

Platinum Complexes of the Tripod-like Ligand Tris(2-diphenylphosphinoethyl)amine (tdpea). X-Ray Crystal Structure of [Pt(tdpea)(CH₂Cl)]BPh₄^{*}

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Treatment of [Pt(C₂H₄)(PPh₃)₂] with the tripod-like ligand tris(2-diphenylphosphinoethyl)amine, N(CH₂CH₂PPh₂)₃ (tdpea), affords the tetrahedral derivative [Pt(tdpea)(PPh₃)]. This species undergoes oxidative-addition reactions allowing the preparation of alkyl, hydrido, chloromethyl, and iodo five-co-ordinated species. An X-ray structure determination for the chloromethyl derivative has been carried out. Crystal data: monoclinic, space group *P*2₁/*n*, *a* = 34.601(9), *b* = 17.136(5), *c* = 10.718(3) Å, β = 94.56(8)°, and *Z* = 4. The structure has been solved by three-dimensional Patterson and Fourier syntheses and refined by least squares to a conventional *R* value of 0.069.

Tripod-like tetradentate ligands are known generally to favour five-co-ordination in transition-metal complexes. However different geometries can be allowed depending on the nature of the metal centre and the ancillary ligands. In this respect tris(2-diphenylphosphinoethyl)amine, (tdpea) shows an unusual flexibility, basically due to the facile dissociation of the apical nitrogen atom. Thus the remarkable reactivity of the tdpea metal species strongly contrasts the inertness of other polydentate phosphine metal complexes.¹

In a recent paper we have reported some palladium complexes of tdpea in which the phosphine in turn acts as a tetra-, ter-, or bi-dentate ligand.² Now we have synthesized the tetrahedral complex [Pt(tdpea)(PPh₃)] and investigated its oxidative-addition reactions allowing the preparation of alkyl, hydrido, chloromethyl, and iodo five-co-ordinated derivatives.

In spite of the very extensive platinum co-ordination chemistry with monophosphines and diphosphines there are few reports concerning platinum polyphosphine complexes.³ A preliminary communication of this work has been published.⁴

Experimental

All reactions were performed under dry nitrogen using standard Schlenk techniques. All solvents were distilled from the usual drying agents prior to use. The starting compound [Pt(C₂H₄)(PPh₃)₂] was prepared by the standard literature method.⁵ Infrared spectra were obtained using a Perkin-Elmer 457 spectrometer, ¹H n.m.r. spectra at 299.940 MHz on a Varian VXR-300 spectrometer, and ³¹P n.m.r. spectra at 32.19 and 121.421 MHz on Varian CFT-20 and VXR-300 spectrometers respectively. Chemical shifts are quoted with respect to internal SiMe₄ (¹H) or external phosphoric acid (³¹P). Concerning the ¹H n.m.r. spectra only the chemical shifts of signals of interest have been reported.

Preparations.—[Pt(tdpea)(PPh₃)]. To a solution of [Pt(C₂H₄)(PPh₃)₂] (200 mg, 0.26 mmol) in benzene (20 cm³) was added the solid tdpea ligand (170 mg, 0.26 mmol), at room temperature. Upon addition of Bu^oOH (20 cm³) yellow crystals of [Pt(tdpea)(PPh₃)] were obtained in nearly quantitative yield, and were filtered off and dried (Found: C, 64.30; H, 5.55; N, 1.20. Calc. for C₆₀H₅₇NP₄Pt: C, 64.85; H, 5.15; N, 1.25%). N.m.r. (C₆D₆): ³¹P-¹H, δ 12.4 [q, ²J(PP) = 80, ¹J(PtP) = 4 438, 1P, PPh₃] and -11.9 p.p.m. [d, ¹J(PtP) = 3 657 Hz, 3P, tdpea].

[Pt(tdpea)H]BPh₄, (2). (a) To a solution of [Pt(tdpea)-

(PPh₃) (200 mg, 0.18 mmol) in dry tetrahydrofuran (thf) (20 cm³) was added NaBPh₄ (70 mg, 0.20 mmol) in EtOH (15 cm³) at 40 °C. The yellow solution slowly cleared, the solvent was evaporated, and white crystals of the complex precipitated. Yield 85%.

(b) By adding CF₃CO₂H in excess to a yellow solution of [Pt(tdpea)(PPh₃)] (200 mg, 0.18 mmol) in thf (20 cm³) a colourless solution was obtained. Addition of solid NaBPh₄ (70 mg, 0.20 mmol) and then n-hexane (20 cm³) caused precipitation of white crystals of [Pt(tdpea)H]BPh₄. Yield 80% (Found: C, 67.35; H, 5.70; N, 1.30. Calc. for C₆₆H₆₃BNP₃Pt: C, 67.70; H, 5.45; N, 1.20%). N.m.r. (CD₂Cl₂): ¹H, δ -19.10 [q, ²J(PH) = 9, ¹J(PtH) = 858]; ³¹P-¹H, δ 22.3 p.p.m. [¹J(PtP) = 3 047 Hz].

[Pt(tdpea)(CH₂Cl)]BPh₄, (3) A yellow solution of [Pt(tdpea)(PPh₃)] (200 mg, 0.18 mmol) in CH₂Cl₂ (25 cm³) was left at room temperature for 24 h. Addition of NaBPh₄ (70 mg, 0.20 mmol) in EtOH (20 cm³) and evaporation of the solvent caused precipitation of yellow crystals of [Pt(tdpea)(CH₂Cl)]BPh₄·CH₂Cl₂. Yield 95% (Found: C, 62.05; H, 5.10; N, 1.20. Calc. for C₆₈H₆₆BCl₃NP₃Pt: C, 62.70; H, 5.05; N, 1.05%). N.m.r. (CD₂Cl₂): ¹H, δ 4.4 [q, ³J(PH) = 7.7, ²J(PtH) = 57, CH₂Cl]; ³¹P-¹H, δ 12.11 p.p.m. [¹J(PtP) = 3 059 Hz].

[Pt(tdpea)R]I [R = Me, (4); or Et, (5)]. To a solution of [Pt(tdpea)(PPh₃)] (200 mg, 0.18 mmol) in thf (20 cm³) was added, RI (R = Me or Et in excess *via* a syringe. When the yellow solution turned white-cream *n*-hexane (30 cm³) was added; after a few minutes clear yellow crystals of [Pt(tdpea)R]I precipitated. Yield 75% [Found: C, 52.10; H, 4.55; N, 1.40. Calc. for C₄₃H₄₅INP₃Pt, (4): C, 51.70; H, 4.50; N, 1.40%). N.m.r. (CD₂Cl₂): ¹H, δ 2.93 [q, ³J(PH) = 8.6, ²J(PtH) = 66, CH₃]; ³¹P-¹H, δ 8.85 p.p.m. [¹J(PtP) = 3 097 Hz]. Complex (5) (Found: C, 52.75; H, 4.50; N, 1.40. Calc. for C₄₄H₄₇INP₃Pt: C, 52.60; H, 4.40; N, 1.40%). N.m.r. (CD₂Cl₂): ¹H, δ 1.16 [tq, ³J(HH) = 7.5, ⁴J(PH) = 1.5, ³J(PtH) = 45, 3H, CH₃] and 2.26 [pseudo-septet, ³J(PH) = 7.3, 2 H, CH₂]; ³¹P-¹H, δ 9.5 p.p.m. [¹J(PtP) = 3 237 Hz].

[Pt(tdpea)Et]_x[Pt(tdpea)H]_y[Pt(tdpea)I]_zBPh₄ (x + y + z = 1). Excess of EtI, *via* a syringe, was added to a yellow

^{*} (Chloromethyl)[tris(2-diphenylphosphino-κ*P*-ethyl)amine-κ*N*]-platinum tetraphenylborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Positional parameters ($\times 10^4$) for $[\text{Pt}(\text{tdpea})(\text{CH}_2\text{Cl})]\text{BPh}_4$

Atom	x	y	z	Atom	x	y	z
Pt	1 366(1)	2 624(1)	-137(2)	C(45)	264(6)	579(13)	2 619(18)
P(1)	1 758(2)	2 520(5)	1 747(9)	C(55)	623(6)	946(13)	2 840(18)
P(2)	1 570(3)	3 483(5)	-1 727(9)	C(65)	761(6)	1 432(13)	1 931(18)
P(3)	714(3)	2 238(5)	-300(9)	C(16)	456(6)	1 930(12)	-1 737(24)
N	1 145(6)	3 696(14)	640(24)	C(26)	575(6)	1 229(12)	-2 245(24)
Cl	1 996(5)	1 428(10)	-1 238(16)	C(36)	402(6)	967(12)	-3 388(24)
C	1 518(12)	1 557(23)	-834(42)	C(46)	109(6)	1 407(12)	-4 024(24)
C(1)	1 538(10)	3 266(18)	2 664(32)	C(56)	-10(6)	2 109(12)	-3 517(24)
C(2)	1 409(9)	3 924(17)	1 827(30)	C(66)	164(6)	2 370(12)	-2 373(24)
C(3)	1 494(9)	4 408(17)	-877(31)	C(17)	4 251(5)	1 351(12)	3 948(24)
C(4)	1 122(8)	4 352(16)	-274(29)	C(27)	4 136(5)	1 494(12)	2 693(24)
C(5)	484(9)	3 156(17)	126(29)	C(37)	4 330(5)	1 135(12)	1 755(24)
C(6)	744(9)	3 574(18)	1 063(31)	C(47)	4 639(5)	634(12)	2 073(24)
C(11)	1 767(7)	1 661(17)	2 716(20)	C(57)	4 755(5)	491(12)	3 329(24)
C(21)	1 897(7)	972(17)	2 196(20)	C(67)	4 561(5)	850(12)	4 267(24)
C(31)	1 911(7)	284(17)	2 892(20)	C(18)	4 297(6)	1 712(10)	6 418(19)
C(41)	1 794(7)	284(17)	4 109(20)	C(28)	4 565(6)	2 289(10)	6 800(19)
C(51)	1 664(7)	972(17)	4 629(20)	C(38)	4 809(6)	2 188(10)	7 888(19)
C(61)	1 651(7)	1 661(17)	3 933(20)	C(48)	4 785(6)	1 508(10)	8 595(19)
C(12)	2 271(7)	2 750(13)	1 826(19)	C(58)	4 517(6)	931(10)	8 213(19)
C(22)	2 501(7)	2 723(13)	2 954(19)	C(68)	4 273(6)	1 032(10)	7 125(19)
C(32)	2 894(7)	2 912(13)	2 981(19)	C(19)	3 581(7)	1 464(12)	5 190(20)
C(42)	3 056(7)	3 128(13)	1 881(19)	C(29)	3 365(7)	1 136(12)	4 167(20)
C(52)	2 825(7)	3 155(13)	754(19)	C(39)	2 980(7)	924(12)	4 268(20)
C(62)	2 433(7)	2 966(13)	727(19)	C(49)	2 810(7)	1 039(12)	5 391(20)
C(13)	2 047(7)	3 579(12)	-2 323(24)	C(59)	3 026(7)	1 367(12)	6 414(20)
C(23)	2 164(7)	3 008(12)	-3 141(24)	C(69)	3 411(7)	1 579(12)	6 314(20)
C(33)	2 525(7)	3 064(12)	-3 629(24)	C(110)	3 999(6)	2 778(14)	4 683(21)
C(43)	2 769(7)	3 692(12)	-3 299(24)	C(210)	4 260(6)	3 117(14)	3 913(21)
C(53)	2 652(7)	4 263(12)	-2 481(24)	C(310)	4 243(6)	3 917(14)	3 672(21)
C(63)	2 291(7)	4 206(12)	-1 993(24)	C(410)	3 967(6)	4 378(14)	4 201(21)
C(14)	1 275(7)	3 564(13)	-3 148(25)	C(510)	3 706(6)	4 039(14)	4 971(21)
C(24)	1 266(7)	4 273(13)	-3 788(25)	C(610)	3 723(6)	3 239(14)	5 212(21)
C(34)	1 028(7)	4 360(13)	-4 893(25)	B	4 046(14)	1 870(27)	5 100(47)
C(44)	800(7)	3 738(13)	-5 358(25)	C(1')	3 932(24)	3 451(49)	8 562(83)
C(54)	810(7)	3 028(13)	-4 718(25)	Cl(1')	3 862(11)	4 036(22)	4 683(37)
C(64)	1 047(7)	2 941(13)	-3 613(25)	Cl(2')	3 931(11)	3 147(23)	9 808(38)
C(15)	540(6)	1 552(13)	800(18)	C(2')	3 000(25)	873(49)	513(83)
C(25)	181(6)	1 185(13)	580(18)	Cl(3')	2 801(8)	7(16)	864(28)
C(35)	43(6)	698(13)	1 489(18)	Cl(4')	3 299(10)	1 170(19)	-8(33)

Primed atoms belong to the solvent molecules, with an occupancy of 0.5.

solution of $[\text{Pt}(\text{tdpea})(\text{PPh}_3)]$ (200 mg, 0.18 mmol) in benzene (20 cm^3). The resulting solution was heated at 40 °C for 20 min, during which time the colour changed to orange-red. Upon adding NaBPh_4 (100 mg, 0.28 mmol) in EtOH (20 cm^3) the solution became red wine in colour and red crystals precipitated. The ^{31}P n.m.r. spectrum of this product and the elemental analysis of the red crystals showed the presence of three species: $[\text{Pt}(\text{tdpea})\text{Et}]\text{BPh}_4$, $[\text{Pt}(\text{tdpea})\text{H}]\text{BPh}_4$, and $[\text{Pt}(\text{tdpea})\text{I}]\text{BPh}_4$ in various percentages. N.m.r. of $[\text{Pt}(\text{tdpea})\text{I}]\text{BPh}_4$ in CD_2Cl_2 : ^{31}P - $\{^1\text{H}\}$ δ 5.6 p.p.m. [$^1J(\text{PtP}) = 2\ 588$ Hz].

Crystallography.—*Crystal data.* $\text{C}_{68}\text{H}_{66}\text{BCl}_3\text{NP}_3\text{Pt}$, $M = 1\ 302.5$, monoclinic, space group $P2_1/n$, $a = 34.601(9)$, $b = 17.136(5)$, $c = 10.718(3)$ Å, $\beta = 94.56(8)^\circ$, $Z = 4$, $U = 6\ 334.8$ Å 3 , $D_c = 1.365$ g cm^{-3} , $\lambda = 0.7107$ Å, $\mu(\text{Mo-K}\alpha) = 24.8$ cm^{-1} , $F(000) = 2\ 640$.

Data Collection and Processing. Yellow prism coated in paraffin, dimensions 0.10 \times 0.15 \times 0.25 mm; CAD4 diffractometer, ω scan with scan width = 0.7 + 0.35 $\tan\theta$, graphite-monochromated Mo-K α radiation, stationary background half the scan time. 6 738 Reflections measured ($5 < 2\theta < 40^\circ$, $\pm h$, $+k$, $+l$) corrected for 30% decay and for absorption, 6 giving 2 260 with $I > 3\sigma(I)$.

Solution and refinement. All the calculations were carried out on a SEL 32/77 computer using the SHELX 76 7 and ORTEP 8 programs. Atomic scattering factors for the appropriate neutral atoms were taken from ref. 9 for non-hydrogen atoms and from ref. 10 for hydrogen atoms. Both the real and imaginary component of the anomalous dispersion were included for the non-hydrogen atoms. 11 The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized during the least-squares refinements, the weights being defined as $w = 1/\sigma^2(F_o)$. The structure was solved by the heavy-atom method. Two solvating CH_2Cl_2 molecules were refined with a population factor of 0.5. Full-matrix least-squares refinements were carried out by assigning anisotropic thermal parameters to the heavier atoms and treating the phenyl rings as rigid groups of D_{6h} symmetry. Hydrogen atoms were introduced in calculated positions but not refined (C-H 0.95 Å). At convergence both R and R' were 0.069. Final positional parameters are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Treatment of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$, in benzene solution, with

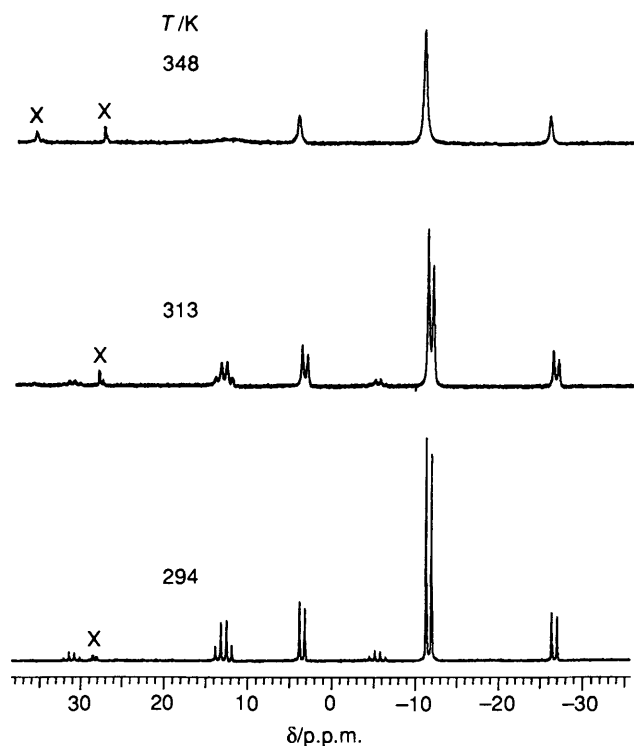


Figure 1. Variable-temperature $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of $[\text{Pt}(\text{tdpea})(\text{PPh}_3)]$ in C_6D_6 ; the signals marked by x are due to impurities

tdpea, at room temperature, affords the yellow derivative $[\text{Pt}(\text{tdpea})(\text{PPh}_3)]$ (1). The complex is stable under a nitrogen atmosphere, but slowly decomposes in air. The i.r. spectrum of the solid (Nujol mull) shows a band at $2\ 800\ \text{cm}^{-1}$, characteristic of metal tdpea complexes in which the phosphine acts as a terdentate ligand, with the apical nitrogen atom uncoordinated.¹² The room-temperature $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of (1), comprised of a quartet (1P) and a doublet (3P), clearly indicates that the three phosphorus atoms of tdpea and PPh_3 are co-ordinated to the metal centre.

Due to the geometrical feature of the tdpea ligand a pseudo-tetrahedral co-ordination must be assigned to (1). Analogous stable platinum(0) tetrahedral complexes of formula $[\text{Pt}(\text{tppme})(\text{PPh}_3)]$ [$\text{tppme} = \text{MeC}(\text{CH}_2\text{PPh}_2)_3$] have been reported.¹³ A comparison with the n.m.r. data for $[\text{Pt}(\text{tppme})(\text{PPh}_3)]$ shows that the Pt-P coupling constants of this latter complex are remarkably different from those of (1): $^1J(\text{PtP}) = 3\ 096$ (tppme) and $5\ 400$ Hz (PPh_3). Chatt *et al.*¹³ found that the magnitude of the directly bonded coupling constant $^1J(\text{PtP})$ for a series of tetrahedral platinum(0) complexes is closely related to the *s* character of the Pt-P bond: the more *s* character the larger is the coupling constant. The n.m.r. data for (1) are consistent with this conclusion. The large difference between the $^1J(\text{PtP})$ - (triphosphine) coupling constants can be accounted for by considering the different bites of tppme and terdentate tdpea ligands in tetrahedral complexes.

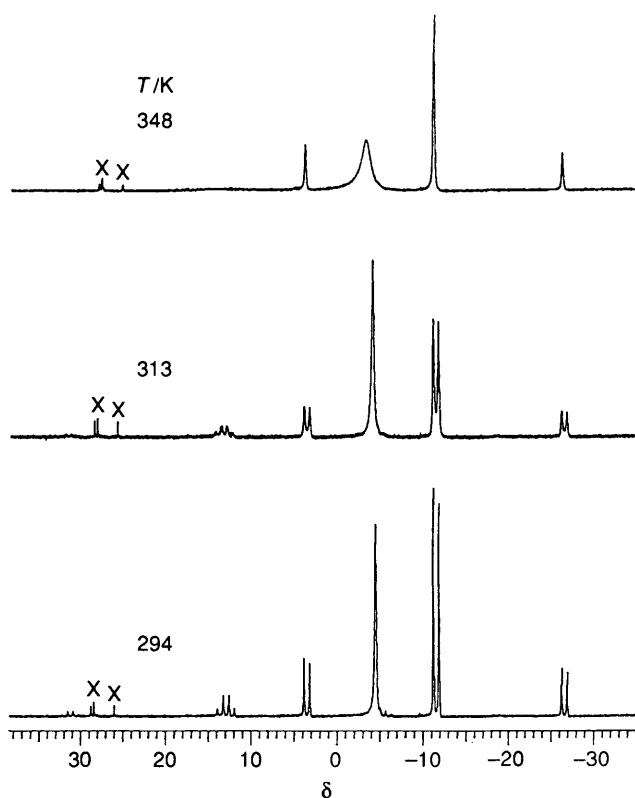
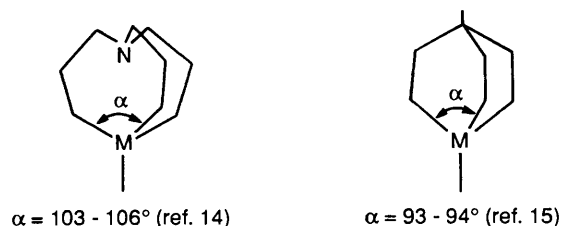


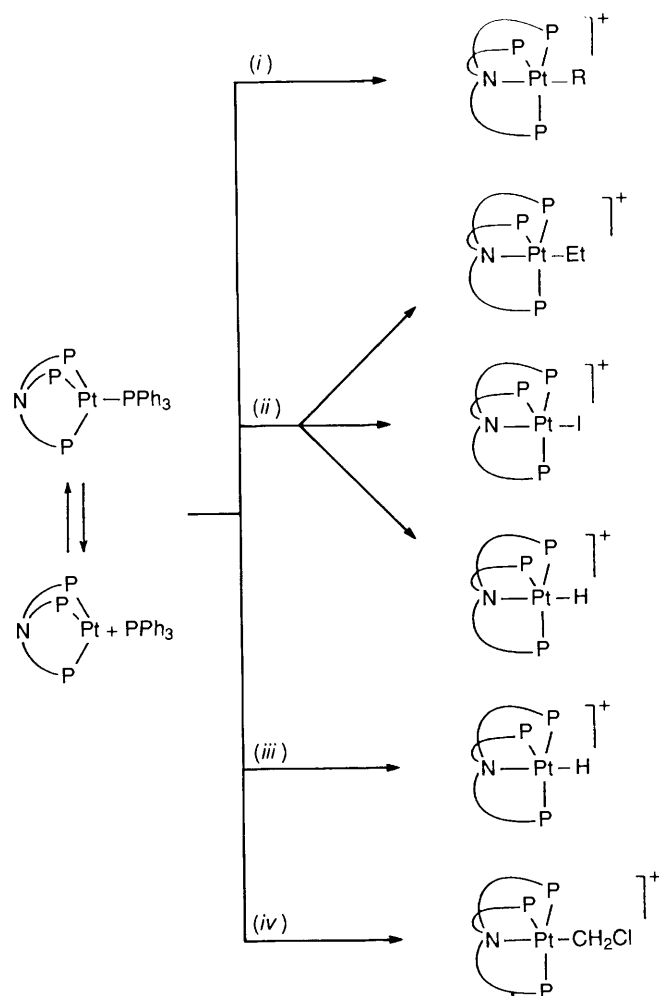
Figure 2. Variable-temperature $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of $[\text{Pt}(\text{tdpea})(\text{PPh}_3)]$ in the presence of excess of free PPh_3 in C_6D_6

Thus in the case of the tppme complex the three Pt-P bonds, being narrower, will have a smaller *s* character than the Pt-P bonds in (1) where the P-Pt-P angles are closer to 'tetrahedral' values. Conversely, because of the rehybridization and redistribution of *s* character, when the $^1J(\text{PtP})$ value for the triphosphine decreases the corresponding value for the monophosphine increases.*

The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra of the two complexes $[\text{PtL}(\text{PPh}_3)]$ ($\text{L} = \text{tppme}$ or tdpea) have been recorded at high temperature in C_6D_6 (Figure 1). Whereas the tppme compound appears stable till 353 K, in the case of (1) the PPh_3 ligand is dissociating at an appreciable rate up to 313 K. On raising the temperature the signal due to PPh_3 broadens together with its satellites and finally coalesces with the baseline at 348 K. The $\text{P}_{\text{tdpea}}\text{-P}_{\text{PPh}_3}$ coupling is lost but the $\text{Pt-P}_{\text{tdpea}}$ one is retained. When the ligand PPh_3 (excess) is added, the broadening of the signals due to co-ordinated and unco-ordinated PPh_3 clearly confirms the above dissociative process (Figure 2).

According to the above findings complex (1) shows a reactivity analogous to that of three-co-ordinated $[\text{Pd}(\text{tdpea})]$.² As previously found for the latter complex, oxidative-addition reactions allow the formation of five-co-ordinate derivatives. Moreover part of the reacting molecule (generally the electrophilic part) co-ordinates to the metal centre, five-co-ordination being attained through the apical nitrogen atom. For these reasons the reactions of platinum(0) and palladium(0) tdpea complexes represent a new kind of oxidative addition for these metals.

* A referee suggested that we have not emphasized sufficiently the presence of an extra CH_2 in the tdpea chain with respect to the tppme. Indeed the different values of the angles α in the two complexes are mainly due to the ligand requirements. The complex $[\text{Pt}(\text{tdpma})(\text{PPh}_3)]$ [$\text{tdpma} = \text{N}(\text{CH}_2\text{PPh}_2)_3$] shows $J(\text{PtP})$ constants fully comparable to that of $[\text{Pt}(\text{tppme})(\text{PPh}_3)]$.¹⁶



Scheme 1. (i) RI (R = Me or Et), thf-hexane; (ii) EtI + NaBPh₄, C₆H₆-EtOH; (iii) CF₃CO₂H or EtOH, NaBPh₄; (iv) CH₂Cl₂

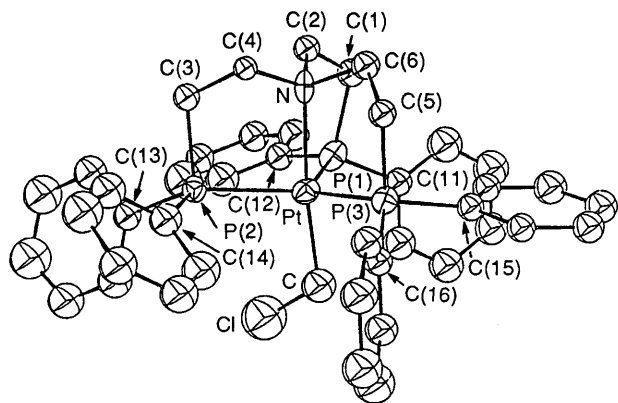


Figure 3. Perspective view of the complex cation [Pt(tdpea)(CH₂Cl)]⁺. ORTEP drawing with 30% probability ellipsoids

The reported reactions of complex (1) are shown in Scheme 1. The alkyl, chloromethyl, hydrido, and iodo derivatives are stable under an inert-gas atmosphere both in the solid state and in solution. These behave as 1:1 electrolytes in CH₂Cl₂ solution. Upon heating in CH₂Cl₂ solution, the complex [Pt(tdpea)Et]I slowly (hours) decomposes with formation of the hydride [Pt(tdpea)H]⁺, probably *via* a β-elimination process.

Table 2. Selected bond distances (Å) and Angles (°)

Pt-P(1)	2.348(9)	P(2)-C(14)	1.77(3)
Pt-P(2)	2.399(9)	P(3)-C(5)	1.84(3)
Pt-P(3)	2.343(9)	P(3)-C(15)	1.80(2)
Pt-N	2.18(2)	P(3)-C(16)	1.80(2)
Pt-C	2.06(4)	N-C(2)	1.55(4)
C-Cl	1.76(5)	N-C(4)	1.49(4)
P(1)-C(1)	1.82(3)	N-C(6)	1.51(4)
P(1)-C(11)	1.80(3)	C(1)-C(2)	1.49(4)
P(1)-C(12)	1.81(2)	C(3)-C(4)	1.49(4)
P(2)-C(3)	1.86(3)	C(5)-C(6)	1.48(4)
P(2)-C(13)	1.83(3)		
P(1)-Pt-P(2)	118.4(3)	C(13)-P(2)-C(14)	99.6(12)
P(1)-Pt-P(3)	121.9(3)	Pt-P(3)-C(5)	100.0(10)
P(2)-Pt-P(3)	117.1(3)	Pt-P(3)-C(15)	120.4(8)
N-Pt-P(1)	86.0(7)	Pt-P(3)-C(16)	123.8(9)
N-Pt-P(2)	83.5(7)	C(5)-P(3)-C(15)	102.8(13)
N-Pt-P(3)	84.4(6)	C(5)-P(3)-C(16)	105.6(12)
C-Pt-P(1)	95.6(12)	C(15)-P(3)-C(16)	101.5(10)
C-Pt-P(2)	100.9(12)	Pt-N-C(2)	108.9(16)
C-Pt-P(3)	89.7(12)	Pt-N-C(4)	112.8(18)
N-Pt-C	173.8(13)	Pt-N-C(6)	110.9(17)
Pt-P(1)-C(1)	100.0(11)	C(2)-N-C(4)	110.3(21)
Pt-P(1)-C(11)	122.7(9)	C(2)-N-C(6)	106.4(23)
Pt-P(1)-C(12)	121.4(8)	C(4)-N-C(6)	107.4(21)
C(1)-P(1)-C(11)	104.6(14)	P(1)-C(1)-C(2)	109.0(23)
C(1)-P(1)-C(12)	105.9(13)	N-C(2)-C(1)	115.6(24)
C(11)-P(1)-C(12)	100.2(11)	P(2)-C(3)-C(4)	108.6(20)
Pt-P(2)-C(3)	96.5(11)	N-C(4)-C(3)	109.3(22)
Pt-P(2)-C(13)	129.0(8)	P(3)-C(5)-C(6)	109.3(21)
Pt-P(2)-C(14)	118.5(9)	N-C(6)-C(5)	112.8(26)
C(3)-P(2)-C(13)	105.2(13)	Pt-C-Cl	118.3(21)
C(3)-P(2)-C(14)	105.2(13)		

The ¹H and ³¹P-(¹H) n.m.r. spectra (see Experimental section) show that in all the complexes the R group (Me, Et, CH₂Cl, or H) is co-ordinated to the metal centre and the three phosphorus atoms of the ligand are co-ordinated and equivalent.

Of particular interest is the activation of CH₂Cl₂ because the synthesis of a (chloromethyl)platinum(II) complex from the reaction with dichloromethane has so far been accomplished only by the photoinduced reaction of CH₂Cl₂ to [Pt-(C₂H₄)(PPh₃)₂]¹⁷.

A complete X-ray determination of complex (3) established that the molecular structure consists of discrete [Pt(tdpea)-(CH₂Cl)]⁺ cations, BPh₄⁻ anions, and CH₂Cl₂ solvating molecules interspersed in the lattice. Figure 3 shows a perspective view of the complex cation, selected bond distances and angles being reported in Table 2.

The geometry of the metal centre is slightly distorted trigonal bipyramidal with the CH₂Cl group in the axial site, *trans* to the central nitrogen ligand. The bond distances and angles within the Pt(CH₂Cl) fragment [Pt-C-Cl 118.3(21)°, C-Cl 1.76(5) Å] are in the expected range. Among the few complexes obtained by CH₂Cl₂ activation the octahedral complex [Rh-(Me₂PCH₂CH₂PM₂)₂Cl(CH₂Cl)]⁺¹⁸ shows fully comparable Rh-C-Cl [118.3(2)°] and C-Cl [1.76(1) Å] values. A comparison with the square-planar complex *cis*-[Pt(PPh₃)₂(CH₂I)]¹⁹ (Pt-C-I 110.5°) reveals in our compound a larger *sp*³ character for the CH₂X carbon, probably attributable to the different crowding of the ligands around the metal centres. The values of the bond distances and angles within the co-ordination polyhedron can be compared with those reported for the related five-co-ordinated palladium complex [Pd(tdpea)Me]⁺, where Pd-P (av.), Pd-N, and Pd-C are 2.357(4), 2.23(2), and 2.10(3) Å respectively.²

Differently from [Pd(tdpea)], but analogously to [Ni(tdpea)],

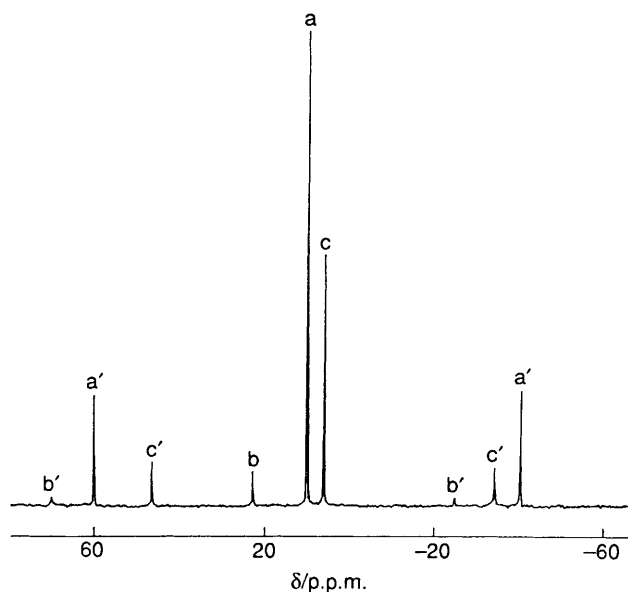
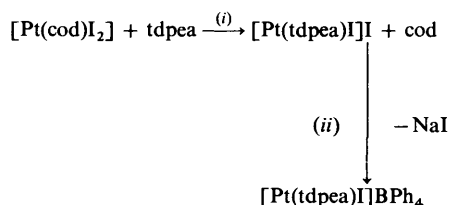


Figure 4. $^{31}\text{P}\{-^1\text{H}\}$ N.m.r. spectrum of a typical sample of $[\text{Pt}(\text{tdpea})\text{Et}]_x[\text{Pt}(\text{tdpea})\text{H}]_y[\text{Pt}(\text{tdpea})\text{I}]_z\text{BPh}_4$ ($x + y + z = 1$) in CD_2Cl_2 ; a = $[\text{Pt}(\text{tdpea})\text{Et}]^+$, b = $[\text{Pt}(\text{tdpea})\text{H}]^+$, c = $[\text{Pt}(\text{tdpea})\text{I}]^+$ primed letters refer to the platinum satellites

complex (1) easily reacts with acids to form the hydride $[\text{Pt}(\text{tdpea})\text{H}]^+$. This complex is formed also by reaction with ethanol, at 40°C , in the presence of NaBPh_4 . The i.r. spectrum of the solid shows a band at $2\,200\text{ cm}^{-1}$, attributable to the Pt-H stretching vibration. The first five-co-ordinated platinum(II) hydride, with the tripodal phosphine $\text{P}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$, was reported only recently.²⁰

Concerning the alkyl derivatives, the reaction with EtI presents some peculiarities. Whereas the pure ethyl complex $[\text{Pt}(\text{tdpea})\text{Et}]\text{I}$ is formed by reaction of (1) with EtI in thf-hexane solution, when the reaction is performed in benzene-ethanol in the presence of NaBPh_4 , at 40°C , red-wine coloured solutions are obtained from which well shaped red crystals can be isolated. The $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectrum of a typical sample of these products (Figure 4) shows the presence of three species, $[\text{Pt}(\text{tdpea})\text{Et}]^+$, $[\text{Pt}(\text{tdpea})\text{H}]^+$, and a third complex which has been identified as the five-co-ordinated $[\text{Pt}(\text{tdpea})\text{I}]^+$. The elemental analysis of the red crystals showed the presence of iodine, and a pure sample of $[\text{Pt}(\text{tdpea})\text{I}]\text{BPh}_4$ was prepared, for comparison, by the reactions in Scheme 2.*



Scheme 2. cod = Cyclo-octa-1,5-diene. (i) C_6H_6 , 50°C ; (ii) CH_2Cl_2 -EtOH, NaBPh_4

The comparison of the elemental analyses of two samples of the solids, and the integrals from ^{31}P n.m.r. spectra have shown that the composition of these mixtures is the same in the solid state and in solution. The percentages of the three species in samples from similar preparations are different, the amounts of

the iodide and hydride derivatives increasing with the time of reaction and heating. The red crystals obtained, when carefully observed by microscopy, appear absolutely homogeneous. X-Ray diffractometer measurements of the crystalline cell dimensions have shown that the crystals of the red samples from different preparations are all isomorphous with those of $[[\text{Pt}(\text{tdpea})(\text{CH}_2\text{Cl})]\text{BPh}_4$. Cell constants of the red sample: $a = 36.23$, $b = 14.11$, $c = 11.47$ Å, $\beta = 96.15^\circ$. The isomorphism of trigonal-bipyramidal complexes of formula $[\text{ML}(\text{X})]\text{BPh}_4$ (L = tetradentate tripod ligand) when X is changed is a general feature.

On this basis the red crystals obtained in this reaction can be considered a solid solution of the three complexes $[\text{Pt}(\text{tdpea})\text{Et}]\text{BPh}_4$, $[\text{Pt}(\text{tdpea})\text{H}]\text{BPh}_4$, and $[\text{Pt}(\text{tdpea})\text{I}]\text{BPh}_4$. Whereas the formation of the hydride must be ascribed to the reaction of (1) with ethanol, the contemporaneous synthesis of the ethyl and iodide complexes deserves some comments. As is well known, two main mechanisms $\text{S}_{\text{N}}2$ or radical have been established in oxidative-addition reactions. In the case of addition of MeI, which allows only the formation of the methyl derivative, whatever the reaction mixture, the reaction seems to follow the $\text{S}_{\text{N}}2$ mechanism, but in the case of the less reactive EtI probably also a radical pathway should be taken into account. The influence of the temperature and the solvent in these reactions provides additional support for a radical mechanism.^{21,22}

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* Alternatively $[\text{Pt}(\text{tdpea})\text{I}]\text{I}$ can be prepared by the oxidative addition of I_2 to (1) in dry benzene.

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