The Platinum(II) Hydride of Tris(2-(diphenylphosphino)ethyl)phosphine: a Novel Five-coordinate Platinum Monohydride

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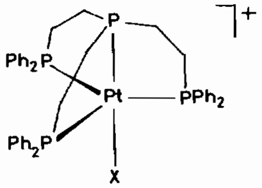
Five-coordinate hydrido species containing tris(2-(diphenylphosphino)ethyl)phosphine (pp$_3$) and related ligands have been prepared with several low-spin d^8 ions including Co(I), Ni(II) and Pd(II) [1–3]. Here the first example of the corresponding five-coordinate platinum(II) monohydrides is reported. The new hydride was obtained by reduction of [(pp$_3$)PtCl]Cl (1) with NaBH$_{4(s)}$ leading to [(pp$_3$)PtH]Cl (2), and isolated as [(pp$_3$)PtH](BPh$_4$).



1, X$^-$ = Cl$^-$ 2, X$^-$ = H$^-$

Experimental

^{195}Pt and ^{31}P NMR spectra were recorded on a Bruker WP 80 spectrometer operating in the FT mode. ^{1}H NMR spectra were obtained on a Jeol, JNM-PMX 60 spectrometer. The positive chemical shifts are downfield from the standards, where 1.0 M Na$_2$PtCl$_6$, 85% H$_3$PO$_4$ and TMS were used as standards respectively. IR – Pye Unicam SP3-300 (KBr); CH-Analyse – Heraeus EH 425.

1: The complex was prepared according to ref. 4.

2: To an aqueous ethanol solution (ν/ν = 1:5) of 1 was added a three-molar excess of NaBH$_{4(s)}$ in small portions. The colorless solution was stirred for 30 min at room temperature and concentrated to a small volume. Complex 2 precipitated and was filtered off. However, it was not possible to obtain 2 in an analytically pure form.

[(pp$_3$)PtH](BPh$_4$): An aqueous ethanol solution (ν/ν = 1:5) of 2 was treated with an equimolar amount of Na(BPh$_4$) in the same solvent and stirred for 2 h at room temperature. The colorless precipitate was filtered off, washed with water and dried *in vacuo*. It was recrystallized from CH$_2$Cl$_2$/n-hexane; melting point 211–213 °C (dec). *Anal.* Found: C, 67.22; H, 5.56. Calc. for C$_{66}$H$_{63}$BP$_4$Pt: C, 66.84; H, 5.35%.

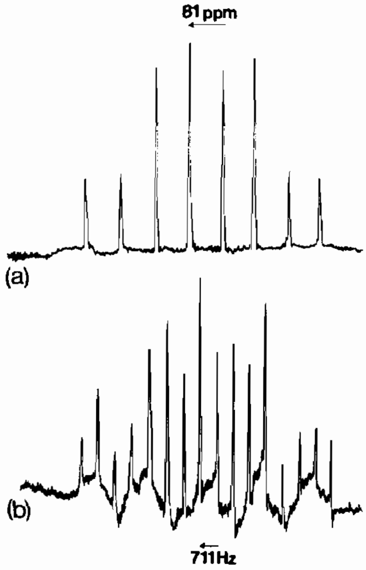


Fig. 1 (a) {H} and (b) coupled ^{195}Pt NMR spectra of 2 in DMSO.

Results and Discussion

The formulation of 1 as a pentacoordinated complex has been established only recently [5, 6]. Treatment of an aqueous ethanol solution of 1 with excess NaBH$_{4(s)}$ should give the corresponding platinum(0) complex [7]. However, no yellow precipitate typical for platinum(0) complexes is observed. Reduction of 1 gives a colorless solution, from which a colorless powder can be separated. In the infrared spectrum it shows a strong asymmetric absorption at 2053 cm^{-1} typical for a terminal ν(Pt–H) [8]. The formation of the five-coordinate hydride 2 is confirmed by the NMR data given in Fig. 1 and Table I. In Fig. 1a and 1b proton decoupled and fully coupled ^{195}Pt NMR spectra are

TABLE I. ^{195}Pt, ^{31}P and ^{1}H NMR Data on 2^a

^{195}Pt	δ(^{195}Pt)	^1J(^{195}Pt, H)	^1J(^{195}Pt, PPh$_2$)	^1J(^{195}Pt, P)
	−5474	755	2975	1467
^{31}P	δ(PPh$_2$)	δ(P)	^2J(P, Pt–H)	
	36.5	137	163	
^{1}H	δ(Pt–H)			
	−0.90 (triplet; J = 81)			

$^a\delta$ (ppm), J (Hz), 300 K. ^{195}Pt and ^{31}P spectra were run in DMSO; ^{1}H spectra in DMSO-d$_6$.

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given respectively. The proton decoupled spectrum consists of a 1:3:3:1 quartet, each line split into a further doublet due to ${}^{1}J({}^{195}\mathrm{Pt}, \mathrm{PPh}_2)$ and ${}^{1}J({}^{195}\mathrm{Pt}, \mathrm{P})$, clearly indicating the presence of a trigonal bipyramidal $[(\mathrm{pp}_3)\mathrm{PtH}]^+$ cation. In Fig. 1b this spectrum is further split into sixteen lines by ${}^{1}J({}^{195}\mathrm{Pt}, \mathrm{H})$. Chemical shifts and coupling constants of **2** are summarized in Table I.

The ^{195}Pt resonance of **2** ($\delta = -5474$ ppm) is strongly shifted towards a higher field compared with the corresponding value of **1** ($\delta = -4372$ ppm) [6]. ${}^{1}J({}^{195}\mathrm{Pt}, \mathrm{H})$ of 755 Hz is located within the range found for a series of terminal hydrides [9]. The magnitude of ${}^{1}J({}^{195}\mathrm{Pt}, \mathrm{P})$ of 1467 Hz indicates the presence of a *trans*-ligand which exhibits a high *trans* influence compared with the *trans*-ligands Cl^- (${}^{1}J({}^{195}\mathrm{Pt}, \mathrm{P}) = 2553$ Hz) and SnCl_3^- (${}^{1}J({}^{195}\mathrm{Pt}, \mathrm{P}) = 1827$ Hz) [5]. This agrees very well with the position of H^- in the *trans* influence series found for a series of tetracoordinated complexes $[(\mathrm{ttp})\mathrm{PtX}]^+$, where ttp is bis(3-(diphenylphosphino)propyl)phenylphosphine and X^- an anionic ligand [10].

The ${}^{31}\mathrm{P}\{{}^{1}\mathrm{H}\}$ NMR spectral pattern of **2** is also consistent with an AX_3 spin-system and a trigonal bipyramidal structure in solution. Both signals show ^{195}Pt satellites, indicating that all four phosphorus nuclei are bonded to the platinum atom. In a fully coupled ^{31}P NMR spectrum the resonance of the apical P-atom is split into a doublet due to ${}^{2}J(\mathrm{P}, \mathrm{Pt{-}H})$. The value of 163 Hz is typical for a *trans* ${}^{2}J(\mathrm{P}, \mathrm{H})$ coupling in a platinum(II) complex [10]. However, no ${}^{2}J(\mathrm{P}, \mathrm{P})$ and ${}^{2}J(\mathrm{P}, \mathrm{CH}_2)$ couplings were observed.

The 60 MHz ^{1}H NMR signal is highly second order presumably arising from virtual coupling effects [11].

Solutions of **2** are air and light sensitive. Irradiation of a deaerated $\mathrm{CH}_2\mathrm{Cl}_2$ solution with a high pressure Xe-lamp leads completely within 30 min to a solvolysis product with an AX_3 ^{31}P NMR spectral pattern.

In an attempt to produce a pp_3-platinum(0) complex LAH in absolute THF was used as reducing agent. However, the reaction is erratic leading to two main products with AB_3 ^{31}P NMR spectral patterns consisting of doublets and quartets together with the corresponding ^{195}Pt satellites. Presumably, the reaction pathway is obscured by the formation of a dimer and oligomers.

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