *et al.*[12] by treating $K_2[PtCl_4]$ with PEt_3 and potassium hydroxide. We found that $[Pt(PEt_3)_4]$ as well as $[Pt(PBu^n_3)_4]$ can also be prepared by treating $[\{Pt(allyl)Cl_3\}_4]$ with an excess of the tertiary phosphine in CH_3OH. This preparative method parallels the one previously reported by us for the palladium analogues.[2] Analogously to the palladium complexes, $[Pt(PEt_3)_4]$ and $[Pt(PBu^n_3)_4]$ lose quantitatively 1 mol of tertiary phosphine *in vacuo*.[9,13] The complex $[Pt\{P(CH_2Ph)_3\}_3]$ is prepared by treating $[Pt(\eta^3\text{-}C_3H_5)\{P(CH_2Ph)_3\}_2][PF_6]$ in methanol with sodium methoxide in the presence of $P(CH_2Ph)_3$. A similar method was attempted for preparing $[Pt\{P(C_6H_{11})_3\}_2]$. However, the reaction of $[Pt(\eta^3\text{-}C_3H_5)\{P(C_6H_{11})_3\}_2][PF_6]$ with sodium methoxide in methanol gave *trans*-$[PtH_2\{P(C_6H_{11})_3\}_2]$ in high yields.[24] Under these reaction conditions the hydrido-complex could be formed through oxidative addition of methanol to $[Pt\{P(C_6H_{11})_3\}_2]$ and subsequent β-hydrogen elimination. In fact, $[Pt\{P(C_6H_{11})_3\}_2]$ does react with methanol to yield the bis-hydrido-complex.[8,14] The complex $[Pt\{P(C_6H_{11})_3\}_2]$ was therefore prepared in thf either from $[Pt(\eta^3\text{-}C_3H_5)\{P(C_6H_{11})_3\}_2][PF_6]$ or $[\{Pt(allyl)Cl\}_4]$ and potassium t-butoxide in the presence of stoicheiometric amounts of $P(C_6H_{11})_3$. This latter reaction route was followed for preparing $[Pt(PBu^t_2Ph)_2]$. Stone and co-workers [16] have prepared $[Pt\{P(C_6H_{11})_3\}_2]$ from $[Pt(cod)_2]$ (cod = η^4-cycloocta-1,5-diene) and $P(C_6H_{11})_3$. Otsuka *et al.*[17] have recently reported the preparation of $[PtL_2]$ [$L = P(C_6H_{11})_3$, PPr^i_3, or PBu^t_2Ph] by sodium-amalgam reduction of $[PtCl_2L_2]$.

N.M.R. Studies.—A number of 10 mm n.m.r. tubes containing various concentrations of the complex and/or free tertiary phosphine were made up, see Table 1. In each case, the samples were investigated in detail by variable-

TABLE 1

Samples used for the ^{31}P n.m.r. investigation of $[PtL_n]$, L = tertiary phosphine, n = 2, 3, or 4 *

(*a*) In toluene–$[^2H_8]$toluene 9 : 1 (v/v)

$[Pt(PMe_3)_4]$	0.051 1		
	0.050 1	PMe_3	0.100
	0.059 1		0.352
$[Pt(PMe_2Ph)_4]$	0.057 5		
	0.059 5	PMe_2Ph	0.101
	0.045 5		0.271
$[Pt(PMePh_2)_4]$	0.053 2		
	0.045 7	$PMePh_2$	0.067 4
	0.045 2		0.206
$[Pt\{P(p\text{-tolyl})_3\}_3]$	0.027 1		
	0.006 8		
$[Pt(PEt_3)_3]$	0.074 9		
	0.083 1		
	0.068 1	PEt_3	0.040 6
$[Pt(PEt_3)_4]$	0.067 4		
	0.015 0		
	0.007 49		
	0.040 4	PEt_3	0.040 6
$[Pt(PBu^n_3)_3]$	0.049 9		
$[Pt(PBu^n_3)_4]$	0.042 3		
	0.008 96		
	0.064 2	PBu^n_3	0.129
	0.079 7		0.953
$[Pt\{P(CH_2Ph)_3\}_3]$	0.033 2		
	0.040 1	$P(CH_2Ph)_3$	0.043 5
	0.036 9		0.251
	0.039 6		1.117
$[Pt(PPr^i_3)_2]$	0.078 6		
$[Pt(PPr^i_3)_3]$	0.051 1		
	0.068 8	PPr^i_3	0.112
	0.074 0		0.369
$[Pt\{P(C_6H_{11})_3\}_2]$	0.056 9		
	0.047 0	$P(C_6H_{11})_3$	0.033 9
	0.050 3		0.119 5
	0.054 9		0.269 2
$[Pt(PBu^t_2Ph)_2]$	0.028 1		
	0.071 9	PBu^t_2Ph	0.128

(*b*) In tetrahydrofuran–$[^2H_{12}]$cyclohexane 8 : 1 (v/v)

$[Pt\{P(C_6H_{11})_3\}_2]$	0.023 1		
	0.035 4	$P(C_6H_{11})_3$	0.059 0

(*c*) In n-heptane–$[^2H_{12}]$cyclohexane 10 : 1 (v/v)

$[Pt(PEt_3)_3]$	0.037 2		
$[Pt\{P(C_6H_{11})_3\}_2]$	0.017 3		
	0.028 9	$P(C_6H_{11})_3$	0.067 9

(*d*) In n-octane–$[^2H_{12}]$cyclohexane 8 : 1 (v/v)

$[Pt(PMe_3)_4]$	0.029 0	PMe_3	0.032 9
	0.028 0		0.065 7
$[Pt(PMe_2Ph)_4]$	0.032 8	PMe_2Ph	0.068 8
$[Pt(PEt_3)_4]$	0.035 9		
$[Pt(PPr^i_3)_3]$	0.033 3		

* Values are concentrations in mol dm⁻³. A 2 cm³ solution was used in each case.

temperature ^{31}P n.m.r. spectra. In most cases two solvents were used, toluene and octane or heptane, or in the case of L = $P(C_6H_{11})_3$, toluene, heptane, and thf. A limited ^1H n.m.r. investigation was also performed. As each tertiary phosphine used in this investigation produced rather different results, they will be discussed separately. The ^{31}P chemical shifts and coupling constants are collected in Table 2 while the thermodynamic parameters are collected in Table 3. Unless otherwise stated, the variable-temperature n.m.r. spectra are reversible.

TABLE 2

Phosphorus-31 n.m.r. data for $[Pt(PR_3)_n]$

Complex	θ_c/°C	$\delta(^{31}P)$/ p.p.m.	$\Delta\delta$/ p.p.m.[a]	$^1J(^{195}Pt-^{31}P)$/Hz
(*a*) In toluene				
$[Pt(PMe_3)_4]$	−74	−53.3	9.2	3 828
$[Pt(PMe_2Ph)_4]$	−74	−34.2	12.9	3 805
$[Pt(PMePh_2)_4]$	−74	−14.8	13.4	3 802
$[Pt\{P(p\text{-tolyl})_3\}_3]$	−74	48.8		4 443
$[Pt(PEt_3)_4]$	−74	−18.1	4.6	3 723
$[Pt(PEt_3)_3]$	−74	41.3	64.0	4 188
$[Pt(PBu^n_3)_4]$	−74	−26.0	7.7	3 700
$[Pt(PBu^n_3)_3]$	−74	31.8	65.6	4 211
$[Pt\{P(CH_2Ph)_3\}_3]$	−74	34.5	45.5	4 377
$[Pt(PPr^i_3)_3]$	−74	64.4	49.2	4 260
$[Pt(PPr^i_3)_2]$	−74	70.7	55.5	4 104
$[Pt\{P(C_6H_{11})_3\}_3]$	−74	53.2	45.0	4 228
$[Pt\{P(C_6H_{11})_3\}_2]$	−74	61.9	53.6	4 120
$[Pt(PBu^t_2Ph)_2]$	−74	83.6	48.3	4 592
(*b*) In heptane				
$[Pt(PEt_3)_3]$	24	42.2	64.9	4 231
$[Pt\{P(C_6H_{11})_3\}_3]$	−52	54.5	43.3	4 229
$[Pt\{P(C_6H_{11})_3\}_2]$	24	63.8	52.6	4 227
(*c*) In octane				
$[Pt(PMe_3)_4]$	−62	−51.9	10.6	3 838
$[Pt(PMe_2Ph)_4]$	−62	−33.2	13.9	3 809
$[Pt(PEt_3)_4]$	−62	−16.9	5.8	3 729
$[Pt(PEt_3)_3]$	−48	43.6	66.3	*b*
$[Pt(PPr^i_3)_3]$	−62	65.6	50.4	4 271
$[Pt(PPr^i_3)_2]$	−62	72.8	57.6	4 202
(*d*) In tetrahydrofuran				
$[Pt\{P(C_6H_{11})_3\}_2]$	24	63.6	52.4	4 192

[a] Co-ordination shifts. [b] Too broadened by exchange to measure.

PMe_3. Only $[Pt(PMe_3)_4]$ could be synthesized and at room temperature only a slightly broadened 1 : 4 : 1 triplet, which sharpens on cooling, is observed in the ^{31}P n.m.r. spectrum. On heating, the 1 : 4 : 1 triplet broadens and collapses to a broad singlet. Lineshape analysis was performed to derive the rate of exchange. No dependence of the rate of exchange on solvent (toluene or n-octane) or on the concentration of added PMe_3 was found. Consequently the $[Pt(PMe_3)_4]$ is undergoing dissociative exchange *via* $[Pt(PMe_3)_3]$ and PMe_3. No evidence was found for the presence of a significant concentration of $[Pt(PMe_3)_3]$. There was, however, significant decomposition of $[Pt(PMe_3)_4]$ in octane on heating especially in the absence of added PMe_3.

The ^1H n.m.r. spectrum of $[Pt(PMe_3)_4]$, containing an excess of PMe_3, at 0 °C shows a sharp doublet, $^2J(^{31}P-^1H)$ = 2.7 Hz at δ 0.82 due to free PMe_3 and a broad multiplet at δ 1.35 with well resolved platinum coupling, $^3J(^{195}Pt-^1H)$ = 19 Hz. On warming to room temperature, the signals broaden due to the commencement of exchange.

PMe_2Ph. The behaviour of $[Pt(PMe_2Ph)_4]$ is very similar to that already described for $[Pt(PMe_3)_4]$. For $[Pt(PMe_2Ph)_4]$, $\delta(CH_3)$ is 1.40 with $^3J(^{195}Pt-^1H)$ = 19 Hz.

$PMePh_2$. According to earlier reports,[11] although $[Pt(PMePh_2)_4]$ is stable in the solid state, it is extensively dissociated in solution to give $[Pt(PMePh_2)_3]$ and $PMePh_2$, even at −30 °C. In agreement with this work, we find that $[Pt(PMePh_2)_4]$ may be prepared and analyses as the tetrakis compound. However, at room temperature the ^1H n.m.r. spectrum in $[^2H_8]$toluene showed only a singlet at δ 1.72 due to the methyl protons, a multiplet at δ 7.20 due to the *o*-protons, and a multiplet at δ 6.92 due to the *m*- and *p*-protons of the phenyl ring. On cooling to −30 °C, the platinum satellites of the methyl group at δ 1.70 became resolved with $^3J(^{195}Pt-^1H)$ = 19 Hz. There is no signal due to free $PMePh_2$. Addition of $PMePh_2$ at −40 °C did not affect the $[Pt(PMePh)_4]$ resonance but merely produced a doublet, $^2J(^{31}P-^1H)$ = 4 Hz, at δ 1.23 and caused severe overlapping of the signals in the phenyl region of the spectrum. The ^{31}P n.m.r. spectrum confirmed these observations. At room temperature, the ^{195}Pt satellites were significantly broadened for $[Pt(PMePh_2)_4]$ at $\delta -13.7$ and no signal was detected in the position due to free $PMePh_2$. On cooling to −17 °C, the platinum satellites sharpened, but the ^{31}P chemical shift did not change markedly, $\delta -14.3$, with $^1J(^{195}Pt-^{31}P)$ = 3 801 Hz. Examination of the data in Table 2 shows that $[Pt(PR_3)_4]$ compounds have ^{31}P co-ordination shifts of *ca.* 10 p.p.m. to high frequency while $[Pt(PR_3)_3]$ compounds have ^{31}P co-ordination shifts of *ca.* 60 p.p.m. to high frequency. For $[Pt(PMePh_2)_4]$ the co-ordination shift is 13.2 p.p.m. to high frequency confirming tetrakis rather than tris co-ordination. Additional evidence for tetrakis co-ordination comes from $J(^{195}Pt-^{31}P)$; for $[Pt(PR_3)_4]$, $^1J(^{195}Pt-^{31}P)$ is *ca.* 3 800 Hz while for $[Pt(PR_3)_3]$, $^1J(^{195}Pt-^{31}P)$ is *ca.* 4 200 Hz. For $[Pt(PMePh_2)_4]$, $^1J(^{195}Pt-^{31}P)$ is 3 801 Hz. It is therefore concluded that, contrary to an earlier report, $[Pt(PMePh_2)_4]$ does not dissociate.

However, as the sample in toluene is warmed, the ^{31}P chemical shift remains reasonably constant ($\delta -14.3$ at −80, −13.7 at 24.5 °C), but after coalescence, at *ca.* 70 °C, the signal begins to move to high frequency. This behaviour is not observed for the other compounds examined, and is probably due to dissociation to $[Pt(PMePh_2)_3]$ and $PMePh_2$. If it is assumed that the ^{31}P chemical shift of $[Pt(PMePh_2)_3]$ is 50 p.p.m. to high frequency of $[Pt(PMePh_2)_4]$ by analogy to $[Pt(PR_3)_3]$–$[Pt(PR_3)_4]$ (R = Et, Bu^n, or *p*-tolyl), see Table 2, then the averaged chemical shift may be used to give an equilibrium constant, using the equations (1)—(4).

$$\begin{aligned}\delta_{obs.} = {} & (4\delta\{Pt(PMePh_2)_4\}[Pt(PMePh_2)_4] \\ & + 3\delta\{Pt(PMePh_2)_3\}[Pt(PMePh_2)_3] \\ & + \delta(PMePh_2)[PMePh_2])/(4[Pt(PMePh_2)_4] \\ & + 3[Pt(PMePh_2)_3] + [PMePh_2]) \qquad (1)\end{aligned}$$

$$[Pt(PMePh_2)_4]_0 = [Pt(PMePh_2)_4] + [Pt(PMePh_2)_3] \qquad (2)$$

$$[PMePh_2] = [PMePh_2]_0 + [Pt(PMePh_2)_3] \qquad (3)$$

$$K = [Pt(PMePh_2)_3][PMePh_2]/[Pt(PMePh_2)_4] \qquad (4)$$

Reasonable agreement was found for the calculated *equilibrium constant* as a function of $PMePh_2$ concentration. From the temperature dependence of the equilibrium constant, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ were calculated. At moderate temperatures, 0—70 °C, the rate of exchange was independent of added $PMePh_2$ concentration, consistent with dissociative exchange of $[Pt(PMePh_2)_4]$. At higher temperatures, the problem became complicated by the partial dissociation of $[Pt(PMePh_2)_4]$. Attempts to isolate $[Pt(PMePh_2)_3]$ by

TABLE 3

Thermodynamic parameters for the equilibrium $[Pt(PR_3)_{n+1}] \rightleftharpoons [Pt(PR_3)_n] + PR_3$ [a]

			Dissociation					Association				
PR_3	n	Solvent [b]	$\Delta H^{\ominus}$/kcal mol^{-1}	$\Delta S^{\ominus}$/cal K^{-1} mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{300}$/kcal mol^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{300}$/kcal mol^{-1}	Tolman [c] cone angle/°	Solid angle [d]
PMe_3	3	Toluene			13.87 ±0.13	−6.6 ±0.4	15.85 ±0.17				118	
	3	Octane			14.35 ±0.17	−4.8 ±0.5	15.8 ±0.2				118	
PMe_2Ph	3	Toluene			14.35 ±0.10	−4.4 ±0.3	15.68 ±0.14				122	2.90
	3	Octane			14.06 ±0.26	−5.1 ±0.8	15.6 ±0.3				122	2.90
$PMePh_2$	3	Toluene	15.1 ±1.0	27.7 ±2.7	15.60 ±0.06	6.3 ±0.2	13.7 ±0.1	0.5 ±1.1 [h]	−21 ±3 [h]	6.8 ±2.0 [h]	136	3.16
PEt_3	3	Toluene	15.2 ±0.6	54.3 ±2.8	16.2 ±0.7 [e]	22.9 ±3.2 [e]	9.3 ±1.7 [e]	0.92 ±0.12	−31.4 ±0.4	10.35 ±0.16	132	3.39
	3	Octane	14.3 ±0.7	48.9 ±3.8	14.8 ±0.9 [e]	11.3 ±4.4 [e]	11.4 ±2.2 [e]	0.47 ±0.16	−37.6 ±0.6	11.76 ±0.07	132	3.39
PBu^n_3	3	Toluene	16.8 ±0.5	63.3 ±2.4	17.0 ±0.5 [e]	22.9 ±2.6 [e]	10.1 ±1.3 [e]	0.15 ±0.04	−40.0 ±0.2	12.3 ±0.1	132	
	2	Toluene			11.2 ±0.3 [f]	−18.9 ±0.8	16.8 ±0.4				132	
$P(CH_2Ph)_3$	2	Toluene			15.26 ±0.16	−5.7 ±0.5	17.0 ±0.2				165	
PPr^i_3	2	Toluene	10.1 ±0.2	40.5 ±1.0	13.9 ±0.3 [e]	12.6 ±1.2 [e]	10.1 ±0.6 [e]	3.79 ±0.05	−27.88 ±0.17	12.16 ±0.07	160	3.96
	2	Octane	13.2 ±0.5	48.6 ±2.3	15.3 ±0.1 [e]	12.7 ±2.5 [e]	11.5 ±0.9 [e]	2.09 ±0.06	−36.1 ±0.2	+12.90 ±0.09	160	3.96
$P(C_6H_{11})_3$	2	Toluene	13.1 ±0.6	48.4 ±2.2	15.6 ±0.7 [e]	16.2 ±2.4 [e]	10.7 ±1.5 [e]	2.54 ±0.07	−32.21 ±0.21	12.20 ±0.09	170	4.42
	2	Heptane	13.8 ±0.7	47.4 ±2.7	14.9 ±1.1 [e]	7.6 ±4.0 [e]	11.6 ±2.7 [e]	1.12 ±0.40	−39.8 ±1.3	13.1 ±0.2	170	4.42
PBu^n_2Ph [g]	2	Anisole						12.1	−29.3	20.1	170	4.68

[a] The quoted errors are for one standard deviation. [b] The toluene contains 10% $[^2H_8]$toluene, while the heptane or octane contains *ca.* 10% $[^2H_{12}]$cyclohexane. [c] Ref. 1*a*. [d] Ref. 18. [e] Calculated from $\Delta H^{\ominus}$, $\Delta S^{\ominus}$, and the association activation parameters. [f] Data are suspect due to possible competing associative exchange. [g] Averaged from ref. 8. [h] Calculated from $\Delta H^{\ominus}$, $\Delta S^{\ominus}$, and the dissociation activation parameters.

pumping off the fourth $PMePh_2$ ligand from $[Pt(PMePh_2)_4]$ resulted in the loss of 2 mol of $PMePh_2$ per mol of $[Pt(PMePh_2)_4]$ to give a mixture of unidentified products.

The complex $[Pt(PMePh_2)_4]$ was not investigated in n-octane on account of its poor solubility in this solvent.

PEt_3. With PEt_3 as the tertiary phosphine, $[Pt(PEt_3)_4]$ was isolated, which when melted in high vacuum yielded $[Pt(PEt_3)_3]$ as previously reported.[9,10,13] The ^1H and ^{31}P n.m.r. spectra are in reasonable agreement with the published values. The discrepancies are acceptable when it is realized that the ^{31}P n.m.r. data are solvent and temperature dependent. Thus for $[Pt(PEt_3)_3]$, in toluene at 24 °C, $\delta(^{31}P) = 41.5$ and $^1J(^{195}Pt-^{31}P) = 4\,211$ Hz, while at −74 °C, $\delta(^{31}P) = 41.3$ and $^1J(^{195}Pt-^{31}P) = 4\,188$ Hz; similarly in n-octane, at 24 °C, $\delta(^{31}P) = 42.2$ and $^1J(^{195}Pt-^{31}P) = 4\,229$ Hz, while at −48 °C, $\delta(^{31}P) = 43.6$ and $^1J(^{195}Pt-^{31}P) = 4\,220$ Hz. The temperature dependence for $[Pt(PEt_3)_4]$ is far less marked. The ^1H n.m.r. spectra of $[Pt(PEt_3)_4]$ in $[^2H_8]$toluene give signals at δ 1.06 (Me) and 1.55 (CH_2) while for $[Pt(PEt_3)_3]$ the signals are at δ 1.10 (Me) and 1.67 (CH_2).

The ^{31}P n.m.r. spectrum of $[Pt(PEt_3)_4]$ shows extensive broadening at room temperature. On cooling, separate signals are observed due to $[Pt(PEt_3)_3]$, $[Pt(PEt_3)_4]$, and PEt_3. It is therefore possible to determine the equilibrium constant as a function of temperature. At low temperatures it was easy to determine the relative concentrations of the species present by integration, but at higher temperatures integration of the exchange-broadened signals proved to be unreliable. Lineshape analysis was then used taking the rate of dissociation and the equilibrium constant as variables until a good match was obtained between the computed and observed spectra. Nevertheless, the temperature range over which reliable dissociation constants were obtained was small. This range was therefore extended by repeating the measurements on more dilute samples where $[Pt(PEt_3)_4]$ was more extensively dissociated and the exchange rate was slower. Analysis of the temperature dependence of the equilibrium constant yielded $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$. These measurements were repeated in n-octane. To a large extent the dissociation constant is the same as in toluene, see Figure 1, but is consistently smaller, by a factor of two. This greater stability of $[Pt(PEt_3)_4]$ compared $[Pt(PEt_3)_3]$ and PEt_3 in n-octane rather than toluene therefore appears to be genuine, albeit small. At higher temperatures severe

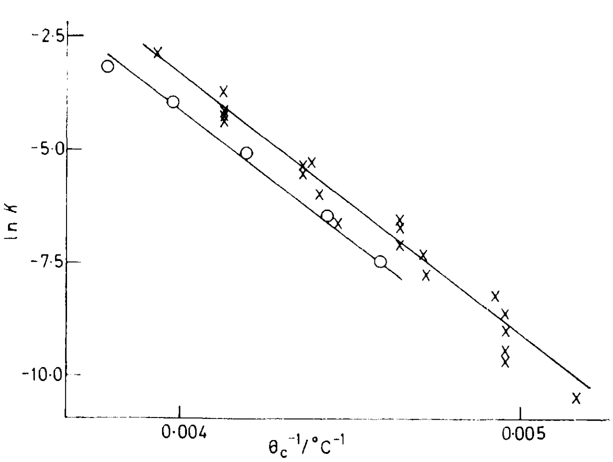

FIGURE 1 Dependence of ln*K* on inverse temperature for the dissociation $[Pt(PEt_3)_4] \rightleftharpoons [Pt(PEt_3)_3] + PEt_3$ in toluene (×) and in heptane (○)

exchange broadening is observed. The rate of exchange depends on the concentration of free PEt_3 showing that the exchange of PEt_3 for $[Pt(PEt_3)_3]$ is associative. Thus for a pure sample of $[Pt(PEt_3)_3]$ in toluene sharp ^{31}P n.m.r. signals are observed up to 50 °C, consistent with this interpretation. Above 50 °C, the ^{31}P n.m.r. signals due to 'pure' $[Pt(PEt_3)_3]$ broaden, even in the absence of a detectable amount of free PEt_3. Indeed the broadening is such at 98 °C that the required concentration of free PEt_3, *ca.* 0.01 mol dm^{-3}, would be readily detected at low temperatures in the form of $[Pt(PEt_3)_4]$. It is therefore concluded that either $[Pt(PEt_3)_3]$ or $[Pt(PEt_3)_3L]$ undergoes dissociative PEt_3 exchange where L is either the toluene solvent or a non-phosphorus containing impurity. Further confirmation of this observation comes from the linear dependence of the rate of PEt_3 exchange on PEt_3 concentration with a non-zero intercept. Hence $[Pt(PEt_3)_3]$ can undergo both associative and dissociative PEt_3 exchange. Rate data for associative exchange were only taken from measurements below 50 °C when dissociative exchange is slow. Nevertheless, it is possible that the calculated value of $\Delta H^{\ddagger}$ may be too large as a result of some contribution from dissociative exchange. Similarly rate data for dissociative exchange were determined only on samples which did not contain free PEt_3. However a trace of free PEt_3 would result in the calculated value of $\Delta H^{\ddagger}$ being too small. No allowance is made for these possible errors in calculating the errors given in Table 3. Only one sample in n-octane was examined. The rates for associative exchange of $[Pt(PEt_3)_3]$ at low temperatures are in good agreement with those measured in toluene, but are significantly smaller at high temperatures suggesting that dissociative exchange is either not occurring or is less significant.

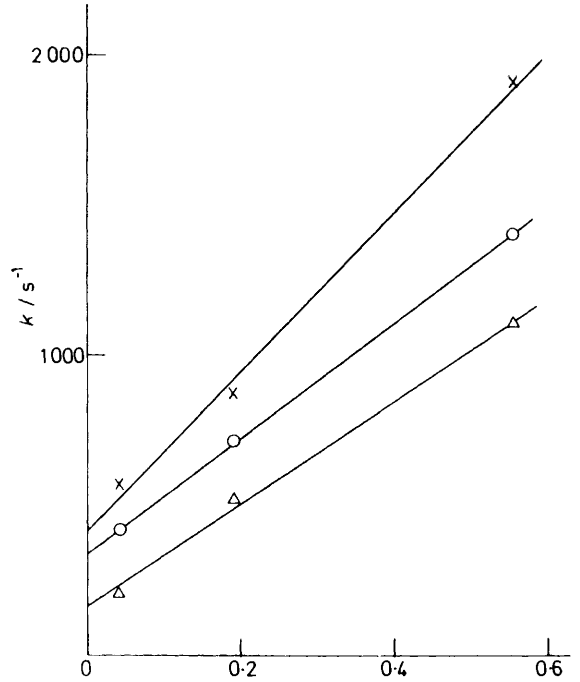

FIGURE 2 Dependence of the rate of PBu^n_3 exchange, k, on PBu^n_3 concentration at 83 (△), 99 (○), and 108 °C (×), for $[Pt(PBu^n_3)_3]$ in toluene

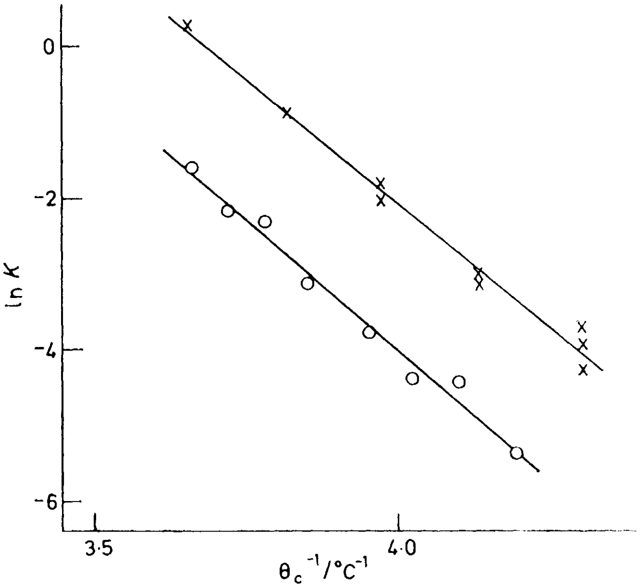

FIGURE 3 The dependence of ln$K$ on inverse temperature for the dissociation $[Pt\{P(C_6H_{11})_3\}_3] \rightleftharpoons [Pt\{P(C_6H_{11})_3\}_2] + P(C_6H_{11})_3$ in toluene (×) and in heptane (○)

PBu^n_3. On the whole the observations on $[Pt(PBu^n_3)_n]$ are very similar to those on $[Pt(PEt_3)_n]$. Thus it was possible to isolate both $[Pt(PBu^n_3)_3]$ and $[Pt(PBu^n_3)_4]$. The ^1H n.m.r. spectrum of $[Pt(PBu^n_3)_3]$ shows CH_2 signals at δ 1.77, 1.64, and 1.46 (apparent sextet J = 7.5 Hz) and the Me signal as a triplet, J = 7.5 Hz, at δ 1.00.

The variable-temperature ^{31}P n.m.r. spectra of the $[Pt(PBu^n_3)_n]$ species proved easier to analyse than those for $[Pt(PEt_3)_n]$ as the associative rate of exchange for $[Pt(PBu^n_3)_3]$ was significantly slower than for $[Pt(PEt_3)_3]$. The equilibrium between $[Pt(PBu^n_3)_3]$, $[Pt(PBu^n_3)_4]$, and PBu^n_3 could be followed more easily without severe exchange broadening and, perhaps more importantly, it was possible to plot the rate of PBu^n_3 exchange against PBu^n_3 concentration and obtain a straight line with a non-zero intercept (see Figure 2) proving that for $[Pt(PBu^n_3)_3]$ there is both associative and dissociative exchange.

The measurements were not repeated in n-octane on account of the similarity to the PEt_3 system.

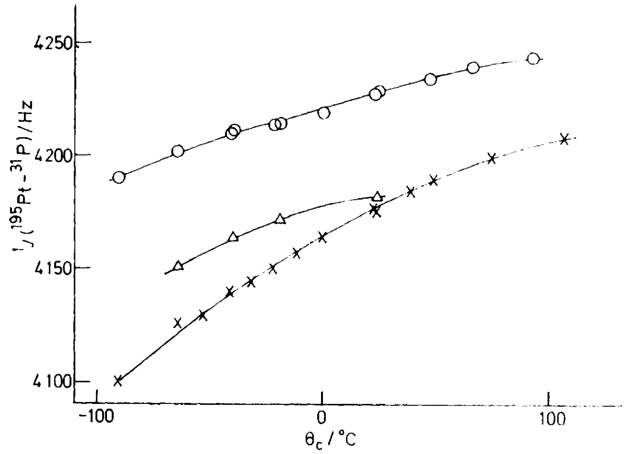

FIGURE 4 Temperature dependence of $^1J(^{195}Pt-^{31}P)$ for $[Pt\{P(C_6H_{11})_3\}_2]$ in toluene (×), heptane (○), and tetrahydrofuran (△)

$P(p\text{-tolyl})_3$. The complex $[Pt\{P(p\text{-tolyl})_3\}_3]$ was examined by ^{31}P n.m.r. spectroscopy. At room temperature the signals were somewhat broadened, but $^1J(^{195}Pt-^{31}P)$ was clearly visible, 4 467 Hz.[6] On warming, the rate of exchange increased slowly, consistent with a small value of $\Delta H^{\ddagger}$ and hence associative exchange but a four-fold dilution produced only a small reduction in the rate, *ca.* 30%, and when the heated sample was re-examined at room temperature the signal was then considerably broader (*ca.* 100%) than previously. It is therefore probable that heating produces decomposition of the compound with the liberation of free $P(p\text{-tolyl})_3$. This behaviour appears to be unique to this particular compound. As the compound is not stable in solution and the n.m.r. spectra are not reversible no conclusions may be drawn on the mechanism of exchange.

Solubility precluded measurements in n-octane.

$P(CH_2Ph)_3$. Only one complex, $[Pt\{P(CH_2Ph)_3\}_3]$, could be isolated. The ^1H n.m.r. spectrum showed that $P(CH_2Ph)_3$ exchange is slow at room temperature with $\delta(CH_2)$ 2.80, $J(^{195}Pt-^1H)$ 25.1 Hz, and aromatic protons at δ 6.97—7.2, but on heating exchange becomes significant.

The variable-temperature ^{31}P n.m.r. spectrum showed only signals due to $[Pt\{P(CH_2Ph)_3\}_3]$ and, when $P(CH_2Ph)_3$ is added, due to $P(CH_2Ph)_3$. No evidence of significant quantities of $[Pt\{P(CH_2Ph)_3\}_2]$ or $[Pt\{P(CH_2Ph)_3\}_4]$ was found. The rate of exchange is independent of the concentration of free $P(CH_2Ph)_3$ showing that the mechanism is dissociative.

$P(C_6H_{11})_3$. Two different crystalline compounds have been isolated and characterized by analysis and *X*-ray crystallography as $[Pt\{P(C_6H_{11})_3\}_2]$ [14] and $[Pt\{P(C_6H_{11})_3\}_3]$.[15] The ^1H n.m.r. spectrum shows signals for $[Pt\{P(C_6H_{11})_3\}_2]$ at δ 2.22, a complex multiplet at 2.0—1.6, and a multiplet at 1.24.

In toluene over the temperature range −40 to 0 °C, it was possible to observe $[Pt\{P(C_6H_{11})_3\}_3]$, $[Pt\{P(C_6H_{11})_3\}_2]$, and $P(C_6H_{11})_3$ in equilibrium in solution, and hence determine the dissociation constant, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$. In n-heptane $[Pt\{P(C_6H_{11})_3\}_3]$ proved to be more stable with the dis-

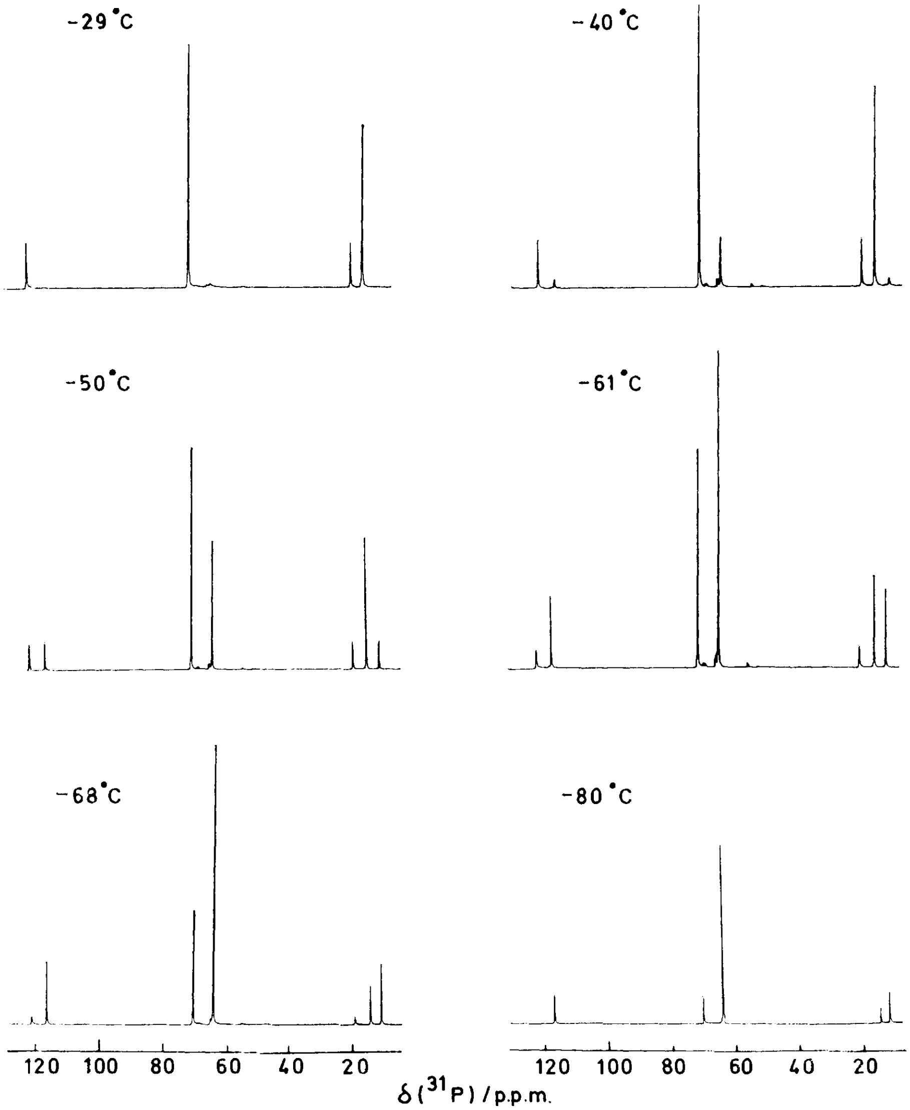

FIGURE 5 Temperature dependence of the ^{31}P n.m.r. spectrum of 0.0511 mol dm^{-3} $[Pt(PPr^i_3)_3]$ in toluene

sociation constant being smaller than in toluene by a factor of about eight resulting in changes in $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$, see Figure 3. Not only the dissociation constant proved to be solvent dependent, but also the ^{31}P chemical shift and coupling constant. The temperature and solvent dependence of the coupling constant is given in Figure 4. It will be observed that the effect of toluene is far more marked than the effect of n-heptane. At higher temperatures, associative exchange for $[Pt\{P(C_6H_{11})_3\}_2]$ becomes significant and the rate of exchange was determined as a function of temperature, solvent, and $P(C_6H_{11})_3$ concentration. No evidence was found for dissociative exchange.

PPr^i_3. The behaviour of the PPr^i_3 complexes is very similar to that of the $P(C_6H_{11})_3$ complexes with the exception that $[Pt(PPr^i_3)_3]$ is less stable than $[Pt\{(C_6H_{11})_3\}_3]$. The complex $[Pt(PPr^i_3)_3]$ is observed in solution from -80 to -29 °C, see Figure 5, and associative exchange for $[Pt(PPr^i_3)_2]$ becomes significant from *ca.* -20 °C.

At room temperature $[Pt(PPr^i_3)_2]$ shows a well resolved ^{1}H n.m.r. spectrum with an apparent quartet for the methyl group at δ 1.24 with $^3J(^1H-^1H) = 7.5$ Hz and $|N(^{31}P-^1H)| = 13.5$ Hz consistent with a virtual triplet arising from a large $^2J(^{31}P-^{31}P)$. The CH proton is a poorly resolved multiplet at δ 1.86. At room temperature the ^{1}H n.m.r. spectrum of $[Pt(PPr^i_3)_3]$ is consistent with a mixture of $[Pt(PPr^i_3)_2]$ and PPr^i_3 in solution with exchange broadening. At low temperatures, $[Pt(PPr^i_3)_3]$ was formed but by -70 °C when it neared complete formation there was considerable broadening of the spectrum (viscosity broadening ?) with the methyl protons as a broad singlet at δ 1.27 and the CH at δ 2.26 with still weak signals due to free PPr^i_3.

The ^{31}P n.m.r. spectrum showed similar behaviour to that observed for the $P(C_6H_{11})_3$ complexes.

An additional complication was found for $[Pt(PPr^i_3)_2]$ to which an excess of PPr^i_3 had been added. The commercial PPr^i_3 used in this work proved to be slightly impure containing small quantities of other tertiary phosphines. Evidence was found for at least two impurities which, on the basis of ^{31}P chemical shifts, are believed to be PPr^i_2R (L′) and PPr^iR_2 (L″) where R may be prop-2-enyl. Consequently at low temperatures not only $[Pt(PPr^i_3)_3]$ was formed, but also $[Pt(PPr^i_3)_2L']$, $[Pt(PPr^i_3)_2L'']$, and $[Pt(PPr^i_3)L'_2]$ giving rise to AB_2 ^{31}P n.m.r. spectra with ^{195}Pt satellites permitting the determination of $^2J(^{31}P-^{31}P) = 148$ Hz.

PBu^t_2Ph. Only $[Pt(PBu^t_2Ph)_2]$ could be synthesized and no evidence was found for the formation of $[Pt(PBu^t_2Ph)_3]$. The ^{1}H n.m.r. spectrum showed a triplet $N = 13.0$ Hz at δ 1.51 due the t-butyl group. As previously noted the phenyl resonance is anomalous. At room temperature the *ortho* protons are at δ 8.57 (broad) but on cooling to -71 °C they become inequivalent. This was attributed to restricted rotation about the phosphorus–carbon bond due to interaction between the *ortho* hydrogen and the metal.[8]

DISCUSSION

The compounds prepared, their relative stability, and their crystal structures when comparable are very similar for $[PtL_n]$ and $[PdL_n]$, L = tertiary phosphine.[2,4,14,17,25] However the investigation in solution of the platinum compounds has proved to be much more rigorous than that of the palladium compounds due to two factors. First the rate of exchange of the tertiary phosphine is slower for the platinum complexes enabling the equilibria to be studied in a wider temperature range. In the cases of $[Pd(PEt_3)_n]$ and $[Pd(PBu^n_3)_n]$ no quantitative information could be obtained from the ^{31}P n.m.r. spectra on the equilibrium between the tris and the tetrakis compounds.[4] From a comparison of, especially, $[Pd(PBu^n_3)_n]$ data with those for the platinum analogues (Table 3) it appears probable that the two-site line shape analysis was not performed on a two-site problem, *i.e.* $[Pd(PBu^n_3)_3]$–PBu^n_3 or $[Pd(PBu^n_3)_4]$–PBu^n_3 but on a three-site problem $[Pd(PBu^n_3)_3]$–$[Pd(PBu^n_3)_4]$–PBu^n_3 leading to erroneous results which should therefore be treated with caution. It is probable that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are considerably smaller than the quoted values. Secondly tertiary phosphine exchange in compounds such as $[Pd(PBu^n_3)_3]$ could not be studied in the absence of added PBu^n_3 while for $[Pd(PBu^n_3)_3]$ the observation of $^1J(^{195}Pt-^{31}P)$ permits the detection of PBu^n_3 exchange, although this dissociative exchange was suspected for $[Pd(PBu^n_3)_3]$ and $[Pd(PEt_3)_3]$ on the basis of ^{13}C n.m.r. data.

Before the dependence of the thermodynamic parameters on the nature of the tertiary phosphine can be discussed, it is necessary to discuss temperature and solvent effects. It has been noted previously[26] that $^1J(^{195}Pt-^{31}P)$ and $\delta(^{31}P)$ for *cis*- and *trans*-$[PtCl_2(PBu^n_3)_2]$ are both solvent and temperature dependent. These observations were interpreted in terms of a competitive solvation at platinum rather than a solvent-cavity model. In the present work, the range of solvents is far more limited but the data appear to be consistent with a specific solvation of the platinum, see Table 2. Thus for the $[PtL_4]$ species, the variations of $^1J(^{195}Pt-^{31}P)$ and $\delta(^{31}P)$ with solvent are minimal. Similarly k values for the dissociation of $[Pt(PMe_3)_4]$ and $[Pt(PMe_2Ph)_4]$ are the same in toluene and n-octane. When $[PtL_3]$ species are examined, $^1J(^{195}Pt-^{31}P)$, k for $[Pt(PEt_3)_3]$ associative exchange, and K for the equilibrium between $[Pt(PEt_3)_4]$, $[Pt(PEt_3)_3]$, and PEt_3 are somewhat solvent dependent. However when $[PtL_2]$, L = PPr^i_3 or $P(C_6H_{11})_3$, species are examined, $^1J(^{195}Pt-^{31}P)$, k for $[Pt(PR_3)_2]$ associative exchange, and K for the equilibrium between $[Pt(PR_3)_3]$, $[Pt(PR_3)_2]$, and PR_3 are markedly solvent dependent, see Figures 3 and 4 and Tables 2 and 3. This behaviour parallels the increasing co-ordinative unsaturation of these species. Thus for $[Pt(PR_3)_4]$ species, where the solvent effects are minimal, the molecule is co-ordinatively saturated, and the formation of a solvate at platinum would require the formation of a 20- (or higher) electron species. For the 16-electron $[Pt(PR_3)_3]$ species, there are solvent effects and the formation of $S \rightarrow [Pt(PR_3)_3]$ is feasible, S = solvent molecule. However there is little evidence for the formation of such species and the formation constant is anticipated to be very small. In contrast the 14-electron species $[Pt(PR_3)_2]$ is known to form a wide range of compounds $[Pt(\eta^2\text{-}S)(PR_3)_2]$, where S = olefin or acetylene. In contrast, arene complexes in this region of the Periodic Table are uncommon, but not unknown, with reports of $[Pt\{\eta^2-C_6(CF_3)_6\}(PR_3)_2]$, $[Rh(\eta\text{-arene})(dppe)]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane],[27] $[Ag(arene)]^+$,[28] and $[Hg(arene)]^{2+}$.[29] It is therefore possible that toluene is not an inert solvent but can co-ordinate to the platinum in $[Pt(PR_3)_2]$, R = Pr^i or cyclohexyl. Although it is difficult to assess the extent of toluene co-ordination to $[Pt\{P(C_6H_{11})_3\}_2]$ and $[Pt(PPr^i_3)_2]$, solvent co-ordination appears to be a possible rationale for the temperature-dependent coupling constant. The absence of temperature effects on $^1J(^{195}Pt-^{31}P)$ for $[Pt(PBu^t_2Ph)_2]$ is attributed to the bulk of the tertiary phosphine and/or partial saturation of the co-ordination sphere of the platinum by the *ortho*-hydrogen of the phenyl ring preventing toluene co-ordination.[17] From a comparison with $^1J(^{195}Pt-^{31}P)$ for $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$ of 3 660 Hz, and $^1J(^{195}Pt-^{31}P)$ for $[Pt(PBu^t_2Ph)_2]$ of 4 653 Hz, it would appear that there is considerable (40—50%) formation of $[Pt(\eta\text{-toluene})(PR_3)_2]$ [R = C_6H_{11} or Pr^i; $^1J(^{195}Pt-^{31}P)$ = *ca.* 4 100 Hz] but the use of these coupling constants is open to question. For n-octane and n-heptane, the temperature dependence of the coupling constant raises the possibility of alkane co-ordination,[30] albeit to a considerably lesser extent than toluene. However these smaller effects may alternatively arise from outer-sphere solvation effects or vibrational effects. Similarly, the co-ordination of toluene to $[Pt(PEt_3)_3]$ is also possible but no conclusions can be reached. As no allowance was made for this solvation in determining the thermodynamic parameters they will be subject to error, but the error is probably relatively small.

When viewed against the gross changes in behaviour due to the tertiary phosphine, the solvent effect is minimal, so that we can next consider the gross changes due to ligand. The ligands, in order of increasing co-ordination number and stability of the higher co-ordination number, are $PBu^t_2Ph < P(C_6H_{11})_3 \sim PPr^i_3 < P(CH_2Ph)_3 < PEt_3 \sim PBu^n_3 < PMePh_2 < PMe_2Ph \sim PMe_3$. This order approximately follows that reported previously by Tolman [1a] based on the concept of cone angle as a measure of the bulk of the tertiary phosphine. Indeed there can be little doubt that the bulk of the tertiary phosphine is the dominant factor in determining the stoicheiometry of the compound. For example, in toluene compare $\Delta H^\ddagger$ for associative exchange of ligand on $[PtL_2]$: for L = PBu^t_2Ph, $\Delta H^\ddagger = 12.1$;[8] L = PPr^i_3 $\Delta H^\ddagger = 3.79$; and L = $P(C_6H_{11})_3$, $\Delta H^\ddagger = 2.54$ kcal mol^{-1}. The dramatic difference between L = PBu^t_2Ph and PPr^i_3 or $P(C_6H_{11})_3$ may be attributed to the greater size of PBu^t_2Ph.

There are a number of anomalies in the order found experimentally for $[PtL_n]$ when compared with either the Tolman cone angle or the solid angle of the ligands as evaluated from available crystal structures.[18] The greatest discrepancy is for PPr^i_3 and $P(C_6H_{11})_3$. From the examined crystal structures it appears that PPr^i_3 is smaller than $P(C_6H_{11})_3$. In part these discrepancies arise from solvation. On going from toluene to n-heptane or n-octane as the solvent, $\Delta H^\ominus$ increases for $[Pt(PPr^i_3)_3]$ dissociation from 10.1 to 13.2 kcal mol^{-1} and for $[Pt\{P(C_6H_{11})_3\}_3]$ dissociation from 13.1 to 13.8 kcal mol^{-1}. If n-heptane or n-octane can also solvate then these measured $\Delta H^\ominus$ may still be further depressed and the true values could have $\Delta H^\ominus$ for $[Pt(PPr^i_3)_3]$ larger than for $[Pt\{P(C_6H_{11})_3\}_3]$ as predicted by the smaller size of PPr^i_3 permitting $[Pt(PPr^i_3)_2]$ to be more readily solvated than the more crowded $[Pt\{P(C_6H_{11})_3\}_2]$. Alternatively this discrepancy may arise from the relative deformabilities of the two ligands with PPr^i_3 being probably less deformable than $P(C_6H_{11})_3$ resulting in greater steric crowding in the PtP_3 plane. Apart from this pair of compounds, examination of the compounds in Table 3 shows no significant evidence for interligand steric interactions reducing $\Delta H^\ominus$ or affecting $\Delta H^\ddagger$ outside experimental error. Indeed the values of $\Delta H^\ddagger$ for the series $[Pt(PMe_3)_4]$, $[Pt(PMe_2Ph)_4]$, and $[Pt(PMePh_2)_4]$ increase with increasing steric bulk. This behaviour may arise from phenyl–phenyl interaction stabilizing the structure, similar to that observed in $[Pt(PPh_3)_3]$ [31] and $[Au(PPh_3)_3]^+$.[32] The crystal structures of the 'crowded' molecules $[Pt(PEt_3)_4]$, $[Pt(PMePh_2)_4]$,[33] and $[Pt\{P(C_6H_{11})_3\}_3]$ [15] show few or no abnormally close interligand distances. We therefore believe that, in general for $[PtL_n]$ complexes, there is little reduction in $\Delta H^\ominus$ due to steric crowding. When steric crowding becomes significant, the effect on $\Delta H^\ominus$ is dramatic resulting in the molecule dissociating. It is possible that, for other compounds where $\Delta H^\ominus$ in the absence of steric crowding is larger, steric crowding may commonly reduce $\Delta H^\ominus$ without dissociation. Although steric crowding may not have a dramatic effect on $\Delta H^\ominus$, it can have a major effect on $\Delta S^\ominus$. For a tertiary phosphine such as PBu^n_3, to avoid major steric interactions in $[PtL_4]$ it is necessary for the n-butyl side chains to orientate with respect to each other in the complex with the consequential loss of freedom and increase in $\Delta S^\ominus$ for dissociation. Thus complexes may become unstable because of a large entropy term rather than a small enthalpy term. It is probable that it is the $\Delta S^\ominus$ term which causes the instability of $[Pt(PEt_3)_4]$, $[Pt(PBu^n_3)_4]$, $[Pt(PPr^i_3)_3]$, and $[Pt\{P(C_6H_{11})_3\}_3]$ rather than a reduction in $\Delta H^\ominus$ by steric crowding. Effects of this sort will almost certainly be present in other series of compounds investigated [34] but the $\Delta S^\ominus$ term could be masked by the larger $\Delta H^\ominus$ term.

It is interesting to examine the values of $\Delta H^\ominus$ for the dissociation of the platinum–phosphorus bond. For $[PtL_4]$ going to $[PtL_3]$ and $[PtL_3]$ going to $[PtL_2]$ it is clear from the values of $\Delta H^\ominus$ and $\Delta H^\ddagger$ given in Table 3 that $\Delta H^\ominus$ is *ca.* 15 kcal mol^{-1} and $\Delta H^\ddagger$ is *ca.* 16 kcal mol^{-1}. These values change markedly on going to $[Pt\{P(OEt)_3\}_4]$ where $\Delta H^\ddagger$ is *ca.* 26 kcal mol^{-1},[5,35] but for $[Pt\{P(OPr^i)_3\}_4]$, $\Delta H^\ddagger$ is 14.7 kcal mol^{-1}. It is possible that both electronic and steric factors are operating in the phosphite complexes. The insensitivity of $\Delta H^\ominus$ and $\Delta H^\ddagger$ to the co-ordination number of $[Pt(PR_3)_n]$ in breaking the third or fourth platinum–phosphorus bond while there is no evidence for the breaking of the second platinum–phosphorus bond indicates that Pt^0 is relatively stable in a 14-electron, configuration and the loss of the third or fourth ligand does not directly destabilize the molecule, but makes room for a more reactive ligand to enter.

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