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Interconversion between Platinum(II) and Platinum(0) with Change of pH: Aqueous Reactions of $\mathrm{Pt(H)(TPPTS)_3^+}$ (TPPTS = $\mathrm{P(\textit{m}\text{-}C_6H_4SO_3Na)_3}$)

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Summary: The oxidation state for platinum complexes of TPPTS can be controlled through variation of the pH of an aqueous solution. Thus $\mathrm{Pt(H)(TPPTS)_3^+}$ *dissolved in* H_2O *gives a well-characterized Pt(II)−H complex at neutral or acidic pH but exists as* $\mathrm{Pt(TPPTS)_3}$ *at pH ≥12.*

Protonation of low-oxidation-state metal compounds by protonic acids is well-known. For $\mathrm{Pt(PPh_3)_3}$, reactions with a variety of acids HX gave $\mathrm{[Pt(H)(PPh_3)_3]X}$ or $\mathrm{Pt(H)(X)(PPh_3)_2}$, depending on the nature of X.[1] The basicity of $\mathrm{Pt(PEt_3)_3}$ was noted by Muetterties et al. 30 years ago through reaction with H_2O, which gave $\mathrm{Pt(H)(PEt_3)_3^+}$ in a reaction reversed by removal of the water.[2] A number of years later $\mathrm{Pt(PEt_3)_3}$ and $\mathrm{Pt(P(\textit{i}\text{-}Pr)_3)_3}$ were used to activate H_2O for H−D exchange and hydration of nitriles.[3] In both of these reactions a Pt(0) complex is changed to a Pt(II) complex by reaction with water. That Pt(0) complexes could be prepared from Pt(II) complexes was shown by reactions of $\mathrm{Pt(Cl)(H)(PPh_3)_2}$ under phase transfer conditions (benzene, 60% KOH, and 18-crown-6), where $\mathrm{Pt(PPh_3)_2}$ was generated and subsequently reacted with alkenes and alkynes.[4] The most pertinent previous example arises from $\mathrm{Pt(P(CH_2OH)_3)_4}$, which was characterized as $\mathrm{Pt(H)(P(CH_2OH)_3)_4^+}$ in aqueous solution.[5] Very recently protonation of $\mathrm{Pd((\textit{i}\text{-}Pr)_2PCH_2CH_2CH_2P(\textit{i}\text{-}Pr)_2)PCy_3}$ was reported.[6] In none of these examples was the ease of converting between Pt(II) and Pt(0) by controlling the pH noted. In this communication we describe the interconversion between $\mathrm{Pt(H)L_3^+}$ and $\mathrm{PtL_3}$ by pH control.

$$\mathrm{Pt(H)(TPPTS)_3^+} \underset{\text{decrease pH}}{\overset{\text{increase pH}}{\rightleftharpoons}} \mathrm{Pt(TPPTS)_3} \qquad (1)$$

The hydride $\mathrm{[Pt(H)(TPPTS)_3^+]Cl^-}$ is readily formed from the reaction of $\mathrm{Pt(Cl)(H)(PPh_3)_2}$ with 3 equiv of TPPTS.[7] The NMR characterization data in water are definitive for a Pt(II) hydride ($^{195}\mathrm{Pt}\{^1\mathrm{H}\}$, δ −5103 (dt) ppm, $J_{\mathrm{Pt-P}trans}$ = 2976 Hz, $J_{\mathrm{Pt-P}cis}$ = 2143 Hz; $^{31}\mathrm{P}\{^1\mathrm{H}\}$, δ 25.4 (t) ppm, $J_{\mathrm{Pt-P}cis}$ = 2143 Hz, $J_{\mathrm{P-P}}$ = 18.9 Hz, 23.8 (d) ppm, $J_{\mathrm{Pt-P}trans}$ = 2976 Hz, $J_{\mathrm{P-P}}$ = 18.9 Hz; ^{1}H (excluding aromatic protons), δ −5.58 (dt) ppm, $J_{\mathrm{P}trans\mathrm{-H}}$ = 120 Hz, $J_{\mathrm{P}cis\mathrm{-H}}$ = 12.0 Hz, $J_{\mathrm{Pt-H}}$ = 780 Hz). In DMSO, free TPPTS and $\mathrm{Pt(Cl)(H)(TPPTS)_2}$[9] are present in solution. The TPPMS (TPPMS = $\mathrm{PPh_2(\textit{m}\text{-}C_6H_4SO_3Na)}$) analogue $\mathrm{[Pt(H)(TPPMS)_3]Cl}$ was reported nearly 25 years ago;[10] the ^{31}P NMR data are consistent with our data.

As the pH is increased in water, the color changes from light yellow to orange,[11] and at pH 12 the NMR characterization confirms the presence of $\mathrm{Pt(TPPTS)_3}$ (^{195}Pt, δ −4519 (quart) ppm, $J_{\mathrm{Pt-P}}$ = 4460 Hz; $^{31}\mathrm{P}\{^1\mathrm{H}\}$, δ 50.1 (s) ppm, $J_{\mathrm{Pt-P}}$ = 4460 Hz; ^{1}H has only aromatic hydrogens). Platinum NMR spectra are shown in Figure 1. At intermediate pH (i.e. pH 10) both complexes are present and are not rapidly interconverting, as indicated by the sharp NMR signals observed. Lowering the pH to 6 completely converts the platinum complex to $\mathrm{Pt(H)(TPPTS)_3^+}$. Reaction 1 can also be entered from $\mathrm{Pt(TPPTS)_3}$.[13] Dissolution of $\mathrm{Pt(TPPTS)_3}$ into water creates a basic solution (0.0195 M is pH 10.5); addition of acid forms exclusively the platinum(II) complex $\mathrm{Pt(H)(TPPTS)_3^+}$. Spectra ($^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR) recorded for $\mathrm{Pt(H)(TPPTS)_3^+}$ in H_2O at pH 13 and pH 4 after 10 cycles

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(7) Into a 25 mL Schlenk flask, equipped with a stir bar, was introduced 0.494 g (0.795 mmol) of TPPTS. The flask was then evacuated and back-filled with N_2 three times. Under N_2 purge 5.0 mL of deaerated DMSO was added via airtight syringe. The solution was stirred until all the complex was dissolved. Under N_2 purge a solution of 0.200 g (0.265 mmol) of $\mathrm{Pt(Cl)(H)(PPh_3)_2}$[8] in 5.0 mL of dry CH_2Cl_2 was added. The resulting solution was heated with gentle reflux for 18 h under N_2 flow. During this time, the solution turned yellow. After cooling, dry dichloromethane was added to encourage precipitation. The cream-colored precipitate was collected by filtration, washed with 3 × 50 mL of CH_2Cl_2 and 3 × 50 mL of Et_2O and dried in vacuo. The crude product was recrystallized from CH_3OH/CH_3NO_2. Yield: 64% (based on starting platinum complex). Anal. Found: C, 33.34; H, 2.24; Cl, 1.68; Na, 10.42; P, 4.66. Calcd for $\mathrm{C_{55}H_{40}ClNNa_9O_{29}P_3PtS_9}$, $\mathrm{[Pt(H)(TPPTS)_3]Cl{\cdot}CH_3NO_2}$: C, 33.06; H, 2.02; Cl, 1.77; Na, 10.36; P, 4.65.

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(9) Characterization data for *trans*-$\mathrm{Pt(Cl)(H)(TPPTS)_2}$ are as follows. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (25 °C, d_6-DMSO): δ 30.4 (s) ppm, $J_{\mathrm{Pt-P}}$ = 2990 Hz; δ −4.3 (s) ppm (free TPPTS, 18% based on integration). ^{1}H NMR (excluding aromatic protons): δ −16.0 (t) ppm, $J_{\mathrm{Pt-H}}$ = 1183 Hz, $J_{\mathrm{P-H}}$ = 14.8 Hz. IR (KBr, cm^{-1}): ν(Pt−H) 2225 (s).

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(11) Oxidation of the ligand becomes significant (25% based on ^{31}P integration) under basic conditions and is irreversible.[12]

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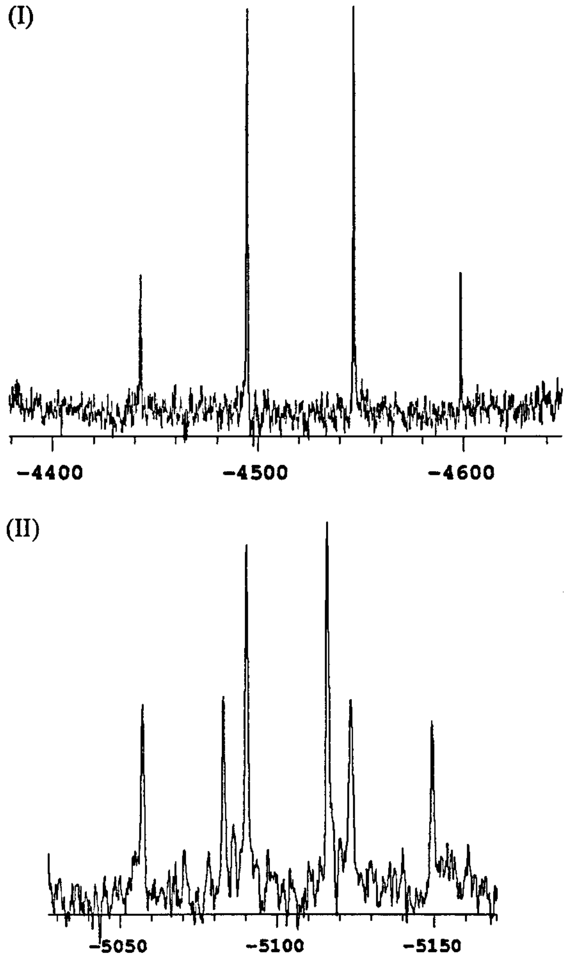

Figure 1. ^{195}Pt NMR spectrum for Pt(TPPTS)$_3$ (I) and ^{195}Pt{^{1}H} NMR spectrum for Pt(H)(TPPTS)$_3^+$ (II) in H_2O.

between pH 4 and 13 are shown in Figure 2. The oxide of TPPTS is present in 25% amount in both spectra (at 34.8 ppm). At pH 13, Pt(TPPTS)$_3$ (at 50 ppm) dominates; the only other product is a trace of Pt$_2$(TPPTS)$_4$(μ-OH)$_2^{2+}$ at 10 ppm.[15] At pH 4, only Pt(H)(TPPTS)$_3^+$ is observed.

By the oxidation number formalism, any protonation of a metal is an oxidation. However, reaction 1 is more than a semantic change. Protonation of a d^{10} PtL$_3$ complex would be expected to result in a tetrahedral geometry unless the platinum is oxidized, while Pt(H)(TPPTS)$_3^+$ is clearly square planar d^8. Similarly, a simple protonation−deprotonation would be expected to rapidly interconvert between Pt(H)L$_3^+$ and PtL$_3$, which is not observed. Furthermore, the hydride ligand of Pt(H)(TPPTS)$_3^+$ does not rapidly exchange with D_2O at pH 6.

While the interconversion between Pt(II) and Pt(0) with pH has not been previously reported, the role of pH in synthesis has been observed. For example, reaction of PtCl$_4^{2-}$ with PPh$_3$ depends on the base added:[8,14a]

$$\mathrm{PtCl_4}^{2-} + 2\mathrm{PPh_3} \rightarrow cis\text{-}\mathrm{PtCl_2(PPh_3)_2} + 2\mathrm{Cl}^- \quad (2)$$

$$\mathrm{PtCl_4}^{2-} + 4\mathrm{PPh_3} \xrightarrow{\text{pH 13}} \mathrm{Pt(PPh_3)_4} + 4\mathrm{Cl}^- \quad (3)$$

These standard syntheses differ only in the amount of PPh$_3$ (and the EtOH required to dissolve it) and the presence of KOH in an amount to give a pH of 13. For reaction 3 it is likely that the ethanol is deprotonated to $OC_2H_5^-$, which replaces a Cl$^-$ on the platinum. β-Hydride elimination would produce, in the presence of PPh$_3$, Pt(H)(PPh$_3$)$_3^+$, which from our work is deprotonated at pH 13 to the Pt(0) complex.

To further demonstrate the relatively slow interconversion between the Pt(II) and Pt(0) complexes, we introduced 3-pentyn-1-ol to the mixture of Pt(H)(TPPTS)$_3^+$ and Pt(TPPTS)$_3$ at pH 10. The alkyne rapidly reacted with the Pt(0) complex, forming Pt(3-pentyn-1-ol)(TPPTS)$_2$,[16] and had no interaction with Pt(H)(TPPTS)$_3^+$. Independent reactions of 3-pentyn-1-ol with each complex confirm rapid complexation of 3-pentyn-1-ol with Pt(TPPTS)$_3$ and slow hydration of 3-pentyn-1-ol with Pt(H)(TPPTS)$_3^+$. Similarly, reaction of Pt(TPPTS)$_3$ with C_2H_4 gives Pt(C_2H_4)(TPPTS)$_2$,[17] while C_2H_4 does not react with Pt(H)(TPPTS)$_3^+$. The reactions with 3-pentyn-1-ol and C_2H_4 confirm the slow interconversion between Pt(H)(TPPTS)$_3^+$ and Pt(TPPTS)$_3$.

The slow interconversion between Pt(H)(TPPTS)$_3^+$ and Pt(TPPTS)$_3$ requires a significant activation barrier. The barrier could arise from the energy to interconvert from square planar to tetrahedral. This energy is not known for Pt(II) but would be expected to be much larger than the ~10 kcal for such conversions for Ni(II).[18] Alternatively the mechanism could involve TPPTS loss and oxidative addition/reductive elimination of water. The latter seems less likely, since PtL$_{3,4}$ complexes react with H_2O to form PtHL$_{3,4}^+$ under similar conditions for the different ligands L = PEt$_3$, P(CH$_2$-

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(13) Into a 25 mL Schlenk flask, equipped with a stir bar, was introduced 0.288 g (0.462 mmol) of TPPTS. The flask was then evacuated and back-filled with N_2 three times. Under N_2 purge 5.0 mL of deaerated DMSO was added via airtight syringe. The solution was stirred until all the complex was dissolved. Into the clear solution was added a solution of 0.151 g (0.154 mmol) of Pt(PPh$_3$)$_3$[14] in 5.0 mL of dry CH_2Cl_2. The resulting solution was heated with gentle reflux for 36 h under N_2 flow. The resulting solution turned orange-yellow. After the solution was cooled, dry CH_2Cl_2 was added to encourage precipitation. The orange precipitate was collected by filtration, washed with 3 × 50 mL of CH_2Cl_2 and then 3 × 50 mL of Et_2O, and dried in vacuo. The crude product was recrystallized from DMSO/CH_2Cl_2. Yield: 52% (based on starting platinum complex).

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(16) Characterization data for Pt(3-pentyn-1-ol)(TPPTS)$_2$ are as follows. ^{31}P{^{1}H} NMR (25 °C, D_2O/NaOH, pH 14): δ 30.5 (d) ppm, $J_{\mathrm{Pt-P}} = 3360$ Hz, $J_{\mathrm{P-P}} = 40$ Hz; δ 30.2 (d) ppm, $J_{\mathrm{Pt-P}} = 3360$ Hz, $J_{\mathrm{P-P}} = 40$ Hz. ^{1}H NMR (excluding aromatic protons): δ 3.10 (t, 2H) ppm; δ 2.15 (m, 2H) ppm; δ 1.68 (d, 3H) ppm, $J_{\mathrm{Pt-H}} = 50$ Hz. ^{195}Pt NMR: δ −4650 (t) ppm, $J_{\mathrm{Pt-P}} = 3360$ Hz.

(17) Pt(C_2H_4)(TPPTS)$_2$ was characterized by NMR. ^{31}P{^{1}H} NMR (pH 14, H_2O, 25 °C): 34.9(s) ppm, $J_{\mathrm{Pt-P}} = 3670$ Hz. ^{1}H NMR (pH 14, H_2O, 25 °C), 2.13 (s), $J_{\mathrm{Pt-H}} = 60$ Hz. These NMR spectra compare excellently with those reported for Pt(C_2H_4)(PPh$_3$)$_2$ (^{31}P NMR, δ 32.5 (s), $J_{\mathrm{Pt-P}} = 3694$ Hz; ^{1}H NMR, δ 2.15 (s), $J_{\mathrm{Pt-H}} = 62$ Hz).[19]

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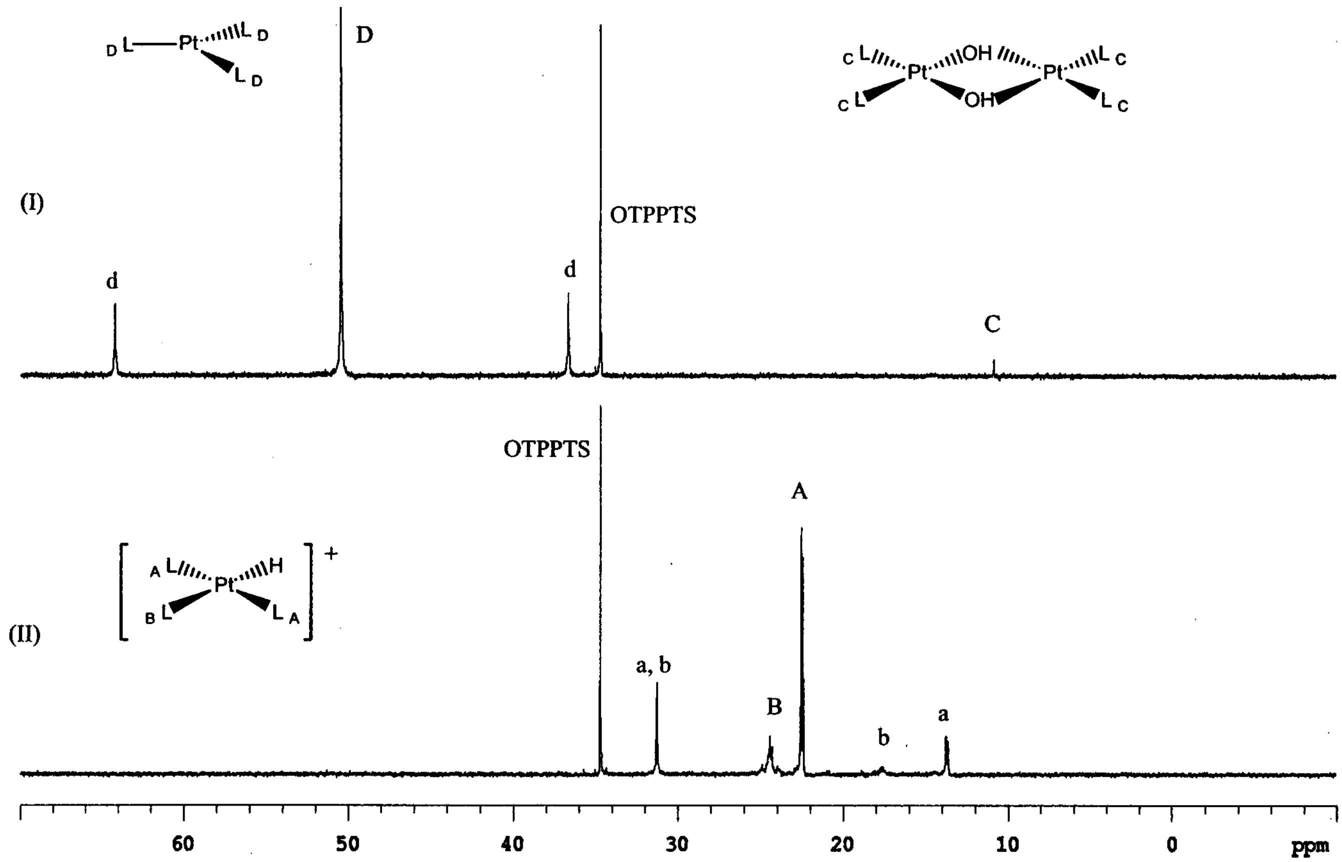

Figure 2. ^{31}P NMR spectra recorded of the same solution after 10 cycles between pH 4 and 13: (I) recorded at pH 13, showing $Pt(TPPTS)_3$; (II) recorded at pH 4, showing $Pt(H)(TPPTS)_3^+$. The lower-case letters indicate the ^{195}Pt satellites (L = TPPTS).

$OH)_3$, TPPTS that would be expected to exchange at different rates, but further mechanistic work is required.

The possible involvement of reactions similar to reaction 1 in water activation and other catalytic reactions in water should be examined.

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