

Synthesis and Characterization of Hydrido–Platinum(II) Complexes containing Mixed Phosphine Ligands

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Several hydrido–platinum(II) complexes containing two non-equivalent phosphine ligands, $[PtH(P-C)(PR_3)]$ (2) [where $(P-C) = Bu_2^tPCMe_2-CH_2$ and $PR_3 = PEt_3, PPh_3, PPr_3^t, PBu_2^tMe, PBu_3, P(C_6H_4-Me)_3, P(OPh)_3$] have been prepared by the reaction of sodium borohydride with the corresponding chloro–platinum(II) complexes, $[PtCl(P-C)(PR_3)]$ (1). A trinuclear platinum cluster, $[Pt(CO)(PBu_3^t)]_3$, has been isolated from a similar reaction of sodium borohydride with $[PtCl(P-C)(CO)]$. Complexes 2 have been characterized by their elemental analysis, infrared, 1H NMR and ^{31}P NMR spectral data. The trans-configuration has been assigned to these complexes on the basis of a 12 line ^{31}P NMR spectra which shows large phosphorus–phosphorus coupling constants ($^2J(PP') = 371-400$ Hz). The trans-effect of the alkyl phosphines has been related to their steric parameters by measuring the platinum–phosphorus coupling constants ($^1J(PtP)$) of the metallated phosphine present at the trans-position.

Introduction

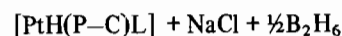
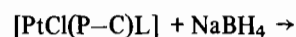
Our interest in the synthesis and structural characterization of hydrido–platinum(II) complexes with the carbon–platinum and platinum–hydrogen bonds and containing mixed phosphine ligands is manifold. In recent years, platinum hydride complexes have been recognized to be important intermediates in the homogeneous hydrogenation and polymerization reactions of unsaturated organic substrates catalyzed by platinum complexes [1–5]. In addition, platinum complexes of low symmetry containing mixed ligands have been shown to be much more active hydrogenation catalysts, compared to the respective

symmetrical diligated complexes [6]. Such low symmetry complexes can also be useful in studies such as *trans*-effect of ligands having variable electronic and steric parameters [7, 8] and homogeneously catalyzed asymmetric synthesis. Although the importance of hydrido alkyl-transition metal complexes in catalytic and stoichiometric process is widely recognized, similar platinum(II) complexes containing carbon–platinum–hydrogen bonds are still rare [9–11].

In the continuation to our studies on the chemistry of mixed ligands complexes of platinum [12, 13] and the platinum hydride complexes [10, 14, 15], we describe here the synthesis and structural characterization of a series of mixed phosphine platinum(II) complexes containing platinum–hydrogen as well as platinum–carbon bonds.

Results and Discussion

The reaction of chloro–platinum complexes containing mixed phosphine ligands, *trans*- $[PtCl(P-C)L]$ (1) ($(P-C) = Bu_2^tPCMe_2CH_2$ and $L = Et_3P, Ph_3P, Pr_3^tP, Cy_3P, Bu_2^tMeP, Bu_3^tP, (Me-C_6H_4)_3P, (PhO)_3P$) with $NaBH_4$ in dry ethanol proceeds exceedingly rapidly at ambient temperatures to yield quantitatively the corresponding hydrido–platinum complexes, $[PtH(P-C)L]$ (2). The reactions are usually complete within a few minutes of the addition of $NaBH_4$ to a suspension of the chloro–platinum(II) complex (1) in ethanol. The hydrido–platinum(II) complexes, $[PtH(P-C)L]$ (2) can be isolated by removing the ethanol and then extracting the reaction mixture with benzene. Further recrystallization in benzene/ethanol (or benzene/ethanol/ H_2O) gives white (or off white) crystalline products. In some cases, due to the poor thermal stability in benzene solution, some decomposition also occurs resulting in lower yields.



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TABLE I. Elemental Analysis and Infrared Spectral (ν Pt-H) Data of the Complexes *trans*-[PtH(P-C)PR₃].

S. No.	[PtH(P-C)PR ₃] PR ₃ =	Solvent of Crystallization	Yield (%)	Analysis (%) Found (Calcd.)			IR ^a , ν Pt-H (cm ⁻¹)
				C	H	P	
1	Et ₃ P	Ethanol/H ₂ O	55	41.5 (41.9)	8.05 (8.16)	12.3 (12.0)	1900 vs
2	Ph ₃ P	Benzene/Ethanol	79	54.5 (54.6)	6.39 (6.37)	9.58 (9.41)	1912 vs
3	Pr ⁱ ₃ P	Ethanol/H ₂ O	68	44.7 (45.2)	8.31 (8.62)	10.9 (11.1)	1875 s
4	Cy ₃ P	Ethanol/H ₂ O	80	53.4 (53.2)	8.75 (8.86)	9.28 (9.16)	1885 s
5	Bu ^t ₂ MeP	Benzene/Ethanol/H ₂ O	70	45.5 (45.2)	8.58 (8.62)	11.3 (11.1)	1910 s
6	Bu ^t ₃ P	Benzene/Ethanol/H ₂ O	82	48.3 (48.1)	9.11 (9.02)	10.7 (10.4)	1970 s
7	(Me-C ₆ H ₄) ₃ P	Benzene/Ethanol/H ₂ O	70	56.1 (56.5)	6.70 (6.85)	8.99 (8.84)	1910 s
8	(PhO) ₃ P	Benzene/Ethanol	72	51.2 (50.9)	5.78 (5.94)	8.51 (8.77)	1930 s

^aSpectra were recorded as nujol mull. s = strong; vs = very strong. Me = Methyl, Et = Ethyl, Ph = Phenyl, Prⁱ = Isopropyl, Cy = Cyclohexyl, Bu^t = Tertiary Butyl.

TABLE II. ³¹P NMR Spectral Data of the Complexes *trans*-[PtH(P-C)PR₃].^a

S. No.	Complex [PtH(P-C)(PR ₃) PR ₃ =	Signals due to Metalated Phosphine			Signals due to Non-metalated Phosphine		
		δ P (ppm)	JPP' (Hz)	JPt-P (Hz)	δ P' (ppm)	JPP' (Hz)	JPt-P' (Hz)
1	Et ₃ P	7.891	398	2383	24.78	398	2744
2	Pr ⁱ ₃ P	14.53	383	2251	54.43	383	2930
3	Ph ₃ P	8.896	398	2407	36.99	398	2920
4	Cy ₃ P	-4.825	400	2253	24.18	400	2822
5	Bu ^t ₃ P	16.79	371	2295	92.48	371	2896
6	(Me-C ₆ H ₄) ₃ P	6.484	398	2515	24.58	398	2778

^aSpectra have been recorded in C₆D₆ at room temperature and chemical shift values are reported with respect to 85% H₃PO₄ (external standard). A 12 line spectrum has been observed in all the cases except in 1 and 6 where right hand side signals collapsed to give only a 10 line spectrum.

The hydrido-platinum complexes (2) are air stable in the solid form and are soluble in most organic solvents including benzene, toluene, *etc.* These tend to decompose slowly in solutions resulting in a brownish material. These also react with CCl₄ to give back the corresponding chloro-platinum complex (1). Infrared spectra of these complexes show a strong band in the region 1875–1970 cm⁻¹ assignable to ν Pt-H. Appearance of this lower position band compared to that in the corresponding chloro-platinum-hydride complexes is indicative of a higher *trans* effect of carbon than that of chlorine [10]. In the ¹H NMR spectra, the hydridic proton signals appear in the region δ -4.03 to -7.73 ppm upfield to TMS as a multiplet (containing as much as 12 lines in some cases, see Table III and Figs. 1 and 2). These

signals appear as a doublet of a double triplet (ddt; 12 peaks) or a doublet of a quartet (dq; 8 peaks) or a doublet of a triplet (dt; 6 peaks). The complex pattern of 12 peaks can be explained by the *cis*-coupling of the two non-equivalent phosphorus nuclei *trans* to each other but *cis*- to hydride (²J(PH) = 20–22.5 Hz; ²J(P'H) = 3.5–10.7 Hz) and the *trans*-coupling of the methylene protons (³J(HH) = 2.4 or 2.9 Hz). These signals are associated with ¹⁹⁵Pt satellites (¹J(PtH) = 791–841 Hz). Appearance of the hydride proton signals, in some cases as multiplet comprised of 6 or 8 peaks, is indicative of a distorted square planar geometry for these complexes. The *trans*-configuration of these species (complex 2) has been further supported on the basis of their ³¹P NMR spectra which show large phosphorus-

TABLE III. Proton NMR Spectral Data of the Complexes *trans*-[PtH(P-C)(PR₃)₂].^a

S No.	PtH(P-C)(PR ₃) PR ₃ =	Signals due to Hydride Proton (Pt-H)				Signals due to Metalated Phosphine (Bu ^t ₂ PCMe ₂ CH ₂)				Signals due to PR ₃		
		δH (ppm)	Pattern	JP-H & JP'-H (Hz)	JH-H (Hz)	JPt-H (Hz)	t-butyl δ (ppm)	(Bu ₂ P) JPH (Hz)	dimethyl δ (ppm)	(PCMe ₂) JPH (Hz)	methylene δ (ppm)	(PCCH ₂ Pt) JPtH (Hz)
1	Et ₃ P	-7.73	(ddt)	20	2.4	835	1.38(d)	11.7	'a' ^b	-	'a' ^c	CH ₃ = 1.25 CH ₂ = 3.86 (m)
2	Ph ₃ P	-4.03	(dq)	19.5	2.9	826	1.41(d)	12.7	1.20(d)	12.7	0.93(m)	Phenyl 7.88 (m; <i>ortho</i>)
3	Cy ₃ P	-5.76	(ddt)	20.0	2.4	804	1.43(d)	11.3	1.54(d)	11.7	'b' ^c	7.03 (m; <i>meta</i> , <i>para</i>)
4	Bu ^t MeP	-5.26	(ddt)	20.4	2.4	810	1.54(d)	12.0	1.38(d)	12.0	0.95(m)	Cyclohexyl 1.5 (br) Bu ^t = 1.40(d) JPH = 11.5
5	Bu ^t ₃ P	-6.90	(ddt)	22.5	2.9	791	1.42(d)	11.7	1.57(d)	12.7	0.96(m)	CH ₃ = 1.49 Bu ^t = 1.51(d) JPH = 11.7
6	(MeC ₆ H ₄) ₃ P	-4.91	(dt)	16.6	2.4	841	1.41(d)	12.7	1.54(d)	11.7	0.81(m)	CH ₃ = 2.49(s) (C ₆ H ₄) = 8.05 7.03 (m; <i>ortho</i>)
7	Pr ⁱ ₃ P	-5.84	(ddt)	21.5	2.4	805	1.50(d)	11.8	1.41(d)	11.8	-	(CH ₃) ₂ C = 1.45 (dd) JPH = 7 CH = 2.3(m)

^aSpectra were recorded in C₆D₆ using TMS as external or internal standard. d = doublet; dt = doublet of triplets; m = multiplet; br = broad. ^b'a', ^c'b' = Signals due to methyl and methylene protons could not be determined accurately due to the overlapping of PEt₃ signals. ^c'a' = Signals due to methylene protons could not be observed due to strong and broad signals of Cy₃P.

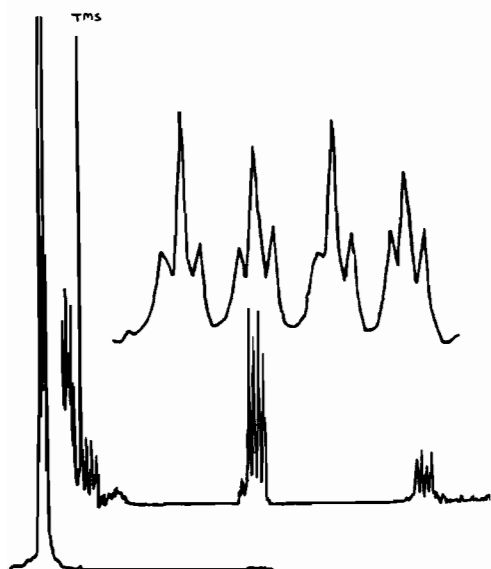


Fig. 1. Proton NMR Spectrum of *trans*-[PtH(P-C)PBu₃^t] in C₆D₆ at Room Temperature. The main signal due to hydridic proton has been expanded and the values of the chemical shifts are given in the Table.

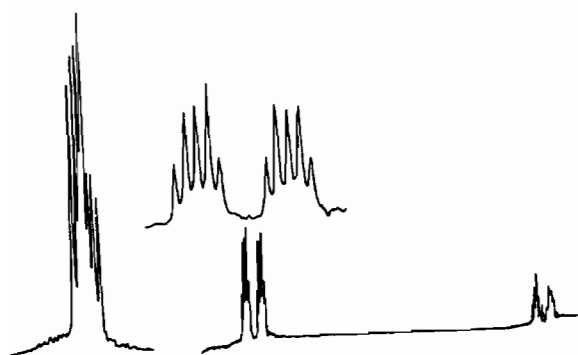


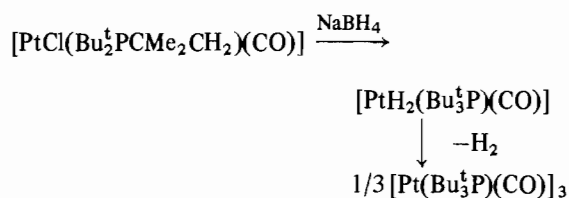
Fig. 2. Proton NMR Spectrum of *trans*-[PtH(P-C)PPt₃^t] in C₆D₆ at Room Temperature. The main signal due to hydridic proton has been expanded and the values of the chemical shifts are given in the Table.

phosphorus coupling constants of the order of ${}^2J_{(PP')} = 371\text{--}400$ Hz (due to magnetically non-equivalent phosphorus nuclei) [7, 8]. With two such phosphorus nuclei, a twelve line spectrum is observed in all the cases (each phosphorus gives a doublet with ${}^{195}\text{Pt}$ satellites) (Table II), except in the cases of the complex 2 [L = Et₃P and (Me-C₆H₄)₃P], where instead of twelve lines, only ten lines are observed. In these spectra, the two phosphine main signals appear as doublets. The ${}^{195}\text{Pt}$ satellites down field from the main doublet signals appear as expected doublets; however, the upfield satellites are observed as singlets. The explanation for this irregular behavior is not clear, but it is interesting to note that the

sum of the [$\frac{1}{2}J(\text{PtP}) + \frac{1}{2}J(\text{PtP}')$] (low field side) obtained by taking the mean values is equal to the sum of [$\frac{1}{2}{}^2J(\text{PtP}) + \frac{1}{2}{}^2J(\text{PtP}')$] (high field side). Analysis of these spectra clearly indicates that platinum satellite signals which appeared as two singlets are not a consequence of accidental overlap of the two doublets. Meek *et al.* [16] have recently observed similar non-uniform spectra in the case of [Pt(tp₃)X]⁺ complexes which have been explained on the basis of a second order approximation.

In these complexes 2, since the metalated phosphine is a constant component for one 'side' of each molecule, the values for JPtP (metalated phosphine) may well then reflect just the effect of the phosphine ligand of the *trans*-position (*trans*-influence of the phosphine ligand) [17]. Upon examination of these values (Table II), it is observed that in the series of alkyl phosphines (Pr^t₃P, Cy₃P and Bu^t₃P), as the size of the ligand increases, the JPtP (metalated) value increases, suggesting a decreasing order of *trans*-influence (*i.e.*, when the size order [18] is Pr^t₃P < Cy₃P < Bu^t₃P, then the *trans*-influence order is Pr^t₃P > Cy₃P > Bu^t₃P). If this generalization is correct, then Et₃P, being smaller than the above phosphines, should exhibit a greater *trans*-influence and hence the value of J(PtP) should be smaller. However, the value of J(PtP) (metalated) for Et₃P is found to be the larger. This inconsistency has also been observed in the parent chloro-platinum(II) complexes (1) series previously [7].

Interestingly, from the reaction of the chloro-platinum complex 1 containing the metalated *t*-butyl phosphine and a CO ligand, [PtCl(P-C)(CO)] with NaBH₄ in ethanol under carbon monoxide atmosphere, a red colored complex has been isolated in high yields. This complex has been characterized as the trinuclear cluster, [Pt(CO)(PBu^t₃)₃] by its elemental analysis, infrared spectrum ($\nu_{\text{CO}} = 1740$ and 1792 cm⁻¹), proton NMR (doublet at δ 1.60 ppm; JPH = 12.7 Hz) and ${}^{31}\text{P}$ NMR spectra [19]. A probable mechanism for the formation of this trinuclear complex is outlined in the following scheme.



A similar conversion of the metalated phosphine to the tertiary phosphine has also been observed earlier [20] in the sodium borohydride reaction with the chloro-platinum complex containing triphenyl stibene ligand, [PtCl(P-C)(Ph₃Sb)]. The product of this reaction has been found to be the dinuclear platinum(II) hydride complex, [Pt(μ -H)(H)(PBu^t₃)₂].

Experimental

Reduction reactions using sodium borohydride were carried out under nitrogen at room temperature. However, other manipulations such as purifications were carried out under open conditions. Ethanol and benzene used were dried and distilled over sodium prior to use. Chloro-bridged dinuclear complex, $[\text{Pt}(\mu\text{-Cl})(\text{Bu}_2\text{PCMe}_2\text{CH}_2)]_2$, was prepared as reported earlier [21] from the reaction of tri-*t*-butyl phosphine with $\text{PtCl}_2(\text{NCPh})_2$. Mixed phosphine platinum(II) chloride complexes, *trans*- $\text{PtCl}(\text{Bu}_2\text{PCMe}_2\text{CH}_2)(\text{PR}_3)$, were obtained by the bridge splitting reaction [7] and a general preparation is given below.

Elemental analyses were performed by M. H. W. Laboratories, Phoenix, Arizona. Proton and ^{31}P NMR spectra were recorded on a Bruker-60 Fourier transform spectrometer. Phosphoric acid (85%) was used as external standard; those ^{31}P chemical shifts to high field (low frequency) are reported as positive. Nujol mull infrared spectra were obtained on a Beckman IR-12 or Perkin-Elmer 621 spectrophotometer.

Preparation of $[\text{PtCl}(\text{Bu}_2\text{PCMe}_2\text{CH}_2)(\text{PR}_3)]$ Complexes

Typically, to a solution of dimeric complex $[\text{PtCl}(\text{P-C})]_2$ in benzene, tertiary phosphine was added in 1:2 molar ratio and the reaction mixture was allowed to react for 1–2 hrs at temperatures 40–50 °C. After concentrating the solution, crystals of the compound $[\text{Pt-Cl}(\text{P-C})\text{L}]$ (I) were obtained in high yields by addition of hexane or ethanol.

Preparation of $[\text{PtH}(\text{P-C})\text{L}]$ from the Reaction of $[\text{PtCl}(\text{P-C})\text{L}]$ with NaBH_4 in Ethanol

Typically, to a suspension of $[\text{PtCl}(\text{P-C})\text{L}]$ (I) (1.0 mmol), in dried ethanol was added an excess of NaBH_4 (5.0 mmol) and the reaction mixture was stirred at room temperature for ~2 hr, during which time gas evolution was noticed. Generally after about 2 hr reaction, no further gas evolution was observed indicating the completion of the reaction. The ethanol was removed under reduced pressure and the residue was extracted with benzene. On concentrating the solution and adding ethanol, white (off white in some cases) crystals of the platinum-hydride complex, $[\text{PtH}(\text{P-C})\text{L}]$ were obtained (55–82% yield). Analytical and spectroscopic data for these complexes are given in Tables I–III.

Reaction of $[\text{Pt-Cl}(\text{P-C})(\text{CO})]$ with NaBH_4

An excess of NaBH_4 (0.38 g, 10 mmol) was added to a suspension of $[\text{PtCl}(\text{P-C})(\text{CO})]$ (0.69 g,

1.5 mmol) in ethanol at room temperature under carbon monoxide atmosphere and the reaction mixture was stirred magnetically for ~3 hrs. The ethanol was stripped off under reduced pressure and the residue was extracted with benzene. On concentrating the solution and adding ethanol, orange-red crystals were isolated in approximately 75% yield. *Anal.*: Found: C, 36.8; H, 6.42; P, 7.41. *Calcd.* for $[\text{Pt}(\text{CO})(\text{Bu}_2\text{P})]_3$: C, 36.7; H, 6.35; P, 7.29.

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