# Synthesis, Characterization, and Reaction Chemistry of $PtCl_2[P(m\text{-}C_6H_4SO_3Na)_3]_2$, an Alkyne Hydration Catalyst

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The preparation and reactions of *cis*-$PtCl_2(TPPTS)_2$ (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$) in aqueous solution are described. In the absence of excess $Cl^-$, *cis*-$PtCl_2(TPPTS)_2$ exists as a mixture with 20% of *cis*-$Pt(Cl)(H_2O)(TPPTS)_2^+$; the aqua complex was prepared independently by reaction with $Ag^+$. As a result of the aquation *cis*-$PtCl_2(TPPTS)_2$ is slightly acidic. Increasing the pH for a solution of *cis*-$PtCl_2(TPPTS)_2$ leads to $Pt_2(TPPTS)_4(\mu\text{-}OH)_2^{2+}$; a subsequent decrease in pH leads to *cis*-$Pt(OH_2)_2(TPPTS)_2^{2+}$ and, ultimately, *cis*-$PtCl_2$-$(TPPTS)_2$. All of these complexes were characterized by $^{31}P$ and $^{195}Pt$ NMR. *cis*-$PtCl_2(TPPTS)_2$ functions as an effective hydration catalyst for the water-soluble alkynes 4-pentyn-1-ol and 3-pentyn-1-ol. Both hydrations are stereospecific to 5-hydroxy-2-pentanone. Hydration of 4-pentyn-1-ol occurs by a 5-exo-dig mechanism, while hydration of 3-pentyn-1-ol occurs through a 5-endo-dig mechanism.



## Introduction

Organic transformations catalyzed by transition metals in aqueous media have become increasingly important due to the benign nature of water and the cost benefits.[1] Water-soluble transition-metal complexes can also be models for biological systems.[2] Much work has been done in recent years to develop water-soluble ligands for transition metals, and sulfonated phosphines such as TPPTS (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$) are now quite common.[3]

Of particular significance have been water-soluble transition-metal-catalyzed transformations of olefins such as hydroformylation,[4,5a] hydrogenation,[5] alkylation,[6] allylic substitution,[7] isomerization,[8] carbonylation,[9] chlorination,[10] and oxidation to form ketones or epoxides.[11] The Markovnikov hydration of olefins to secondary alcohols has also been demonstrated.[12] Transition-metal-catalyzed anti-Markovnikov hydration of olefins to primary alcohols remains a challenge,[13,14] although it has been shown to occur via hydroboration.[15]

The hydrations of nitriles to amides[16] and of alkynes to ketones or aldehydes have also been reported. Alkyne hydrations to ketones can be catalyzed by a variety of

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**Table 1. $^{31}P$ and $^{195}Pt$ NMR Data for Complexes 1−6, $PtCl_2$, and $K_2PtCl_4$**

| | $^{31}P$ NMR[a,b] | | | $^{195}Pt$ NMR[a,b] | |
|---|---|---|---|---|---|
| complex | $\delta$(TPPTS) | $J$(P−P) | $J$(P−Pt)[c] | $\delta$(Pt)[d] | $J$(P−Pt) |
| *cis*-$PtCl_2$(TPPTS)$_2$ (**1a**) | 14.3 br s | | 3720 | −4437 t | 3720 |
| *cis*-$PtCl_2$(TPPTS)$_2$ (**1a**)[e] | 15.5 s | | 3720 | −4390 t | 3720 |
| *trans*-$PtCl_2$(TPPTS)$_2$ (**1b**) | 22.3 s | | 2600 | −4072 t | 2600 |
| $Pt_2$(TPPTS)$_4$($\mu$-OH)$_2$ (**2**) | 10.7 s | | 3530 | −4083 t | 3530 |
| *cis*-[Pt(OH$_2$)$_2$(TPPTS)$_2$][O$_3$SCF$_3$]$_2$ (**3**) | 9.2 br s | | 3680 | −3839 t | 3680 |
| *cis*-[Pt(OH$_2$)(Cl)(TPPTS)$_2$][O$_3$SCF$_3$] (**4**) | 17.6 br d | 20 | 3740 | −4280 dd | 3740, 3920 |
| | 4.6 br d | 20 | 3920 | | |
| [PtCl(TPPTS)$_3$]Cl (**5**) | 23.8 d | 18 | 2500 | −4731 dt | 3680, 2500 |
| | 12.6 t | 18 | 3680 | | |
| [$PtCl_3$TPPTS] (**6**) | 18.9 s | | 3850 | −3916 d | 3810 |
| $K_2PtCl_4$[37] | | | | −1627 | |
| $PtCl_2$ | | | | −3096 | |

[a] $^{31}P$ and $^{195}Pt$ NMR spectra were recorded in water at room temperature with a capillary insert of $D_2O$ for the lock signal unless otherwise noted. [b] Chemical shifts ($\delta$) are recorded in ppm, and coupling constants ($J$) are recorded in Hz. [c] Coupling constants refer to Pt satellites. [d] Referenced to 0.2 M $K_2PtCl_6$ in $H_2O$. [e] Recorded in DMSO.



metal complexes,[17] frequently halide complexes of Ru,[18a] Rh,[19] Pd,[20] and Pt.[21] Platinum catalysts are often based on Zeise's dimer, [($C_2H_4$)$PtCl_2$]$_2$.[22] Hartman et al.[22b] showed enhanced regioselectivity for hydration of internal alkynes to the ketone moiety on the most substituted carbon (Markovnikov). This selectivity was augmented when chelating atoms such as oxygen were present on the alkyne. Tokunaga and Wakatsuki reported the first example of an anti-Markovnikov hydration of terminal alkynes to aldehydes using a water-soluble ruthenium catalyst.[18b]

Although it is well-known that water-soluble phosphine complexes of transition metals are excellent catalysts for a variety of organic transformations, the exact nature of these complexes is less well understood. TPPTS and $PPh_3$ are similar spectroscopically and have nearly coincident $^{31}P\{^1H\}$ NMR signals (−5.6 ppm for TPPTS and −6.0 ppm for $PPh_3$). Therefore, spectroscopic properties of complexes containing TPPTS are often similar to those of their organic-soluble analogues.

Bis-phosphine complexes of Pt(II) exist as either *cis* or *trans* isomers. The literature is not definitive on the thermodynamic preference for *cis* or *trans* in $PtCl_2L_2$ complexes; for $PtCl_2(PPr_3)_2$ (Pr = *n*-propyl) the preference is for 97% *trans*,[23] while for $PtCl_2(PPh_3)_2$ the preference is for 90% *cis*.[24] Similar results were noted for *cis*-$PtCl_2(P(OEt)_3)_2$ (100%) and $PtCl_2(PBu_3)_2$, which was 95% *trans*.[5] *cis*-$PtCl_2(PPh_3)_2$ can be prepared in several ways,[26] including by addition of $PPh_3$ to $K_2PtCl_4$ in aqueous EtOH/$H_2O$[27] and in refluxing xylene[28] or by addition of $PtCl_2$ to molten $PPh_3$.[29] *trans*-$PtCl_2(PPh_3)_2$ is prepared by a combination of Zeise's salt, K[$PtCl_3$($C_2H_4$)], with 2 equiv of $PPh_3$. *trans*-$PtCl_2(PPh_3)_2$ can be isomerized to *cis*-$PtCl_2(PPh_3)_2$ in the presence of excess $PPh_3$ with heat.[30]

Literature procedures[31] for the preparation of *cis*-$PtCl_2$(TPPTS)$_2$ consist of the dissolution of $K_2PtCl_4$ with 2 equiv of TPPTS in water at room temperature. Pure *cis*-$PtCl_2$(TPPTS)$_2$ was claimed to be isolated in high yields after drying. Our efforts to reproduce this synthesis were unsuccessful. In this paper we report the synthesis of $PtCl_2$(TPPTS)$_2$ from $PtCl_2$ in water, yielding pure complex with no ancillary KCl. This complex has been characterized by $^{31}P$ NMR, $^{195}Pt$ NMR, and elemental analysis. Its solution behavior in water vs DMSO has been examined via $^{31}P$ NMR. This complex is an efficient catalyst for the room-temperature Markovnikov hydration of 4-pentyn-1-ol to 5-hydroxy-2-pentanone. Hydration is also regiospecific for the hydration of 3-pentyn-1-ol to 5-hydroxy-2-pentanone under the same reaction conditions.

## Results and Discussion

**Synthesis of *cis*-$PtCl_2$(TPPTS)$_2$ (1).** Complex **1** (the compound numbering scheme is shown in Table 1) can be prepared from the addition of 2.05 equiv of TPPTS in water to an 80 °C brown suspension of $PtCl_2$[36] in

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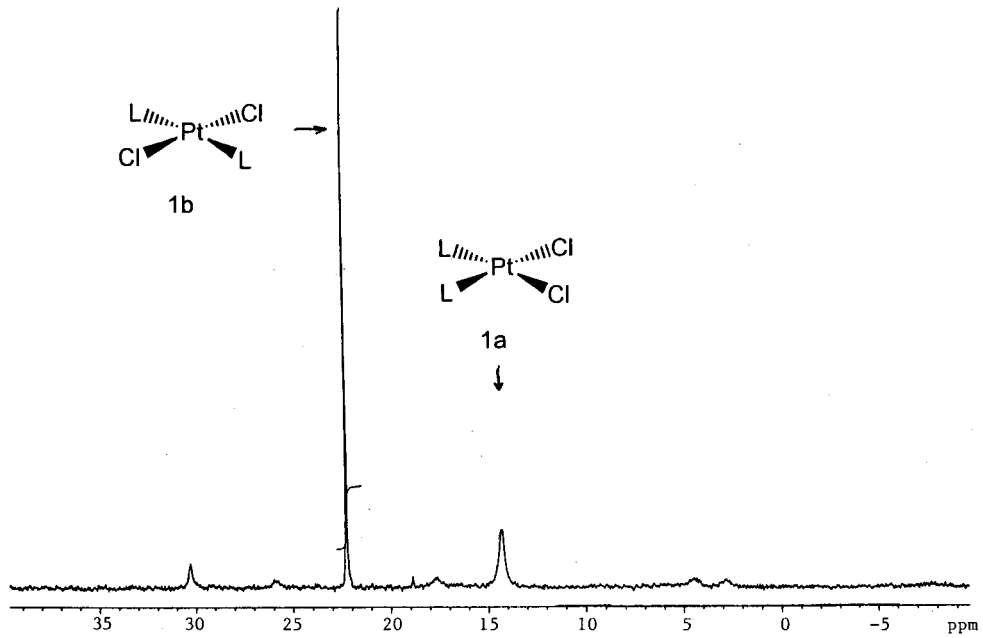


**Figure 1.** $^{31}P$ NMR spectrum for 1:1 *cis*-$PtCl_2(TPPTS)_2$ (**1a**) and *trans*-$PtCl_2(TPPTS)_2$ (**1b**).



water (eq 1). After 12 h at 80 °C, all of the $PtCl_2$ is

$$PtCl_2 + 2TPPTS \xrightarrow[80\ °C,\ 12\ h]{H_2O} \underset{\mathbf{1}}{PtCl_2(TPPTS)_2} \qquad (1)$$

consumed and the resulting pale yellow solution is filtered and dried in vacuo to afford a pale yellow solid (yield 88%). $PtCl_2(TPPTS)_2$ (**1**) can also be prepared by adding 2.05 equiv of TPPTS in DMSO to an 80 °C DMSO solution of $PtCl_2$ (soluble at this temperature). After 12 h at 80 °C, a pale solution forms. The product can be precipitated with $CH_2Cl_2$ and isolated via filtration with a yield of 98%.

$PtCl_2(TPPTS)_2$ (**1**) exists as *cis* and *trans* isomers (Figure 1) in the room-temperature $^{31}P$ NMR spectrum. The syntheses described above form both isomers of **1** in a 3:1 *cis*:*trans* ratio. The *trans* isomer is converted into the *cis* isomer at temperatures over 80 °C. Performing the synthesis at temperatures over 80 °C produces TPPTS-oxide (OTPPTS, $\delta$ 34.5 ppm). Higher concentrations of the *trans* isomer are favored when the reaction is done in DMSO at lower temperatures. When TPPTS is added to a room-temperature DMSO solution of $PtCl_2$, up to 50% *trans*-$PtCl_2(TPPTS)_2$ (**1b**) is formed.

The $^{31}P$ NMR spectrum of **1** in water (all NMR spectra were taken in $H_2O$ with a capillary insert of $D_2O$ for the lock) shows a broad peak at 14.3 ppm ($J_{Pt-P} = 3720$ Hz) corresponding to *cis*-$PtCl_2(TPPTS)_2$ (**1a**; 60%), and a sharp peak at 22.3 ppm ($J_{Pt-P} = 2600$ Hz) corresponding to *trans*-$PtCl_2(TPPTS)_2$ (**1b**; 20%) (see Table 1 for $^{31}P$ and $^{195}Pt$ data for all complexes). Also in the $^{31}P$ NMR spectrum in water are two broad doublets appearing at 17.6 ppm ($J_{P-P} = 20$ Hz, $J_{Pt-P} = 3740$ Hz) and 4.6 ppm ($J_{P-P} = 20$ Hz, $J_{Pt-P} = 3920$ Hz) accounting for 20% of the products, assigned to *cis*-$[PtCl(H_2O)(TPPTS)_2]^+$. This complex can be made independently by the addition of 1 equiv of AgOTf ($OTf = O_3SCF_3^-$) to **1a**, giving 55% *cis*-$[PtCl(H_2O)(TPPTS)_2][OTf]$ (**4**) by $^{31}P$ NMR (discussed in detail later in the paper). Trace amounts of $[PtCl_3TPPTS]^-$ (**6**) are often observed in the preparation of **1**. Complex **6** exists in higher concentrations during the reaction, accounting for 30% of the products when 30% of the $PtCl_2$ remains unreacted (as determined by $^{195}Pt$ NMR). $[PtCl_3TPPTS]^-$ (**6**) is characterized by a singlet at 18.9 ppm ($J_{Pt-P} = 3850$ Hz) in the $^{31}P$ NMR and a doublet at 3916 ppm in the $^{195}Pt$ NMR.

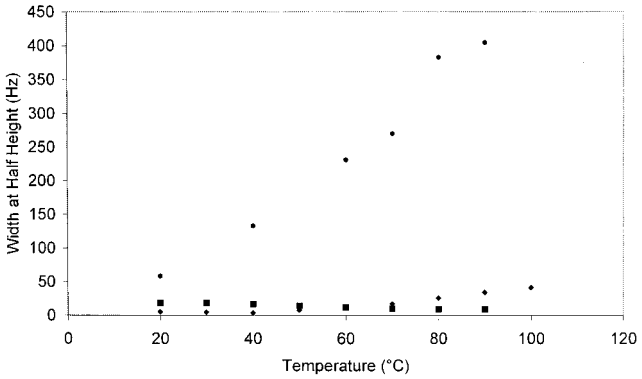


**Figure 2.** Line width vs temperature for *cis*-$PtCl_2TPPTS_2$ (**1a**): (◆) $PtCl_2(TPPTS)_2$ in DMSO; (■) $PtCl_2(TPPTS)_2$ in DMSO; (●) $PtCl_2(TPPTS)_2 \cdot 2KCl$ in $D_2O$.

The broadness of the $^{31}P$ NMR resonance for *cis*-$PtCl_2(TPPTS)_2$ in $H_2O$ is striking (line width 50 Hz) in comparison to *trans*-$PtCl_2(TPPTS)_2$ in $H_2O$ (line width 5 Hz) or to *cis*-$PtCl_2(TPPTS)_2$ in DMSO (line width 2 Hz).[33] When the compound is heated in $H_2O$ the resonance continues to broaden (line width 405 Hz at 90 °C) (as shown in Figure 2). The line broadening probably arises from chemical exchange of $H_2O$ for $Cl^-$. The broad resonances for *cis*-$PtCl(H_2O)(TPPTS)_2^+$ further broaden and disappear upon heating. Studies on *cis*- and *trans*-$PtCl_2(PEt_3)_2$ show that the rate constant for associative substitution of $Cl^-$ by pyridine is more

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(33) In all of the spectra recorded at high field, the $^{31}P$ resonances arising from $^{195}Pt$ coupling are broader than the center, uncoupled peak. This is a well-established consequence of chemical shift anisotropy.[34]

than $10^3$ greater for the *cis* complex than for the *trans*.[35] If the rapid substitution for a *cis* complex continues to $PtCl_2(TPPTS)_2$ in $H_2O$, the *cis* complex could be broadened by chemical exchange of $Cl^-$ for $H_2O$ while the *trans* complex is less affected. After a sample that had been heated to 95 °C is cooled, the peak for **4** reappears and again accounts for 20% of the sample, while the remaining 80% is now all *cis*-$PtCl_2(TPPTS)_2$ (**1a**).

In DMSO, the room-temperature $^{31}P$ spectrum shows only $PtCl_2(TPPTS)_2$ in a 80/20 *cis*/*trans* ratio. *trans*-$PtCl_2(TPPTS)_2$ (**1b**) is seen as a sharp singlet at 25.3 ppm ($J_{Pt-P} = 2580$ Hz), and *cis*-$PtCl_2(TPPTS)_2$ (**1a**) is a sharp singlet at 15.5 ppm ($J_{Pt-P} = 3720$ Hz). No other peaks are observed, and sharp lines in the spectrum indicate no $Cl^-$ exchange with DMSO is occurring on the NMR time scale. When the temperature is raised to 100 °C, broadening of the peaks occurs, perhaps indicating some exchange of the chloride ligand for DMSO at higher temperatures (Figure 2). Heating also causes a slight increase in the concentration of the *trans* isomer (20−30%).

In the synthesis of $PtCl_2(TPPTS)_2$ (**1**), addition of more than 2.05 equiv of TPPTS leads to formation of the tris-phosphine complex $[PtCl(TPPTS)_3]Cl$ (**5**) in addition to complex **1**. Complex **5** can be synthesized quantitatively by the reaction of 3 equiv of TPPTS with $PtCl_2$ in water at 80 °C (eq 2). All the $PtCl_2$ is consumed after 12 h,

$$PtCl_2 + 3TPPTS \xrightarrow[80\ °C,\ 12\ h]{H_2O} \underset{\mathbf{5}}{[PtCl(TPPTS)_3]Cl} \quad (2)$$

resulting in a yellow solution. Water is removed in vacuo to produce yellow crystals of **5** in 88% yield. $[PtCl(TPPTS)_3]Cl$ (**5**) is characterized by a doublet in the $^{31}P$ NMR spectrum at 23.8 ppm corresponding to the two phosphines *trans* to each other ($J_{P-P} = 18$ Hz, $J_{Pt-P} = 2500$ Hz), and a triplet at 12.6 ppm ($J_{P-P} = 18$ Hz, $J_{Pt-P} = 3680$ Hz) corresponding to the unique phosphine *trans* to chloride.[36]

Also, in contrast to previously published results,[31] addition of 2 equiv of TPPTS to $K_2PtCl_4$ at room temperature in water leads to formation of *cis*-$PtCl_2(TPPTS)_2$ (**1a***)* plus $[PtCl(TPPTS)_3]Cl$ (**5**) in a 3/1 ratio (eq 3). In water, the $^{31}P$ resonance corresponding to **1**

$$K_2PtCl_4 + 2TPPTS \xrightarrow[\text{room temp}]{H_2O} \underset{\mathbf{1},\ 75\%}{cis\text{-}PtCl_2(TPPTS)_2} + \underset{\mathbf{5},\ 25\%}{[PtCl(TPPTS)_3]Cl} + 2KCl \quad (3)$$

is broad while the peaks for **5** are sharp and well-resolved. This indicates that the process causing the broadening of the peaks for **1** and **4** does not involve phosphine exchange for chloride. The product mixture was evacuated to dryness and redissolved in DMSO. The $^{31}P$ NMR in DMSO shows *cis*-$PtCl_2(TPPTS)_2$ (**1a**) plus free TPPTS ($\delta$ −5.6 ppm) in an 85/15 ratio. Performing the reaction in DMSO gives the same results (eq 4).

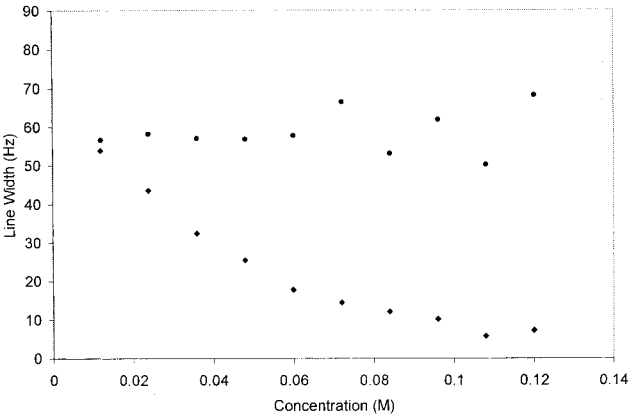


**Figure 3.** Concentration vs line width for *cis*-$PtCl_2(TPPTS)_2$ (**1a**) in $D_2O$: (◆) $PtCl_2(TPPTS)_2$·2KCl in $D_2O$; (●) $PtCl_2(TPPTS)_2$ in $D_2O$.

$$K_2PtCl_4 + 2TPPTS \xrightarrow[\text{room temp}]{DMSO} \underset{\mathbf{1},\ 85\%}{cis\text{-}PtCl_2(TPPTS)_2} + \underset{15\%}{TPPTS} + 2KCl \quad (4)$$

Addition of only 1.5 equiv of TPPTS to $K_2PtCl_4$ in water produces a crystalline product that is light coral, compared to the expected pale yellow. The $^{31}P$ NMR spectrum shows only *cis*-$PtCl_2(TPPTS)_2$ (**1a**; a broad singlet at 14.3 ppm, $J_{Pt-P} = 3730$ Hz), but the $^{195}Pt$ NMR spectrum shows the presence of unreacted $K_2PtCl_4$ ($\delta$(Pt) −1627 ppm), accounting for about 30% total platinum. Addition of more than 1.5 equiv of TPPTS produced some of the tris-phosphine product $[PtCl(TPPTS)_3]Cl$ (**5**), even if all the $K_2PtCl_4$ was not consumed. This reaction was attempted at various temperatures up to 100 °C with the same results.

As with *cis*-$PtCl_2(TPPTS)_2$ (**1a**), *cis*-$PtCl_2(TPPTS)_2$ with 2KCl (prepared from $K_2PtCl_4$ and 1.5 equiv of TPPTS) in water exhibits a broad peak in the $^{31}P$ NMR spectrum. However, unlike **1a**, no peaks corresponding to *cis*-$[PtCl(H_2O)(TPPTS)_2]^+$ (cation of **4**) are observed. Increasing the concentration of *cis*-$PtCl_2(TPPTS)_2$ with 2KCl causes the phosphine resonance to narrow, while increasing the concentration of **1a** (without excess KCl) has virtually no effect on its line width (Figure 3) or the ratio of **1a** to **4** present. The extra $Cl^-$ in *cis*-$PtCl_2(TPPTS)_2$ with 2KCl inhibits formation of **4**. Accordingly, addition of 10 equiv of KCl to a solution of *cis*-$PtCl_2(TPPTS)_2$ (**1a**) causes a decrease in line width for **1a** from 54 to 3 Hz and a disappearance of the peaks corresponding to **4**.

All complexes have been characterized by $^{195}Pt$ NMR spectroscopy (Table 1); peaks are referenced to an internal standard of 0.2 M $K_2PtCl_4$ in 0.4 M KCl/$D_2O$ set to −1627 ppm (vs 0.2 M $K_2PtCl_6$ in $D_2O$).[37] *cis*-$PtCl_2(TPPTS)_2$ (**1a**) is characterized by a triplet at −4437 ppm with a phosphorus coupling constant of 3720 Hz, in the

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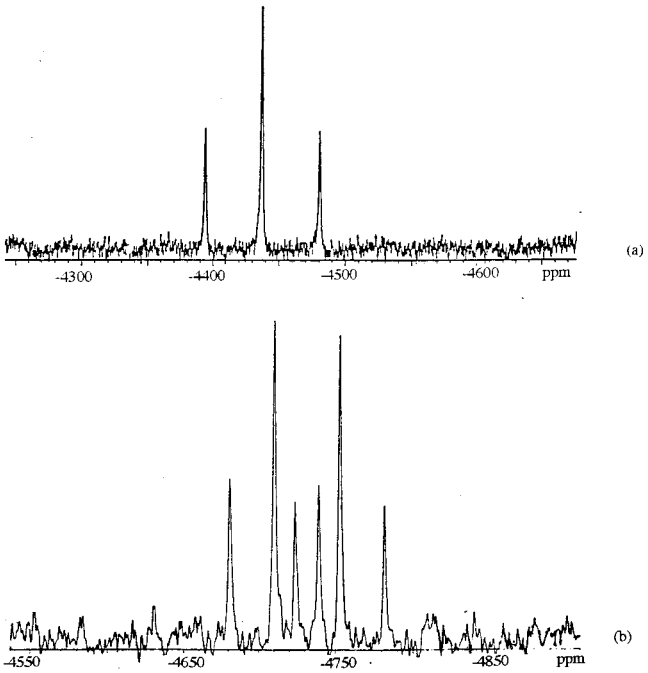


**Figure 4.** $^{195}Pt$ NMR spectra in $D_2O$: (a) *cis*-$PtCl_2(TPPTS)_2$ (**1a**); (b) $[PtCl(TPPTS)_3]Cl$ (**5**).

range for complexes of this type (Figure 4a).[37,38] *trans*-$PtCl_2(TPPTS)_2$ (**1b**) resonates as a triplet at −4072 ppm ($J_{Pt-P}$ = 2600 Hz). $[PtCl_3TPPTS]^-$ (**6**) appears as a doublet at −3916 ppm ($J_{Pt-P}$ = 3850 Hz). $[PtCl(TPPTS)_3]^+$ (cation of **5**) is seen as a doublet of triplets at −4371 ppm with phosphorus coupling of 3680 Hz for the unique phosphine *trans* to a chloride and 2500 Hz for the two phosphines *trans* to each other (Figure 4b).

**Reactions of *cis*-$PtCl_2(TPPTS)_2$ in Water.** Dissolving **1a** in water in the absence of $Cl^-$ produces about 20% of *cis*-$Pt(Cl)(H_2O)(TPPTS)_2^+$ (cation of **4**), which has two broad doublets in the $^{31}P$ NMR (17.6 and 4.6 ppm) with typical coupling (20 Hz) for *cis* phosphine ligands. The same complex can be made in 55% yield by reaction of 1 equiv of AgOTf with **1a**. This reaction mixture also contains 10% of **1a** and 30% of *cis*-$[Pt(H_2O)_2(TPPTS)_2]^{2+}$ (cation of **3**; a broad singlet at 9.2 ppm in the $^{31}P$ spectrum and a $^{195}Pt$ resonance at −3839(t) with $J_{P-Pt}$ = 3680 Hz); the reaction mixture is light yellow. Reaction of *cis*-$PtCl_2(TPPTS)_2$ with 2 equiv of AgOTf produces complex **3** (55%) with several unidentified species (a singlet at 5.6 ppm (10%, $J_{Pt-P}$ = 3990 Hz), two doublets at 12.6 and 4.6 ppm (20%, $J_{P-P}$ = 21 Hz, $J_{Pt-P}$ = 3830 Hz, 3630 Hz respectively), and a singlet at 12.6 ppm (10%, $J_{Pt-P}$ = 3790 Hz)).

Direct base hydrolysis of *cis*-$PtCl_2(TPPTS)_2$ with 2 equiv of NaOH (pH 12) produces **2**, $Pt_2(TPPTS)_4(\mu\text{-}OH)_2$ ($^{31}P$, $\delta$ 10.7(s) ppm; $^{195}Pt$, $\delta$ −4083(t) ppm, $J_{P-Pt}$ = 3530 Hz[21]), in 80% yield and 20% of OTPPTS. Basic conditions are known to promote OTPPTS formation.[39] Base hydrolysis with 1 equiv of NaOH (pH 9) produces **2** and **3** in a 1/1 ratio. The $^{31}P$ resonance for **2** is sharp, while **3** has a broad $^{31}P$ resonance. Acidification of **2** with HCl (2 equiv, pH drops from 12 to 3) produces **3** as the major product. Over the course of a few hours **3** is converted to **1a**, *cis*-$PtCl_2(TPPTS)_2$.

Aqua, hydroxo, and oxo complexes of platinum have been reported,[40−46] although the reaction chemistry in water is limited by the low solubility of the platinum complexes. Sharp and colleagues have reacted $PtL_2Cl_2$ (L = phosphine ligands) with $Ag^+$ salts in methanol or ethanol with small amounts of water to produce binuclear complexes with bridging hydroxy ligands, $Pt_2L_4(\mu\text{-}OH)_2^{2+}$.[42] Deprotonation with base gives the bridging oxo complexes, $Pt_2L_4(\mu\text{-}O)_2$. These reactions are accomplished in nonaqueous solvents. For L = $PPh_3$ the oxo complex reacts with $H_2O$ to regenerate the bridging hydroxy complex.[42] Thus, it is unlikely that our reactions in aqueous solution produce an oxo complex. Miyamato et al.[43] prepared $Pt(OH)_2L_2$ (L = $PMe_3$) under basic conditions; reaction with 1 equiv of $HNO_3$ gave $Pt_2L_4(\mu\text{-}OH)_2^{2+}$, and reaction of $Pt(OH)_2L_2$ with 2 equiv of $HNO_3$ gave $Pt(H_2O)_2L_2^{2+}$. No evidence of a bridging oxo ligand was found in these studies in water.[43] Reactions of $PtL_2Cl_2$ ($L_2$ = 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy)) have also been examined.[41,46] Reaction with 2 equiv of $Ag^+$ produces $[PtL_2(\mu\text{-}OH)]_2^{2+}$ with hydroxo bridges.[41] Further addition of NaOH to pH 8 produces a deep red color indicative of the binuclear complex triply bridged by hydroxide, $Pt_2(L_2)_2(\mu\text{-}OH)_3^+$.[41] Base hydrolysis of $PtL_2Cl_2$ ($L_2$ = bipy) rapidly produces $PtL_2(OH)_2$.[41] Acidification of the dihydroxo complex produces the binuclear complex $Pt_2(L_2)_2(\mu\text{-}OH)_2$ at intermediate pH (pH 4); at pH 1 acidification with $HNO_3$ produces the nitrate complex $PtL_2(ONO_2)_2$ upon evaporation of the water.[41] A number of studies have focused on *cis*-$PtL_2Cl_2$ (L = $NH_3$ (cisplatin), other amine ligand) to understand the interactions with biomolecules in vivo.[44−46] Most pertinent to our observations is the $^{195}Pt$ and $^{15}N$ NMR study of the hydrolysis of *cis*-$Pt(NH_3)_2Cl_2$.[44] Reaction with $Ag^+$ in weak $HNO_3$ produced the diaqua complex $Pt(NH_3)_2(OH_2)_2^{2+}$, which formed the hydroxide-bridged dimer and trimer when the pH was adjusted above 6.65.[44] The $Pt_2(NH_3)_4(\mu\text{-}OH)_2^{2+}$ and $Pt_3(NH_3)_6(\mu\text{-}OH)_3^{3+}$ dissociate rapidly to *cis*-$Pt(NH_3)_2(OH_2)_2$ upon treatment with acid (10 min). The formation of dimer and trimer is considered to occur through the monohydroxo intermediate $PtL_2(OH)(OH_2)^+$.[45]

The previous observations on Pt(II) aqua and hydroxo complexes can be summarized by the pH-dependent



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equilibria (shown in order of increasing pH)

$$PtL_2(OH_2)^{2+} \rightleftarrows Pt_2L_4(\mu\text{-}OH)_2^{2+} \rightleftarrows Pt_2L_4(\mu\text{-}OH)_3^{+} \rightleftarrows PtL_2(OH)_2$$

This scheme does not include $PtL_2(OH)(H_2O)^+$, the presumed intermediate to the dimer,[45] and does not include the trimer or higher oligomers. For L = $NH_3$ the pH for conversion of the diaquo complex to the dimer is pH ≅7, while for $L_2$ = bipy the pH ≅1. For the most reasonable assignment of **2** and **3** the formation of the binuclear complex for L = TPPTS occurs at pH ≅9. For TPPTS, even at pH 12 the distinctive red of $Pt_2L_4(\mu\text{-}OH)_3^+$ is not observed. The broadness of the $^{31}P$ resonance for the cation of **3**, *cis*-$Pt(H_2O)_2(TPPTS)_2^{2+}$, is most consistent with an aqua ligand that is exchangeable as observed for **1** and **4**. The sharpness of the $^{31}P$ resonance for **2** is consistent with the unusually stable binuclear complex $Pt_2(TPPTS)_4(\mu\text{-}OH)_2^{2+}$. Acidification of **2**, which quickly produces **3**, is consistent with the observation for L = $NH_3$ of a rapid dissociation of $Pt_2L_4(\mu\text{-}OH)_2^{2+}$ and $Pt_3L_6(\mu\text{-}OH)_3^{3+}$ upon treatment with acid. The subsequent rearrangement of **3** to **1** is a ligand substitution of $Cl^-$ for $H_2O$, where the $H_2O$ is more than $10^4$ in excess. $Cl^-$ substitution was quite slow for L = $NH_3$ complexes also.[44] Thus, our assignments are **2** as $Pt_2(TPPTS)_4(\mu\text{-}OH)_2^{2+}$ and **3** as $Pt(OH_2)_2(TPPTS)_2^{2+}$. The assignments and spectroscopic characteristics are given in Table 1. Equations 5−8 summarize the aqueous chemistry of $PtCl_2(TPPTS)_2$.

$$\underset{\textbf{1a}}{cis\text{-}PtCl_2(TPPTS)_2} \xrightarrow[H_2O,\ room\ temp]{NaOH\ (2\ equiv)} \underset{\textbf{2},\ 80\%}{Pt_2(TPPTS)_4(\mu\text{-}OH)_2^{2+}} + \underset{20\%}{OTPPTS} \quad (5)$$

$$\underset{\textbf{1a}}{cis\text{-}PtCl_2(TPPTS)_2} \xrightarrow[H_2O,\ room\ temp]{NaOH\ (1\ equiv)} \underset{\textbf{2},\ 33\%}{Pt_2(TPPTS)_4(\mu\text{-}OH)_2^{2+}} + \underset{\text{cation of }\textbf{3},\ 67\%}{Pt(OH_2)_2(TPPTS)_2^{2+}} \quad (6)$$

$$\underset{\textbf{2}}{Pt_2(TPPTS)_4(\mu\text{-}OH)_2^{2+}} + 2HCl \xrightarrow[room\ temp,\ 1\ min]{H_2O} \underset{\text{cation of }\textbf{3}}{2cis\text{-}[Pt(OH_2)_2(TPPTS)_2]^{2+}} \xrightarrow[room\ temp,\ 12\ h]{-H_2O,\ +Cl} \underset{\textbf{1a}}{cis\text{-}PtCl_2(TPPTS)_2} \quad (7)$$

$$\underset{\textbf{1a}}{cis\text{-}PtCl_2(TPPTS)_2} + 2AgOTf \xrightarrow[room\ temp,\ 12\ h]{H_2O} \underset{\textbf{3},\ 55\%}{cis\text{-}[Pt(OH_2)_2(TPPTS)_2][OTf_2]} \quad (8)$$

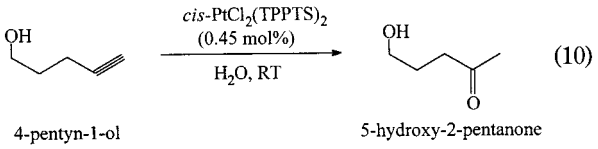
**Synthesis of *cis*-$[PtCl(H_2O)(TPPTS)_2]^+$ (Cation of 4).** Complex **4** is observed in the $^{31}P$ NMR spectrum along with *cis*-$PtCl_2(TPPTS)_2$ (**1a**) when **1a** is dissolved in water. *cis*-$[PtCl(H_2O)(TPPTS)_2]^+$ (cation of **4**) can be synthesized independently by the addition of 1 equiv of AgOTf to a water solution of *cis*-$PtCl_2(TPPTS)_2$ (**1a**). The resulting white precipitate (AgCl) can be removed via filtration through Celite. Removing the solvent from the pale yellow solution yields a pale yellow crystalline solid in 74% yield. $^{31}P$ NMR indicates that, upon dissolution in water, this solid exists as a mixture of 55% $[PtCl(H_2O)(TPPTS)_2]^+$ (cation of **4**), 30% *cis*-$[Pt(OH_2)_2(TPPTS)_2]^{2+}$ (cation of **3**), and 10% *cis*-$PtCl_2(TPPTS)_2$ (**1a**) (eq 9). The other 5% are various unidentified byproducts.

$$\underset{\textbf{1a}}{cis\text{-}PtCl_2(TPPTS)_2} \xrightarrow[room\ temp]{AgOTF,\ H_2O\ (1\ equiv)} \underset{\text{cation of }\textbf{4},\ 55\%}{cis\text{-}[Pt(Cl)(OH_2)(TPPTS)_2]^+} + \underset{\text{cation of }\textbf{3},\ 30\%}{cis\text{-}[Pt(OH_2)_2(TPPTS)_2]^{2+}} + \underset{\textbf{1a},\ 10\%}{cis\text{-}PtCl_2(TPPTS)_2} \quad (9)$$

$[PtCl(H_2O)(TPPTS)_2]^+$ (**4**) is characterized by a doublet of doublets in the $^{31}P$ NMR spectrum resonating at 17.6 ppm ($J_{P-P}$ = 20 Hz, $P_{Pt-P}$ = 3740 Hz) and 4.6 ppm ($J_{P-P}$ = 20 Hz, $P_{Pt-P}$ = 3920 Hz). The peak at 17.6 ppm is assigned to the phosphorus *trans* to the Cl ligand, while the peak at 4.6 ppm with larger Pt coupling corresponds to the phosphorus *trans* to the weaker $H_2O$ ligand. The platinum nucleus resonates as two overlapping doublets at −4280 ppm with phosphorus coupling of 3740 and 3920 Hz.

**Hydration of Water-Soluble Alkynes.** *cis*-$PtCl_2(TPPTS)_2$ (**1a**) in water is an effective catalyst for the room-temperature hydration of the water-soluble alkynes 3-pentyn-1-ol and 4-pentyn-1-ol. Standard reaction conditions consist of 6 mg (0.45 mol %) of *cis*-$PtCl_2(TPPTS)_2$ (**1a**) in 1 mL of water. The solution is nearly colorless and has a pH of 5. Upon addition of ∼200 equiv of substrate, the solution turns pale yellow and the pH drops to 3 due to the acidity of the substrate. The reaction is monitored by $^1H$ NMR spectroscopy.

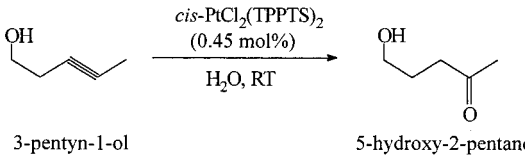
Hydration of the terminal alkyne 4-pentyn-1-ol using *cis*-$PtCl_2(TPPTS)_2$ (**1a**) yields 5-hydroxy-2-pentanone (eq 10). Over the course of several hours at room temperature, the $^1H$ resonances for 4-pentyn-1-ol disappear and the resonances for 5-hydroxy-2-pentanone grow. The pH remains at 3 during the course of the reaction. However, the ketones themselves only have a pH of 5, very similar to that of the complex in water. The low pH of the final reaction mixture must result from the loss of protons from the platinum center in the first step. The reaction is clean, and no other products are observed. Complete conversion of 4-pentyn-1-ol occurs within 24 h under these conditions, with a turnover frequency (TOF) of 175 $h^{-1}$ at 20% conversion. When the reaction is performed at 80 °C, complete conversion of the substrate occurs within 1 h. The $^{31}P$ NMR spectrum at the end of the reaction exhibits an AB pattern with platinum satellites, denoting a complex with inequivalent groups *trans* to the phosphine ligands. Using a modeling program, peaks were found to resonate at 16.3 ppm ($J_{Pt-P}$ = 3735 Hz) and 15.6 ppm ($J_{Pt-P}$ = 3915 Hz) with $J_{P-P}$ = 16 Hz. This complex is stable for several weeks in the




(10)

reaction mixture; however, in the presence of a large excess of chloride the major species in solution becomes *cis*-$PtCl_2(TPPTS)_2$ (**1a**). While we were unable to isolate the product, its characteristics are consistent with the alkyne complex $Pt(H_2O)(alkyne)(TPPTS)_2^{2+}$.

Hydration of the internal alkyne 3-pentyn-1-ol is expected to be less selective and should form a mixture of 5-hydroxy-2-pentanone and 5-hydroxy-3-pentanone. Surprisingly, hydration of 3-pentyn-1-ol with catalytic amounts of *cis*-$PtCl_2(TPPTS)_2$ (**1a**) yields 5-hydroxy-2-pentanone as the only product (eq 11). Conversion of




(11)

3-pentyn-1-ol 5-hydroxy-2-pentanone

the alkyne to 5-hydroxy-2-pentanone can be observed using $^1H$ NMR spectroscopy. The reaction is clean and no other products are observed. The conversion of 3-pentyn-1-ol to 5-hydroxy-2-pentanone is complete after 48 h at room temperature. This corresponds to a TOF of 115 $h^{-1}$ at 20% conversion. The process is somewhat slower than the conversion of 4-pentyn-1-ol under the same reaction conditions. As with the hydration of 4-pentyn-1-ol, the pH of the solution drops from 5 to 3 upon substrate addition, and the pH remains at 3 throughout the course of the reaction.

Unlike the clean formation of one phosphorus-containing species during the hydration of 4-pentyn-1-ol, many phosphorus-containing species are present during the hydration of 3-pentyn-1-ol. The predominant complex exhibits a singlet in the $^{31}P$ NMR at $\delta$ 26.6 ppm with a platinum−phosphorus coupling constant of 3035 Hz. This value is intermediate between *cis* ($J_{Pt-P} \sim$ 3200−3600 Hz) and *trans* ($P_{Pt-P} \approx$ 2200−2400 Hz) coupling constants for weak ligands but typical of *trans*-$Pt(R)XL_2$ (R = alkyl, aryl).[47] If a large excess of chloride ion is present (∼100 equiv), the predominant complex in solution after all the alkyne is converted is the starting catalyst *cis*-$PtCl_2(TPPTS)_2$ (**1a**) along with the unknown species in a 2:1 ratio. Some of the aqua complex *cis*-$[PtCl(H_2O)(TPPTS)_2]^+$ (**4**) is also present in the reaction mixture.

The rate of hydration for both 3-pentyn-1-ol and 4-pentyn-1-ol varies with KCl concentration (Figure 5) but, unexpectedly, in opposite directions. Reactions were carried out using 0.45 mol % *cis*-$PtCl_2(TPPTS)_2$ (**1a**) with 0, 1, 4.5, and 45 mol % KCl (0, 2, 10, and 100 equiv with respect to **1a**) added to monitor the effect of KCl on the rate of hydration. For 4-pentyn-1-ol a decrease in hydration rate is observed. Without KCl added to the catalyst solution, 62% of 4-pentyn-1-ol converted to 5-hydroxy-2-pentanone after 2 h at room temperature. With 100 equiv (45 mol %) of KCl added to the catalyst mixture before alkyne addition, the amount converted drops to 35% after 2 h. The rate of hydration of 3-pentyn-1-ol to 5-hydroxy-2-pentanone shows an increase in conversion rate with increased concentration of KCl added. With no KCl added to the catalyst

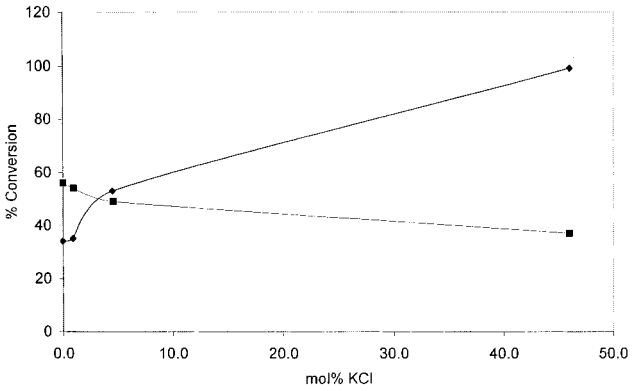



**Figure 5.** Hydration of functionalized alkynes (*cis*-$PtCl_2(TPPTS)_2$ (**1a**, 0.45 mol %) with 200 equiv of alkyne, 2 h reaction time): (◆) 3-pentyn-1-ol; (■) 4-pentyn-1-ol.

solution, 30% of the 3-pentyn-1-ol is converted to 5-hydroxy-2-pentanone after 2 h of reaction time. With 100 equiv (45 mol %) of KCl added to the catalyst solution, 3-pentyn-1-ol is completely converted to 5-hydroxy-2-pentanone (by $^1H$ NMR) after 2 h (initial TOF over 550 $h^{-1}$).

The product of both catalytic hydrations arises through cyclization of the alkynes followed by hydrolysis of the heterocycle (Scheme 1). 5-Hydroxy-2-pentanone is formed from 4-pentyn-1-ol by a 5-exo-dig mechanism followed by hydrolysis, while 5-hydroxy-2-pentanone is formed from 3-pentyn-1-ol by a 5-endo-dig mechanism.[48] Similar cyclizations have been reported using $PdCl_2$ in aqueous $CH_3CN$. Under anhydrous conditions, the heterocycles are the observed products.[49]

The Pt(II) complex serves to activate the alkyne toward intramolecular nucleophilic attack by the pendant OH upon coordination. Alkynes bind to Pt(II) perpendicular to the square plane and offset such that the midpoint of the carbon−carbon bond of the alkyne is above the square plane.[50−52] For 4-pentyn-1-ol, this binding mode accentuates the inherent charge separation of the alkyne carbons (evidenced by the acidic nature of the terminal hydrogen). This makes the carbon leading to exo attack more positive. In 3-pentyn-1-ol, the carbon leading to endo attack is less positive than the exo carbon of 4-pentyn-1-ol. Accordingly, the hydration of 3-pentyn-1-ol is slower than 4-pentyn-1-ol under standard reaction conditions.

With excess $Cl^-$ added, the hydration of 4-pentyn-1-ol is inhibited. The chloride could coordinate along the *z* axis, probably on the side with the least steric inhibition from alkyne. This coordination mode would place the chloride in close proximity to the exo carbon of the alkyne and would inductively reduce the charge distribution that facilitates nucleophilic attack.

For 3-pentyn-1-ol, a similar coordination mode would be expected for added chloride. The chloride would then be in close proximity to the endo carbon, thereby increasing the positive charge on that carbon. The endo carbon would then be more reactive toward nucleophilic

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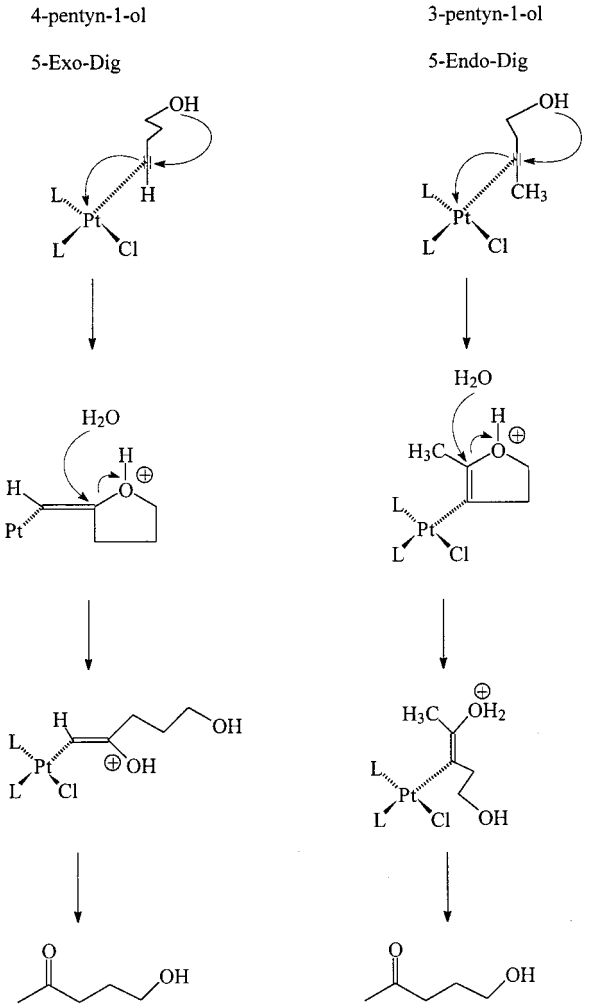
**Scheme 1. Proposed Mechanism for the Catalytic Hydration of 4-Pentyn-1-ol and 3-Pentyn-1-ol with 1a**




attack by OH. Accordingly, there is a dramatic acceleration in rate when 3-pentyn-1-ol is hydrated in the presence of excess $Cl^-$.

As noted previously, standard reaction conditions result in an acidic reaction mixture. In fact, no hydration of 3-pentyn-1-ol or 4-pentyn-1-ol occurs at a pH over 7. Under basic conditions, $PtCl_2(TPPTS)_2$ forms $Pt_2(TPPTS)_4(\mu\text{-}OH)_2^{2+}$, which was shown to be inactive toward alkyne hydration. The catalytic intermediates in the proposed mechanism have not been observed spectroscopically.

As a check on our mechanistic interpretation, we have also examined hydration of 5-hexyn-1-ol, which would be expected to produce 6-hydroxy-2-hexanone by a 6-exo-dig mechanism. Under the same reaction conditions as for hydration of 3- and 4-pentyn-1-ol, 5-hexyn-1-ol gave 6-hydroxy-2-hexanone in 100% yield. This reaction was identical in all aspects to the hydration of 4-pentyn-1-ol. Excess $Cl^-$ inhibited the reaction. The hydration of 5-hexyn-1-ol provides further evidence that excess $Cl^-$ inhibits exo attack of the OH on the coordinated alkyne.

Note that reactions 10 and 11 are hydration reactions. No evidence for the cyclic products from the mechanism is found, but the specificity of the products and the differing $Cl^-$ dependences are consistent with an intramolecular attack by the OH.

## Experimental Section

**Materials and Methods.** Reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Water was triply distilled and deionized and was purged with nitrogen prior to use. All other solvents were purged with nitrogen and used without further purification. Deuterium oxide was purchased from Isotec, Inc. DMSO-$d_6$ and methanol-$d_4$ were obtained from Aldrich. $K_2PtCl_4$ and $H_2PtCl_6{\cdot}6H_2O$ were purchased from Strem Chemicals and used as received. TPPTS[53] and $PtCl_2$[32] were prepared using literature procedures. All other reagents were obtained from commercial sources and used without further purification.

$^1H$ NMR (400 MHz), $^{31}P$ NMR, and $^{195}Pt$ NMR were recorded on a Varian XL 400 spectrometer. $^{31}P$ NMR spectra were measured at 161.9 MHz, proton-decoupled and referenced to an external sample of 85% $H_3PO_4$ in $D_2O$ set at 0.00 ppm. $^{195}Pt$ NMR spectra were measured at 85.97 MHz and referenced using an internal standard of 0.2 M $K_2PtCl_4$ in 0.4 M KCl/$D_2O$ set to −1627.0 ppm (vs 0.2 M $K_2PtCl_6$ in $H_2O$).[37,54] Analyses were conducted by E and R Microanalytical Laboratory in Parsipanny, NJ. pH measurements were performed using a Fisher Scientific Accumet pH meter with a glass pH electrode with a silver/silver chloride reference electrode, referenced to three buffers (pH 4, 7, 10).

**$PtCl_2(TPPTS)_2$ (1). Method A.** Into a Schlenk flask was weighed 102 mg (0.383 mmol) of $PtCl_2$ followed by 10.0 mL of $H_2O$. The brown suspension was heated in an 80 °C oil bath. To this was added 499 mg (0.774 mmol, 2.02 equiv) of TPPTS in 10.0 mL of $H_2O$. Over 12 h, a yellow solution formed. Filtration from any insoluble material followed by solvent removal in vacuo gave a pale yellow, oily solid of **1** in 88% yield.

**Method B.** Into a Schlenk flask was weighed 113 mg (0.425 mmol) of $PtCl_2$ followed by 10.0 mL of DMSO. The brown suspension was heated in an 80 °C oil bath until all the $PtCl_2$ went into solution, about 5 min. To the resulting brown solution was added 533 mg (0.853 mmol, 2.01 equiv) of TPPTS in 10.0 mL of DMSO. Over 12 h, a light yellow solution formed. Precipitation with $CH_2Cl_2$ followed by filtration and drying in vacuo produced a cream-colored solid in 98% yield. $^{31}P\{^1H\}$ NMR ($D_2O$; $\delta$ (ppm)): 22.3 s ($^1J_{P-Pt} = 2600$ Hz), **1b** (20%); 14.3 broad s ($^1J_{P-Pt} = 3720$ Hz), **1a** (60%); 17.6 d ($^2J_{P-P} = 20$ Hz, $^1J_{P-Pt} = 3740$ Hz), 4.6 d ($^2J_{P-P} = 20$ Hz, $^1J_{P-Pt} = 3920$ Hz), *cis*-$[Pt(Cl)(H_2O)(P\text{-}(C_6H_4\text{-}SO_3Na)_3)_2]^+$ (cation of **4**, 20%). $^{31}P\{^1H\}$ NMR (DMSO; $\delta$ (ppm)): 25.3 s ($^1J_{P-Pt} = 2580$ Hz), **1b** (20%); 15.5 s ($^1J_{P-Pt} = 3720$ Hz), **1a** (80%). $^{195}Pt$ NMR ($D_2O$; $\delta$ (ppm)): −4072.4 t ($^1J_{P-Pt} = 2600$ Hz), **1b**; −4437.2 t ($^1J_{P-Pt} = 3720$ Hz), **1a**. Anal. Calcd for $PtCl_2P_2C_{36}H_{24}S_6O_{18}Na_6$: C, 30.82; H, 1.80; S, 13.71; Cl, 5.05. Found (method A): C, 30.10; H, 1.91; S, 13.60; Cl, 4.37. Found (method B): C, 29.99; H, 2.43; S, 14.29; Cl, 5.05. The product from A carries two water molecules, while the product from B has some DMSO and $CH_2Cl_2$ in the crystalline material.

**$Pt_2(TPPTS)_4(\mu\text{-}OH)_2^{2+}$ (2).** To a solution of 75 mg (0.049 mmol) of $PtCl_2(TPPTS)_2$ (**1**) in 1.0 mL of $H_2O$ was added 0.180 mL of a 0.55 M aqueous NaOH solution (0.10 mmol, 2 equiv). A color change from pale yellow to dark yellow was observed, along with an increase in pH from 4 to 12. Formation of $Pt_2(TPPTS)_4(\mu\text{-}OH)_2^{2+}$ was confirmed by $^{31}P$ NMR in 80% yield, along with 20% OTPPTS. $^{31}P\{^1H\}$ NMR ($D_2O$; $\delta$ (ppm)): 10.7 s ($^1J_{P-Pt} = 3530$ Hz), 34.5 s (OTPPTS). $^{195}Pt$ NMR ($D_2O$; $\delta$ (ppm)): −4082.7 t ($^1J_{P-Pt} = 3530$ Hz).

***cis*-$[Pt(H_2O)_2(TPPTS)_2][OTf]_2$ (3).** Into a Schlenk flask were weighed 134 mg (0.088 mmol) of $PtCl_2(TPPTS)_2$ (**1**) and 48 mg (0.19 mmol, 2.1 equiv) of AgOTf. Dissolution in 3.0 mL of $H_2O$ formed a pale yellow solution. The reaction was stirred

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at room temperature overnight in the absence of light, resulting in formation of a white precipitate which was removed via Celite filtration. Following solvent removal in vacuo, a pale yellow solid was isolated in 72% yield. $^{31}P$ NMR showed a mixture of products; the major product was identified as *cis*-$[Pt(H_2O)_2(TPPTS)_2][OTf]_2$ (**3**). $^{31}P\{^1H\}$ NMR ($D_2O$; $\delta$ (ppm)): 9.2 broad s ($^1J_{P-Pt} = 3680$ Hz). $^{195}Pt$ NMR ($D_2O$; $\delta$ (ppm)): −3838.8 t ($^1J_{P-Pt} = 3680$ Hz).

***cis*-[PtCl(H$_2$O)(TPPTS)$_2$][OTf] (4).** Into a Schlenk flask were weighed 160 mg (0.106 mmol) of $PtCl_2(TPPTS)_2$ (**1**) and 28 mg (0.109 mmol, 1.03 equiv) of AgOTf. To this was added 4.0 mL of $H_2O$ to form a pale yellow solution. The reaction was stirred at room temperature overnight in the absence of light, resulting in the formation of a white precipitate, which was removed via Celite filtration. Following solvent removal in vacuo, a pale yellow solid was isolated in 74% yield. $^{31}P$ NMR showed a mixture of products; the major product was identified as *cis*-$[Pt(H_2O)(Cl)(TPPTS)_2][OTf]$ (**4**). $^{31}P\{^1H\}$ NMR ($D_2O$; $\delta$ (ppm)): 17.6 broad d ($^2J_{P-P} = 20$ Hz, $^1J_{P-Pt} = 3740$ Hz, P *trans* to Cl), 4.6 broad d ($^2J_{P-P} = 20$ Hz, $^1J_{P-Pt} = 3920$ Hz, P *trans* to $H_2O$). $^{195}Pt$ NMR ($D_2O$; $\delta$ (ppm)): −4279.7 dd ($^1J_{P-Pt} = 3740$, 3920 Hz).

**[PtCl(TPPTS)$_3$]Cl (5).** Into a Schlenk flask was weighed 71 mg (0.267 mmol) of $PtCl_2$ and 504 mg (0.806 mmol, 3.02 equiv) of TPPTS followed by the addition of 10.0 mL of $H_2O$. The brown suspension was heated in an 80 °C oil bath. Over 12 h, a yellow solution formed. Filtration from any remaining insoluble material followed by solvent removal in vacuo gave a pale yellow solid of **5** in 88% yield. $^{31}P\{^1H\}$ NMR ($D_2O$; $\delta$ (ppm)): 23.8 d ($^2J_{P-P} = 19$ Hz, $^1J_{P-Pt} = 2500$ Hz, P *trans* to P), 12.6 t ($^2J_{P-P} = 19$ Hz, $^1J_{P-Pt} = 3680$ Hz, P *trans* to Cl). $^{195}Pt$ NMR ($D_2O$; $\delta$ (ppm)): −4731.2 dt ($^1J_{P-Pt} = 2500$, 3680 Hz).

**General Procedure for Hydration Reactions.** Into a NMR tube (containing a fused capillary with $D_2O$ for NMR lock) was weighed 6 mg (0.004 mmol) of **1** plus 0, 2, 10, or 100 equiv of KCl. The tube was sealed with a rubber septum and purged with $N_2$ for 15 min. $H_2O$ (1.0 mL) was added to form a pale yellow solution, to which was added 200 equiv of alkyne. A color change to yellow along with a drop in pH from 5 to 3 was observed. Formation of ketone was monitored by $^1H$ NMR spectroscopy.

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